ANIONIC COPPER(I), SILVER(I), AND GOLD(I) HALIDE COMPLEXES: STRUCTURE, SYMMETRY, AND LUMINESCENCE

By

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INTRODUCTION AND BACKGROUND

Associated with the current interest in solid-state materials with useful properties is a focus on materials with a physical response to changes in their environment. For example, the response of certain crystalline solids to pressure alters their unit cell parameters, and the altered electrical conductivity provides an indication of the magnitude of the pressure applied. This property is useful in the quantization of forces applied to systems such as analytical balances and bridge structural supports. Chemically tuned emission properties of luminescent materials are important in sensing technology, such as coatings on spectroscopic detectors. [1-3]

The copper(I) halides are of interest as a result of potential applications based on luminescent properties, and because of the large variety of motifs observed in these solid state materials. Complexes of copper(I), a d^{10} species, show coordination numbers of one to four. These complexes form solid state materials containing multiple tetrahedral metal centers built up of Cu_2X_2 units. In cases where X is larger, trigonal planar CuX_3^{-2} anion forms may be observed. Copper(I) is also reported as a linear, two coordinate species. [4]

These solid state complexes emit in the visible when excited in the ultraviolet. Pervious work in this laboratory has established the identity of large numbers of these complexes, both of the neutral form, $Cu_xX_x(\text{ligand})_n$, and anionic types with formula Cu_xX_y (y>x). [5,6] Complexes of the first type tend to be more stable and to show no emission when oxygen atoms are coordinated to copper. Emission is present when the ligand is an amine or other nitrogen donor compound. Complexes of the anionic type exist in many stoichiometries and structural forms that are typically built up of tetrahedral Cu_2X_2 subunits, or are linear, two-coordinate dihalide anions.[7,8] A summary of known copper(I) halides is given in Table 1.

Complexes of the three IB metal(I) halides show increasing stability in the order: F<Cl<Br<I. This trend corresponds to the Pearson Hard-Soft acid-base theory that suggests the greatest stability in forming complexes is seen when hard acid-hard base or soft acid-soft base groups combine.[9] The relationship of the IB metals in order of increasing softness is: Cu<Ag<Au, while that of the halides is F<Cl<Br<I. Copper (I) fluoride complexes are unknown in the literature.

Copper, silver and gold are d^{10} metals forming structures that may be influenced significantly by ligand and cation size. Previous investigations suggest coordination numbers for both silver(I) and copper(I) species increase with decreasing cation size, within a series containing cations of similar shape and charge distribution.[10] Studies by Hoffman et al. suggest that the bridging angle requirements for the halides of copper(I) and silver(I) complexes result in the extensive structural variety.[11] These metals show metallophilic behavior, where close metal-metal contact distances within homo-polymetallic molecules are similar to those in the pure metal form, instead of reflecting the nuclear repulsion expected of a closed shell system. This metallophilic behavior is reported to be a result of the mixing of the d and s or p orbitals of the metal centers. It may increase the bond order in clusters where it is observed.[12,13]

Several mechanisms have been used to describe the source of emission of metal-ligand systems:[14]

1) Metal to Ligand Charge Transfer (MLCT). An electron from the metal d orbital is promoted to a π^* orbital of the ligand. This occurs generally when an unsaturated ligand system (olefin or aryl) is coordinated to the metal.

2) Ligand to Ligand Interaction (LLI) also known as inter-ligand excitation. The promotion of ligand electrons from $\pi \rightarrow \pi^*$ occurs as a transition between unsaturated systems that are physically close in space.

3) Metal-Metal Interaction (MM). This transition is between two metal centers giving a $d^{10},d^{10} \rightarrow d^9,d^{10}s^1$ transition. This occurs when two or more metal centers are in close proximity such that contact distances are equal to or less than the van der Waals radius.

4) Single Metal Excitation (SME). Isolated metal centers, where no metal-metal interaction can take place, may promote an electron to the higher s orbital resulting in a change of electron configuration of $d^{10} \rightarrow d^9s^1$.

5) Ligand to Metal Charge Transfer (LMCT) or Donor-Acceptor Pair (DAP). The ligand system promotes an electron to a metal center upon excitation.

BACKGROUND

Investigations by H. D. Hardt, et al. reported an observed shift in the wavelength of emitted light at different temperatures from copper(I) species with heteroaromatic and non-aromatic ligands such as pyridine, pyrrolidine and quinoline.[15] The suspicion of thermochromic fluorescence resulted in further study by Weber and Hardt in which powder diffraction studies of a number of luminescent copper(I) carboxylate salts revealed a relationship between thermochromic shifts and small differences in cell packing.[16] There was no structural identification of the complexes involved.

Schramm, et al. proposed that thermochromicity in copper(I) complexes was directly related to the crystallographic symmetry of the copper-ligand moiety.[17] For the tetrameric $Cu_4I_4L_4$, where L = piperidine, no thermochromic shift was observed. Crystallographic structural analysis indicated the presence of an S_4 inversion symmetry element, and the conclusion was that no thermochromism should be displayed if the nitrogen ligands of the tetrameric copper are symmetrical.

In a comparison of $Cu_4I_4L_4$ moieties by Hardt and Pierre where L = morpholine, pyridine and piperidine, an increasing red shift upon lowering the temperature was observed in each tetrameric compound.[18] The red shift for the Cu_4I_4(piperidine)$_4$ was 15 nm, for Cu_4I_4(morpholine)$_4$, 35 nm, and for Cu_4I_4(pyridine)$_4$, 50 nm. However, in this study, the symmetry elements present were a fourfold axis for Cu_4I_4(piperidine)$_4$, a two-fold axis for Cu_4I_4(morpholine)$_4$, and a single-fold for Cu_4I_4(pyridine)$_4$. The structural analysis indicated very similar Cu-Cu distances, and the conclusion was that the red shift increased inversely with increasing symmetry of the molecule.

Work in this laboratory was unable to reproduce the solid state thermochromism of the complexes as reported in the literature.[19,20,21] Separate work published by these previous authors on the influence of solvent identity, suggested that the thermochromic studies might have been performed on wet samples and thus are not indicative of isolated solid state behavior.

Bao et al. suggested that crystallographic symmetry might influence the emission maxima of structurally similar compounds exhibiting differing symmetry elements within the molecule in the solid state.[22] Copper(I) complexes with aliphatic amine ligands were synthesized to eliminate the ligand-based emission characteristics of previous examples, allowing a focus on the relationship between metal based luminescence and symmetry of the molecule. Two cubic clusters were among those investigated: Cu_4I_4(acetonitrile)$_2$(morpholine)$_2$ and Cu_4I_4 (morpholine)$_4$. The Cu_4I_4(acetonitrile)$_2$(morpholine)$_2$ crystallized with no internal symmetry, and had an emission maxima of 575 nm, while the second compound had a two-fold rotation axis in the solid state and emitted at 640 to 680 nm. The two-fold axis effectively reduced the frontier energy between the HOMO and the LUMO, resulting in a lower energy emission. Four rhombohedral compounds having a $Cu_2I_2L_4$ motif with the following stoichiometries: Cu_2I_2(1-methylpiperizine)$_4$, Cu_2I_2(4-methylpiperidine)$_4$, Cu_2I_2(3,3-dimethylpiperidine)$_4$, and Cu_2I_2(3-azaspiro[5.5]undecane)$_4$ were studied in the solid state. With excitation at 330 nm, the first two compounds had emission maxima at 495-500 nm and contained no symmetry elements. The last two compounds contained a crystallographic center of symmetry within the cluster and the emission maximum was at 650 nm for both.

Hu et al. studied the luminescent properties of linear copper halide complexes seeking relationships between symmetry elements in the molecule and the wavelength maxima with the aid of X-ray crystallographic characterization, variable temperature spectrofluorimetry, and *ab initio* calculations.[23] The study of the linear di-coordinate copper halide anions with halides, bromine, chlorine and iodine, indicate the the transfer of electron density occurs from the halide p orbitals to the copper p orbital system. There was little effect on the HOMO-LUMO frontier energy due to symmetry elements (mirrors, 2-fold axes, and centers of symmetry) within the samples examined via *ab initio* computations This suggests that all of the CuX_2^- compounds should emit at about the same wavelength, in agreement with the experimental results, in which a range of emission of 465-515 nm was observed. Exceptions to this emission profile were copper(I) dihalides having aromatic functionality in the phosphorus ligand system serving as a cation in the cell, where no emission was observed in the visible spectrum. This has demonstrated that the cation should contain no aromatic groups bound to electron rich centers because these lead to quenching of the copper emission. Thus, in a series of dihalide (Cl, Br, and I) copper(I) compounds having triphenylphosphine or tetraphenylphosphine ligands, no emission was observed in the visible spectrum. The identity of the halide present had no measurable effect on the emission properties, although calculations suggested small decreases in the frontier energy when the ligand was changed from Cl to Br to I. This would indicate that the wavelength of emission should increase in the series, Cl, Br, I.

Nurtaeva et al. examined $Cu_2I_4^{-2}$ anions with trigonal planar copper(I) metal centers bridged by two halide atoms and each metal center coordinated to a terminal halide, in a rhombohedral motif. This study sought to relate symmetry elements within the structures and the emission characteristics of the solid crystalline material.[24] Also utilizing X-ray diffraction studies, variable temperature spectrofluorimetry, and *ab initio* calculations, the study evaluated eight structures and found these structures to be of four different types distinguished by the symmetry elements present. Three of these structures were found to exist as a planar rhomb with a center of symmetry and emission maximum at 452-453 nm. Calculations showed that the transition between HOMO (orbital 26) and LUMO (orbital 27) was forbidden resulting in a minimum absorption energy for transitions to LUMO + 2 (orbital 29). A fourth similar structure displayed an interfering ionic interaction with one of the terminal iodine ligands of the cluster, thus changing the available electron density on the terminal halide atom to be donated to Cu(I) on excitation. The emission maximum for this compound was 422 nm.

A second type of $Cu_2X_4^{-2}$ rhomb was bent about a line passing through the bridging ligands, resulting in a non-planar and symmetry-free motif. An emission maximum at a much longer wavelength, 675 nm, was observed. The frontier transition for the bent rhomb, in the absence of symmetry induced forbiddeness, was thought to be a HOMO to LUMO transition.

The third group of structures contained two symmetry elements passing through the crystallographic center of symmetry, 2/m. All atoms were on a mirror plane perpendicular to a two-fold rotation axis which passes through the center of symmetry. These symmetry operations impose symmetry constraints on the allowed transitions from HOMO to LUMO, resulting in symmetry forbidden transitions from HOMO to the first two LUMO orbitals. The first $A_u \rightarrow A_g$ transition allowed is the HOMO to the LUMO + 2 orbital, but apparently with a reduced frontier energy compared to that seen when an inversion center is present. The fourth group contained both the centrosymmetric and bent species within the same unit cell, and the emission profile exhibited both the 478 nm component of the centrosymmetric group and the longer wavelength of the bent type at 675 nm.

Table 1. Known Copper(I) Halides

Compound	Motif Type	Unit cell, A	Cell Ang.	Space Grou	Ref.
$K[C_{40}H_{72}O_{12}]CuI_2$	$[CuX_2]^-$	a =9.126 b =9.211 c =10.877	α =103.37 β =93.40 γ =126.86	P-1	25
$(C_{38}H_{36}Br_3CuP_2)[CuBr_2]Br$	$[CuX_2]^-$	a =11.439 b =14.862 c =21.659	α = β =91.56 γ =	P21/c	26
$(C_{38}H_{36}Br_3CuP_2)[CuBr_3]$	$[CuX_3]^{2-}$	a =32.65 b =23.96 c =9.196	α = β =96.11 γ =	Fdd2	26
$(C_{60}H_{52}P_4S_2)[CuI_3]$	$[CuX_3]^{2-}$	a =29.207 b=9.929 c=22.083	α = β =110.78 γ =	P21/c	27
$(C_{60}H_{52}P_4S_2)[CuBr_3]$	$[CuX_3]^{2-}$	a=58.950 b =10.390 c =21.589	α = β =104.33 γ =	C2/c	27
$(C_{38}H_{36}P_2)[CuI_3]$	$[CuX_3]^{2-}$	a =9.580 b =12.476 c =16.410	α = β =102.71 γ =	P21/m	28
$(C_8H_{24}P_2)[CuBr_3]$	$[CuX_3]^{2-}$	a =7.878 b = c =	α = β =79.08 γ =	R32	29
$(C_{16}H_{40}P_2)[Cu_2Br_4]$	$[CuX_4]^{3-}$	a =12.545 b=8.300 c =14.629	α = β =110.76 γ =	P21/m	29
$(C_{56}H_{60}P_4)[CuI]_4$	$[Cu_4X_4]$	a =21.058 b=12.059 c =23.425	α = β =111.50 γ =	C2/c	30
$[Pt_3(C_3H_8N_2)_6]$ $[Pt_3(C_3H_8N_2)_6Cl_6][CuCl_4]$	$[CuX_4]^{3-}$	a =15.657 b =15.657 c=10.522	α =90 β =90 γ =120	P63/m	31
$[Na(C_{10}H_{20}O_5)]_2$ $[Na(C_{10}H_{20}O_5)]_2[Cu_2I_4][Cu_4I_6]$	$[Cu_2X_4]^{2-}$	a =14.046 b =33.013 c =8.425	α = β =96.11 γ =	P21/c	32
$[C_{16}H_{40}P_2][Cu_2Cl_4]$	$[Cu_2X_4]^{2-}$	a =11.881 b =7.976 c =14.296	α = β =112.46 γ =	P21/n	33
$(C_{12}H_{36}N_3)[Cu_2Br_5]$	$[Cu_2X_5]^{3-}$	a=14.119 b =11.246 c=15.178	α = β =95.12 γ =	C2/c	34
$(C_{12}H_{40}N_2)[Cu_2Br_4]$	$[Cu_2X_4]^{2-}$	a =8.375 b =13.817 c =11.086	α = β =97.03 γ =	P21/c	35

Table 1 (continued)

$(C_{10}H_{10}Co)[Cu_3I_6]$	$[Cu_3X_6]^{3-}$	a =12.002 b= 13.431 c= 18.096	α = β= 116.98 γ =		36
$(C_{10}H_{10}Co)[Cu_4I_8]$	$[Cu_4X_8]^{4-}$	a =18.640 b= 9.154 c= 11.446	α = β =100.20 γ =	P21/m	36
$(C_{38}H_{36}P_2)Cu_4I_6$	$[Cu_4\,X_{6]}^{2-}$	a =15.603 b = c =	α = β= 53.133 γ =	R3c	37
$(CoN_{24}H_{-72})[Cu_5Cl_{17}]$	$[Cu_5X_{17}]^{11-}$	a = 21.80 b = c =	α =90 β = γ =	Fd3	38
$(C_{10}H_{12}N_2)[Cu_5Br_7]$	$[Cu_5X_7]^2$	a =12.230 b =12.543 c =33.031	α = β =115.04 γ =	P21/c	39
$(C_7H_{18}N)_6[Cu_6Br_9]$	$[Cu_3X_6]^{3-}$	a =11.591 b =16.640 c =21.250	α =90 β =90 γ =90	Cmcm	40
$I(C_8H_{20}N)_6[Cu_6I_{11}]$	$[Cu_6X_{11}]^{5-}$	a =19.474 b = c =12.129	α =90 β =90 γ =120	P63/m	41
$(C_8H_{20}N)_3[Cu_7Cl_{10}]$	$[Cu_7X_{10}]^{3-}$	a =19.052 b=16.296 c =13.782	α = β =98.95 γ =	C2/c	42
$K_7(C_{72}H_{144}O_{24})(Cu_4I_6)[Cu_8I_{13}]$	$[Cu_8X_{13}]^{5-}$	a =17.702 b= 17.715 c =10.581	α =90 β =90 γ =90	P-4	43
$Rb_4Cu_9Cl_{13}$	$[Cu_9X_{13}]^{4-}$	a=19.541 b = c =	84.43 β = γ =	R-3c	44
$(C_5H_6N)_{24}I_4[Cu_{36}I_{56}]$	$[Cu_{36}X_{56}]^{20-}$	a =38.252 b = c =	α = β = γ =	Fm3c	45
$(C_8H_{20}N)[Cu_2I_3]$	$[Cu_2X_3]^-$	a =8.420 b =17.755 c=10.736	α = β = γ =	Pna21	46
$(C_{10}H_{14}N)[Cu_2I_3]$	$[Cu_2X_3]^-$	a =15.72 b=12.27 c=8.50	α = β =108.26 γ =	C2/c	46
$[N(CH_3)_4](Cu_2I_3)$	$[Cu_2X_3]^-$	a =9.443 b=24.993 c =8.105	α =94.09 β =94.19 γ =100.12	P-1	47

Table 1 (continued)

$(C_{23}H_{17}S)(Cu_2I_3)$	$[Cu_2X_3]^-$	a =13.856 b = c=20.778	α = β = γ =	P61	48
$[S_2C_3SCH_3)_3(Cu_2I_3)$	$[Cu_2X_3]^-$	a=10.856 b=18.992 c =8.630	α = β =106.74 γ =	P P21/c	49
$[N(C_3H_7)_4]_2(Cu_2I_4)$	$[Cu_2X_4]^{2-}$	a=9.017 b =12.683 c =16.140	α = β =93.15 γ =	P21/n	50
$[(C_4H_9)_4]_2(Cu_2I_4)$	$[Cu_2X_4]^{2-}$	a =9.042 b =21.231 c =11.734	α = β =92.88 γ =	P21/n	51
$(As_2C_{48}H_{40})(Cu_2I_4)$	$[Cu_2X_4]^{2-}$	a=12.040 b =18.046 c =22.683	α = β =102.73 γ =	P21/c	52

Silver(I) halides are typically discrete three-coordinate dinuclear silver rhombohedra, or polymeric forms built up of these units.

Silver halide compounds have long been of interest as a result of their photographic imaging properties. Exposure to light causes some silver halide molecules fixed in an emulsion to become reduced via a ligand to metal charge transfer (LMCT) mechanism, whereupon they dissociate to silver particles. This is the basis for the development of a negative image.[53]

Other specific interests have been in the metal-metal bonding interactions and the charge transfer process between metal centers and ligands. [54-58] A summary of known silver halide anionic complexes is given in Table 2.

Coetzer et al., synthesized hexamethylenediamine complexes of silver iodide resulting in early reports of trigonal planar and tetrahedral structure of silver iodide as anionic complexes.[59] These structures exhibited no metal-metal interactions, nor were emission properties reported. Jagner et al. synthesized two rare trigonal planar silver(I) halides with potassium and rubidium dibenzo-18-crown-6 cationic complexes.[60] These $AgCl_3$ and $AgBr_3$ anions were synthesized with the goal of controlling coordination number by cation size as in the copper(I) halides. This group suggests that a correlation exists for halogeno-argentates such that the decreasing stoichiometric ratio of halogen ligand influences the coordination of the metal, given a similar unipositive cation.

Vogler et al. was the first to evaluate the emission properties of tetrameric silver(I) complexes by synthesizing and measuring the room and low temperature luminescence of $[Ag(PPh_3)Cl]$ and $Ag[P(OCH_3)_3]_4ClO_4$ in the solid state.[61,62] The first compound had an emission maximum at 434 nm, which corresponds to the emission of triphenylphosphine. The luminescent properties of the material was therefore attributed to this substance, present as an impurity. The second compound did not show emission under any conditions. Two other compounds synthesized by this group, $[Ag_4Cl_4(P(OCH_3)_3)_4]$ and $[Ag_4Cl_4(PPh_3)_4]$, showed luminescence with a maxima at ~480 nm in the solid state. The emission was described as originating from silver centered d-s mixing in the excited state and to be strongly influenced by silver-silver metal interaction.

The promotion of an electron from the antibonding d orbital of silver to a bonding s orbital increases the bond order between the metals, resulting in a contraction of the cluster. This distorted, excited state condition was reported to be responsible for the large stokes shift observed between the UV absorption band and the emission band in the tetrameric complexes.

In a study by Pichè and Harvey, di-metallic silver halides with tetrahedral coordination and including isocyanate ligands (Ag_2X_2)[1,8-isocyano-*p*-menthane](X=Cl, Br, I), were synthesized and evaluated for photoluminescent properties.[63] In addition, extended Hückel calculations were used to model the electronic transition states. The X-ray crystal structure of the compound indicated close metal-metal contact as well as metal to ligand interactions. Luminescence measurements of the solid-state compounds revealed maxima of 440, 458 and 443 nm for the Cl, Br, and I halides, respectively. In addition, it was determined that the metal-metal interactions were not the lowest energy excited states in the complexes. A metal to ligand charge transfer (MLCT) process was determined to have the lowest energy in the excited state where the ligand receiving the electron density is the π^* orbital of the CNR ligand. Surprisingly, the less polarizable bromide bridging ligand produced the species with the longest emission wavelength, rather than the iodide species. This group suggested that luminescence phenomena are absent for many d^{10} species, possibly as a result of a photochemically induced lability of the bridging ligands of the Ag (I) compounds.

Luminescence properties of both chair and cube forms of tetrameric silver(I) iodide phosphines were reported by Henary and Zink.[64] Solid samples of both forms showed luminescent maxima at 418 nm for the chair form, and 455 nm for the cube shaped tetramer. The emission was assigned to the d-s silver centered excited state modified by metal-metal interaction. The lower energy emission was accounted for by the resulting delocalization over more d and s orbitals of the silver(I) centers in the cube isomer. Each silver center has three neighbors in the cube form, while two centers are neighbors in the chair form of the molecule. Interestingly, the closest metal center distance in the cube form of the tetramer is 3.12 Å while for the chair form it is 3.09 Å.

This suggested that metal-metal contacts could not be judged from distance information alone, but other factors, such as ligand polarizability, must be considered.

Two hexanuclear silver(I) thiolate clusters [Ag_6(dtc)$_6$] and [Ag_6(mtc)$_6$] (dtc = di-*n*-propyldithiocarbamate; mtc = di-*n*-propylmonothiocarbamate) were synthesized by the Vogler group and found to be luminescent with maxima at 644 and 545 nm, respectively. Assignment of the excited state was a ligand-to-metal charge transfer (LMCT) from the non-halide ligands to the silver metal centers.

Table 2.
Known Silver Halide Complexes

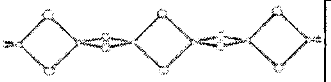
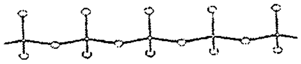
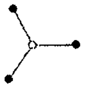
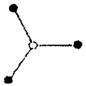
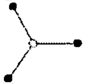
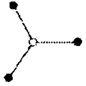
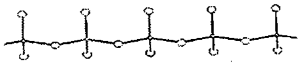
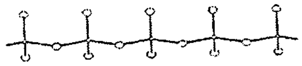
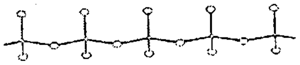
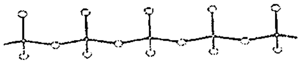
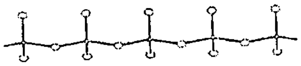
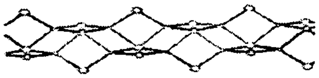
Structure	Compound	Motif Type	Unit cell, A	Cell Ang.	Space Group	Ref.
	$AgCl_2(C_{18}H_{36}KN_2O_6)$	$[AgX_2]^-$	a =14.248 b =15.695 c =11.614	α = β =95.63 γ =	P2/c	65
	$Ni(en)_2AgBr_2$	$[AgX_2]^-$	a =16.557 b =23.864 c =14.070	α = β =107.44 γ =	C2/m	66
	$Ni(en)_2AgCl_2$	$[AgX_2]^-$	a =6.877 b =13.075 c =9.359	α = β =99.16 γ =	C2/m	66
	$AgCl_2(C_4H_{12}N)$	$[AgX_2]^-$	a =8.825 b =14.526 c =6.570	α =90 β =90 γ =90	Immm	67
	$Ag_2I_4(C_8H_{22}N_2)$	$[AgX_2]^-$	a =14.190 b =9.720 c =7.130	α =90 β =90 γ =90	Pnma	68
	$SrAg_2I_4\ 8H_2O$	$[AgX_2]^-$	a =12.86 b =12.86 c =5.56	α =90 β =90 γ =90	I422	69
	$AgI_2(C_4H_{12}N)$	$[AgX_2]^-$	a =9.228 b =15.353 c =6.889	α =90 β =90 γ =90	Immm	70
	$AgI_3(C_{38}H_{36}P_2)$	$[AgX_3]^-$	a =16.469 b =12.514 c =9.673	α = β =103.64 γ =	P21	71
	$K(C_{30}H_{38}O_6)[AgBr_3]$	$[AgX_3]^{2-}$	a =14.154 b =14.154 c =19.045	α =90 β =90 γ =120	P63/m	72
	$Rb(C_{30}H_{38}O_6)[AgBr_3]$	$[AgX_3]^{2-}$	a =14.000 b =14.000 c =19.591	α =90 β =90 γ =120	P63/m	72
	$K(C_{30}H_{38}O_6)[AgCl_3]$	$[AgX_3]^{2-}$	a =14.012 b =14.012 c =18.958	α =90 β =90 γ =120	P63/m	72
	$Rb(C_{30}H_{38}O_6)[AgCl_3]$	$[AgX_3]^{2-}$	a =13.768 b =13.768 c =19.507	α =90 β =90 γ =120	P63/m	72
	$CsAgI_3$	$[AgX_3]^-$	a =14.39 b =15.16 c =5.02	α =90 β =90 γ =90	Pnam	73
	$CsAgI_3$	$[AgX_3]^-$	a =13.19 b =13.74 c =4.57	α =90 β =90 γ =90	Pnam	73
	K_2AgI_3	$[AgX_3]^{2-}$	a =21.3 b =10.9 c =4.6	α =90 β =90 γ =90	Pbnm	74
	K_2AgI_3	$[AgX_3]^{2-}$	a =10.01 b =4.78 c =	α =90 β =90 γ =90	Pnma	75
	Rb_2AgI_3	$[AgX_3]^{2-}$	a =10.258 b =4.886 c =20.063	α =90 β =90 γ =90	Pnma	76
	$AgI_3(N_2H_6)$	$[AgX_3]^-$	a =21.20 b =10.84 c =4.629	α =90 β =90 γ =90	Pbnm	77

Table 2 (continued)

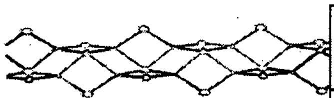
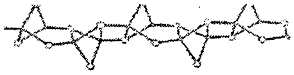
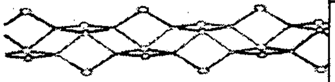
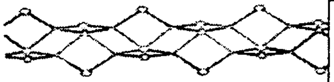
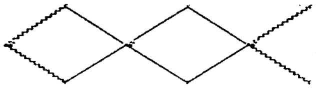
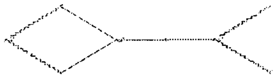
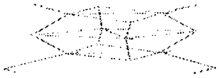
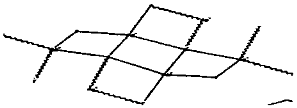
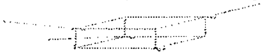
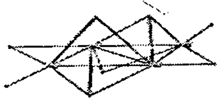
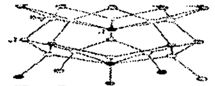
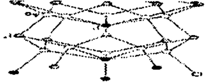
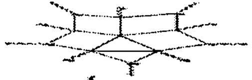
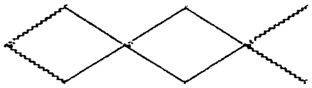
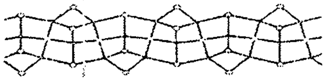
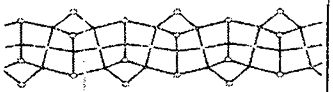
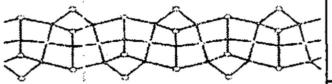
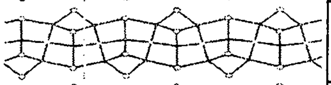
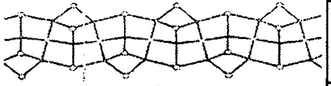
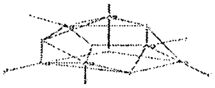
	$Ag_2I_3(NC_4H_{12})$	$[Ag_2X_3]^{2-}$	a =17.760 b =10.077 c =7.431	α =90 β =90 γ =90	Pnam	77
	$CsAg_2I_3$	$[Ag_2X_3]^{2-}$	a =11.08 b =13.74 c =6.23	α =90 β =90 γ =90	Pbnm	78
	$Ag_2Cl_3(C_8H_{20}N)$	$[Ag_2X_3]^{2-}$	a =20.773 b =11.895 c =26.683	α =90 β =90 γ =90	Pnma	79
	$Ag_2Br_3(C_8H_{20}N)$	$[Ag_2X_3]^{2-}$	a =17.063 b =7.0356 c =9.702	α =90 β =90 γ =90	Pnma	80
	$Ag_2I_4(C_{26}H_{28}CuN_4O_2)$	$[Ag_2X_4]^{2-}$	a =8.540 b =10.029 c =10.584	α =110.22 β =95.48 γ =93.42	P-1	81
	$Ag_2I_4(C_8H_{22}N_2)$	$[Ag_2X_4]^{2-}$	a =14.190 b =9.720 c =7.130	α =90 β =90 γ =90	Pnnm	82
	$Ag_2I_4(C_4H_{12}N)_2$	$[AgX_2]^{-}$	a =9.228 b =15.353 c =6.899	α =90 β =90 γ =90	Immm	83
	$Ag_2I_4(C_{36}H_{72}K_2N_4O_{12})$	$[Ag_2X_4]^{2-}$	a =11.330 b =12.365 c =10.343	α =103.49 β =101.72 γ =86.66	P-1	84
	$Ag_2Cl_4(C_{48}H_{40}P_2)$	$[Ag_2X_4]^{2-}$	a =14.190 b =8.062 c =19.177	α = β =101.64 γ =	P21/n	85
	$Ag_2Br_4(C_{48}H_{40}P_2)$	$[Ag_2X_4]^{2-}$	a =14.525 b =7.914 c =20.010	α = β =103.16 γ =	P21/n	85
	$Ag_2Cl_4(As_2C_{48}H_{40})$	$[Ag_2X_4]^{2-}$	a =14.280 b =8.200 c =19.118	α = β =101.19 γ =	P21/n	86
	$Ag_2Br_4(As_2C_{48}H_{40})$	$[Ag_2X_4]^{2-}$	a =14.456 b =8.072 c =19.854	α = β =102.73 γ =	P21/n	86
	$Ag_2Cl_5(NH_3)_6AuCl_4$	$[Ag_2X_5]^{3-}$	a =20.86 b =11.20 c =6.61	α =90 β =90 γ =90	Immm	87
	$Ag_2I_6(C_4H_{16}I_2N_4Pt)_2$	$[Ag_2X_6]^{4-}$	a =15.576 b =18.451 c =24.645	α =90 β =90 γ =90	Fddd	88
	$(C_{16}H_{21}N)_4[Ag_3I_6]$	$[Ag_3X_6]^{3-}$	a =9.450 b =15.770 c =18.880	α = β =101.13 γ =	P21/c	89
	$(C_{16}H_{21}N)[Ag_3I_4]$	$[Ag_3X_4]^{-}$	a =9.450 b =15.770 c =18.880	α = β =101.8 γ =	P21/c	90
face sharing iodide polyhedra	$RbAg_4I_5$	$[Ag_4X_5]^{-}$	a =11.24 b =11.24 c =11.24	α =90 β =90 γ =90	P4(1)3	91
face sharing iodide Icosohedra	$Ag_4I_5(C_5H_{12}ON)$	$[Ag_4X_5]^{-}$	a =13.167 b =23.437 c =12.758	α =90 β =90 γ =90	P212121	92

Table 2 (contimued)

	$Ag_4I_6(C_4H_{12}N_2)(C_2H_6OS)_4$	$[Ag_4X_6]^{2-}$	a =12.960 b =11.540 c =6.540	α =93.80 β =100.70 γ =104.20	P-1	93
	$Ag_4I_8(C_{12}H_{28}N)_4$	$[Ag_4X_8]^{4-}$	a =26.836 b =12.535 c =24.509	α = β =118.54 γ =	C2	94
	$Ag_4I_8(C_{15}H_{30}N_2)_2$	$[Ag_4X_8]^{4-}$	a =15.316 b =15.083 c =20.777	α =90 β =90 γ =90	Pbca	95
	$Ag_4I_8(C_{24}H_{20}P)_4$	$[Ag_4X_8]^{4-}$	a =13.453 b =16.607 c =11.068	α =102.83 β =103.94 γ =82.96	P-1	86
	$Ag_4I_8(C_{24}H_{20}As)_4$	$[Ag_4X_8]^{4-}$	a =13.446 b =16.712 c =11.293	α =103.84 β =103.36 γ =83.43	P-1	86
	$Ag_4Br_8(C_{72}H_{144}K_4N_8O_{24})$	$[Ag_4X_8]^{4-}$	a =16.557 b =23.864 c =14.070	α = β =107.446 γ =	P2(1)/c	96
	$Ag_5I_6(C_5H_9ON)$	$[Ag_5X_6]^-$	a=15.93 b =21.82 c =7.935	α =90 β =90 γ =90	P212121	97
	$Ag_5I_6(C_6H_{13}ON)$	$[Ag_5X_6]^-$	a =7.926 b =21.170 c =18.39	α =90 β =90 γ =90	Pnma	97
	$Ag_5I_6(C_{19}H_{17}IP)$	$[Ag_5X_6]^-$	a =15.004 b =27.190 c =7.898	α = β =97.18 γ =	P21/c	98
	$Ag_5I_7(C_{54}H_{66}AgO_{18}P_2)_2$	$[Ag_5X_7]^{2-}$	a =22.010 b =19.980 c =16.480	α =94.49 β =92.46 γ =116.76	P-1	99
	$Ag_5Br_8(C_{18}H_{42}N_3O_3)$	$[Ag_5X_8]^{3-}$	a =28.84 b =6.350 c =36.48	α = β =108.25 γ =	C2/c	100
	$Ag_6I_8(C_8H_{22}N_2)$	$[Ag_6I_8]^{2-}$	a =10.47 b =9.58 c =7.86	α =101.4 β =101.8 γ =95.5	P-1	101
	$Ag_6I_8(C_{16}H_{36}N)_2$	$[Ag_6I_8]^{2-}$	a =9.450 b =15.770 c =18.880	α = β =101.13 γ =	P2(1)/c	102
	$Ag_6I_8(C_{24}H_{20}P)_2$	$[Ag_6I_8]^{2-}$	a =13.380 b =26.536 c =8.504	α = β =108.09 γ =	P21/c	103
	$Ag-_6I_8(C_{24}H_{20}As)_2$	$[Ag_6I_8]^{2-}$	a =13.448 b =26.723 c =8.546	α = β =107.99 γ =	P21/c	103
	$Ag_6I_8(C_{19}H_{18}As)_2$	$[Ag_6I_8]^{2-}$	a =12.783 b =25.800 c =8.388	α = β =108.36 γ =	P21/c	104
	$Ag_6Cl_2I_6(C_{19}H_{18}As)_2$	$[Ag_6I_{8-n}X_n]^{2-}$	a =12.448 b =25.339 c =8.372	α = β =109.96 γ =	P21/c	104
	$Ag_6Br_2I_6(C_{19}H_{18}As)_2$	$[Ag_6I_{8-n}X_n]^{2-}$	a =12.448 b =25.339 c =8.372	α = β =108.75 γ =	P21/c	104
	$Ag_6I_{11}(C_8H_{20}N)_6$	$[Ag_6X_{11}]^{5-}$	a =19.750 b =19.750 c =12.240	α =90 β =90 γ =90	P63/m	105
electrolytic solid state polymer	$Ag_{13}I_{15}(C_8H_{24}N_2)$	$[Ag_{13}X_{15}]^{2-}$	a =11.52 b =11.52 c =11.52	α =67.35 β = γ =	R-3m	106
electrolytic solid state polymer	$Ag_{13}I_{15}(C_{12}H_{32}N_2)$	$[Ag_{13}X_{15}]^{2-}$	a =25.151 b =11.367 c =21.665	β =120.38	C2/c	107

Gold(I) complexes are predominantly linear or bent (180 to 155.4 degrees) single metal centered complexes, both in the free anionic form or within larger molecular ligands. The higher oxidation numbers (III to VII) can lead to a more complex motif, with up to 12 coordination found in some organometallic structures. Metallic gold is frequently found in nature and shows great stability to chemical change, but enjoys a facile reduction-oxidation chemistry that drives research in the synthesis of new compounds. A summary of known gold(I) iodide complexes is provided in Table 3.

Gold(I) complexes show strong luminescence with phosphine, thiolato, polypyridyl and organometallic ligand systems. The three-coordinate gold(I) complexes generally exhibit luminescence while the free, mononuclear linear and four coordinate complexes exhibit no photoluminescent properties. Linear gold(I) moieties bonded with psuedo-halide, phosphino, thiolato ligands or supramolecular ring systems appear to support emission activity.[108] Several gold(I) complexes follow the same closed shell trend as the copper(I), and to a lesser extent silver(I) metal centers, in showing significant metal-metal interactions. These interactions are implicated when the metal-metal distances are similar to those in the pure metal, and which are not dictated by the geometric stresses of the molecule.[109] Several mechanisms have been invoked to describe the origin of this interaction, with some experimental support for each argument.

In 1970 Ziolo et al synthesized several triphenylphosphine gold(I) halide compounds in an effort to produce photographic sensitizers.[110] These compounds displayed photoluminescence after irradiation with near-UV light and sparked a continuous and productive search for luminescent gold(I) compounds. In fact, many researchers commonly have the habit of irradiating all gold compounds to check for luminescence.

Two groups began synthesis of macrcyclic polynuclear gold(I) complexes. Mason and Rogers et al. synthesized simple di-gold macrocycles to create a close interaction of gold-gold metal centers in linear opposition within the cycles. Systematic synthesis of $[Au_2(dmpm)_2]$ and $[Au_2(dmpe)_2]$ cycles (dmpm = $((Ph_2P)_2CH_2)_2$; dmpme = $((PMe_2)_2CH_2)_2$) with Br_2, Cl_2, I_2, and $(ClO_4)_2$ counter ions resulted in structures where obvious interaction between the metal centers occurred.[110] Balch et al. began synthesis of polynuclear gold(I) complexes with a variety of bridging hetero-metals.[111,112] Macrocyclic compounds *trans*-$PdCl_2(dpmaAu_2Cl_2)_2$ (dpma=bis(di-phenylphosphinomethyl)arsine) and $[Au_2Rh(CO)Cl(\mu\text{-dpma})_2][PF_6]_2$ were synthesized and the latter complex showed photoluminescence at 620 nm when irradiated in the UV at room temperature. Short contact distances between two different Au-Rh metal contacts (3.028 Å, 3.025 Å) indicated a metal-metal interaction between gold and rhodium centers in this macrocycle, while the palladium bridged moiety showed no interaction with a Pd-Au distance of 8.88 Å. No luminescent behavior was observed for the Pd containing macrocycle.

The first trigonal planar gold(I) complex was synthesized by McLesky and Gray using 1,2-bis(dicyclohexylphosphino)ethane (=dcpe) producing a strongly emitting complex where no Au-Au interactions were evident.[113] The group attributed luminescence to a metal to ligand charge transfer (MLCT) excited state.

A series of syntheses from Fackler et al. resulted in several macrocyclic compounds where X-ray crystallographic analysis of metal-metal contacts, absorption and photoluminescence studies, and electronic characterization by computational methods were carried out to establish the relationship between metals in the close contact environment.[114-117] This group synthesized aryl ([Au(dppm)]$_2$) and non-aryl ([Au($H_2PCH_2PH_2$)]$_2$) phosphine di-gold(I) systems and determined solution absorption and luminescent behavior for each. Utilizing SCF-Xα-SW molecular orbital investigations, an attempt was made to understand bonding between the metals and their luminescence behavior.[114] Under the hypothesis that luminescent behavior is generated by the metal-metal contacts in the non-aryl phosphine system, MO studies on this compound revealed the HOMO to be 78% Au in character with 41% from the 6s orbital and 41% from the 5dz^2 orbital. A contribution of 10% from the ligand s orbital was noted, and ligand identity was assumed to be significant in the luminescent characteristics of these compounds. The bonding between metal centers was assumed zero order. The computational study showed the interactions were generated from s, p, and d atomic orbitals of the Au center. These are symmetry forbidden in C_{2h} symmetry of this species and, as a result, the hypothesis that δ bond formation occurs between the metal centers was not invoked from this study.

Another series of investigations by Fackler et al. utilized TPA (TPA = 1,3,5,-triaza-7-phosphaadamantane) in hopes of reducing or eliminating steric interactions between aurophilic centers.[115] Synthesis of [AuX(TPA)], (X = Cl, Br, I, AuI_2, HCl)[144] and Au(TPPTS)$_4$ (TPPTS = Tris-3,3',3''-phosphinidynetris(benzenesulfonic acid) trisodium salt)[116] produce two coordinate luminescent systems where interaction between Au centers was from packing within the unit cell and not by geometric constraints of a macrocyclic structure. These luminescent systems were evaluated by computational techniques utilizing extended Hückel MO methods having relativistic corrections for the gold centers. The resulting HOMO-LUMO analysis indicated that as two isolated linear gold centers are brought together, the frontier energy between HOMO and LUMO decreases as a result of close interaction. The decrease in the energy was attributed to the destabilization of the σ_u HOMO orbital. Thermal studies indicated a relationship between close approach distances of the metal centers and the blue shift emission characteristics. As the temperature was increased from 77 K to 298 K, the emission energy increased (blue shift), consistent with an increasing HOMO-LUMO energy.

A series of studies by Che et al began with luminescence studies of [Au_2(2,6-bisdiphenylphosphinopyridine)] a linear P-Au-P complex having a metal-metal contact distance of 4.866 Å, assumed without interactions.[118] The system showed luminescence in solution at 520 nm, and the absorption spectrum indicated electronic interaction was π^*, $6p \leftarrow 5d_{xy}, 5d_{x2-y2}$ transition MLCT, a result similar to the Fackler group.

A synthesis of $[Au_4(dpmp)_2(SCN)_2][SCN]Cl$ and $[Au_3(dpmp)_3][SCN]$ by Che et al., produced complexes having three and four Au-Au interactions. The luminescent characteristics of the two species indicated a shift in HOMO-LUMO energy on the Au centers to a lower energy state (decreased frontier energy) with increasing Au-Au interactions. The metal-metal interaction distances were 3.013 and 3.004 Å, respectively. This group attributed the decrease in frontier energy to a lowered $p_\sigma \leftarrow d_{\sigma*}$ energy, a result of the weak metal-metal interaction.

In another study by the Fackler group, thiolate macrocycles were synthesized ($[AuS_2PPh(OCH_2CH{=}CH_2)]_2$; $[AuS_2P(4\text{-}C_6H_4OCH_3)(OSiPh_3)]$) and their luminescence properties measured.[119] An X-ray crystallographic study indicated a metal-metal distance of 3.096 Å and was assumed to include a metal-metal interaction for the first compound, while the second system had no such metal-metal interaction. Emission profiles for the two compounds differed in energy by 100 nm, which suggested to this group that the excitation is from the sulfur orbital of the ligand, and not from the associated phenyl ring π orbital. An emission difference would be much smaller if only the metal-metal interaction was the mechanism involved. The emission properties were assigned to LMCT from the sulfur to the metal center.

Pyykkő et al. studied the MP2 geometry and HF relativistic electronic interactions of metal-metal contacts in model structures.[120] Both 8-membered macrocycles containing Au-Au close contacts and the smaller $[M_2X_4]^{2-}$ rhombohedral species for Cu and Ag were evaluated at both levels of theory with quasi-relativistic pseudopotentials to determine the dependence of the interaction on correlated electronic effects. The studies revealed a dependence on electron correlation in those structures with short contacts between metals as the MP2 derived geometries suggested a contraction of metal-metal distances and a reduction in bridging angles. Another study by this group postulated a theoretical consideration to view this interaction as a $d \rightarrow p$ transition rather than the $p_z \rightarrow d_\sigma$ assignment by the other groups.

The synthesis and photophysical properties of closed shell gold(I) complexes have attracted considerable attention as a result of the close Au-Au interactions which have been attributed to relativistic effects and electron correlation. Photoluminescence studies have shown that most derivatives with such weak interactions display luminescence in the visible region, with the metal-centered electronic excited states being modified by this close metal-metal interaction. Several structurally similar cases reveal photoluminescence in the absence of metal-metal interactions, but ligand contributions to the luminescent behavior of these structures makes definitive determination of this mechanism difficult.

The use of polyphosphines and N or S-donor ligands modify the emission properties of gold(I) complexes. In all cases, mononuclear free anionic two-coordinate gold(I) species do not emit, but linear two-coordinate gold(I) species bonded within these systems do show emission. Three-coordinate gold(I) species have shown luminescent behavior.

Copper(I) and silver(I) complexes are numerous, and emission of copper(I) complexes is common. Silver(I) complexes do not readily produce emission in the visible spectrum, and although many structural examples exist, little study of the luminescent behavior of silver(I) complexes has been attempted.

Considerable study of the electronic nature of IB metal emission and bonding by relativistic quantum mechanical computations has been inconclusive, with several studies available to suggest the presence or absence of metal-metal interactions. Clearly, more straightforward examples of related structures are necessary to reduce ambiguity in the understanding of photophysical behavior in closed shell complexes.

The compounds evaluated for emission and computational study to date have been of mixed ligand types with pseudohalides, chalcogens, or rare earth metals included to induce luminescence in the molecules. There have been no clear, systematic efforts to relate symmetry and emission in related structures as has been done for copper(I) complexes. This study focuses on the synthesized silver and gold halide moieties with different crystallographic symmetries charge-balanced with non-emitting crown ether coordinated cations.[121] This reduces computational challenges, and allows a more straightforward evaluation of the electronic character of the luminescence properties of the species without ligand complications. Computational studies were undertaken to allow comparison of electronic features found experimentally.

Table 3. Gold(I) Halides

compound	Motif Type	Unit cell, A	Cell Ang.	Space Group	Ref.
$(C_{20}H_{20}N_4)[Au_4I_4]$	$[AuX_2]^-$	a =7.222 b =14.250 c =14.773	α =90.00 β =90.00 γ =90.00	Pnnm	122
$(C_6H_{12}Au_1N_4S_2)[AuI_2]$	$[AuX_2]^-$	a =6.540 b =14.089 c =8.184	α =90.00 β =99.75 γ =90.00	P21/c	123
$(C_{16}H_{32}S_4)[Au_4I_4]$	$[AuX_2]^-$	a =8.149 b =11.460 c =15.956	α =90.00 β =90.00 γ =90.00	Pc21n	124
$(C_{10}H_8S_8)_2[AuI_2]$	$[AuX_2]^-$	a =6.603 b =9.015 c =15.403	α =94.95 β =96.19 γ =110.66	P-1	125
$(C_{10}H_8S_8)_2[AuI_2]$	$[AuX_2]^-$	a=6.802 b=14.822 c =33.387	α =90.00 β =90.00 γ =90.00	Pbcm	126
$(C_{10}H_8S_8)_2[AuI_2]$	$[AuX_2]^-$	a=6.570 b =8.891 c =15.299	α =95.84 β =96.22 γ =110.67	P-1	127
$(C_{10}H_8S_8)_2[AuI_2]$	$[AuX_2]^-$	a =12.833 b =7.738 c =34.160	α =90.00 β =90.00 γ =90.00	Abam	128
$(C_{10}H_8S_8)_2[AuI_2]$	$[AuX_2]^-$	a =6.540 b =8.845 c =15.253	α =95.94 β =96.25 γ =110.78	P-1	129
$(C_{10}H_8\ S_8)_2[AuI_2]$	$[AuX_2]^-$	a =6.790 b =14.595 c =33.460	α =90.00 β =90.00 γ =90.00	Pbcm	130
$(C_{16}H_{36}N_1)[AuI_2]$	$[AuX_2]^-$	a=13.009 b=10.665 c=16.412	α =90.00 β =93.48 γ =16.412	C2/c	131
$(C_{16}H_{36}N\text{-}_1)[AuI_2]$	$[AuX_2]^-$	a =13.043 b =10.724 c =16.500	α =90.00 β =93.62 γ =90.00	C2/c	132
$(C_{10}H_8S_8)(C_{10}H_8S_8)_{.98}(I_3)_{.02}[AuI_2]$	$[AuX_2]^-$	a =10.076 b =33.853 c =4.994	α =90.00 β =90.00 γ =90.00	Pnma	133
$(C_{10}H_8S_8)(C_{10}H_8S_8)_{.98}(I_3)_{0.02}[AuI_2]$	$[AuX_2]^-$	a =10.068 b =33.851 c =4.970	α =90.00 β =90.00 γ =90.00	Pnma	134

Table 3. (cont.)

$(C_8H_{20}N_1)[AuI_2]$	$[AuX_2]^-$	a =12.806 b =9.053 c =12.811	α =90.00 β =111.50 γ =90.00	P21/n	135
$(C_{24}H_{21}N_1P_1)[AuI_2$	$[AuX_2]^-$	a =8.249 b =10.220 c =14.762	α =89.23 β =87.41 γ =85.65	P-1	136
$(C_6H_{15}S_1)n[Au_2I_4]$	$[AuX_2]^-$	a =8.772 b =10.220 c =14.762	α =105.07 β =95.25 γ =115.25	P-1	137
$(C_6H_{15}S_1)[AuI_2]$	$[AuX_2]^-$	a =27.110 b =11.101 c =15.309	α =90.00 β =123.35 γ =90.00	C2/c	138
$(C_{14}\text{-}H_{10}S_{12})_4[AuI_2]_2$	$[AuX_2]^-$	a =39.620 b =11.097 c =4.993	α =90.00 β =93.36 γ =90.00	P21/n	139
$(C_{20}H_{32}As_4I_1)[AuI_2]$	$[AuX_2]^-$	a =16.570 b =18.260 c =9.200	α =90.00 β =97.70 γ =90.00	P21	140
$(C_{20}H_{32}As_4I_1)[AuI_2]$	$[AuX_2]^-$	a =21.600 b=8.920 c=16.100	α =90.00 β =107.00 γ =90.00	C2/c	141
$(C_{30}H_{32}N_4)(ClO_4)(C_4H_{10}O_1)[AuI_2]$	$[AuX_2]^-$	a =10.030 b =15.915 c =25.210	α =90.00 β =101.63 γ =90.00	P21/c	142
$(C_{24}H_{64}Au_4I_4P_82)(C_2H_3N_1]$	$[AuX_2]^-$	a =10.436 b =24.970 c =20.383	α =90.00 β =96.53 γ =90.00	P21/c	143
$(C_7H_{12}N_2S_2I_3)[AuI_2]$	$[AuX_2]^-$	a =8.204 b =15.994 c =8.080	α =96.68 β =112.40 γ =92.20	P-1	144
$2(C_{10}H_8O_2S_6)2[AuI_2]$	$[AuX_2]^-$	a =7.485 b =7.485 c =34.032	α =90.00 β =90.00 γ =90.00	P42cm	145
$(C_{10}H_8O_2S_6)_2[AuI_2]$	$[AuX_2]^-$	a =6.621 b =7.248 c =33.239	α =90.00 β =90.00 γ =90.00	A222	146
$(C_{15}H_{11}S_2)[AuI_2]$	$[AuX_2]^-$	a =7.524 b =22.525 c =10.628	α =90.00 β =95.59 γ =90.00	P21/c	147

Table 3. (cont.)

$(C_{10}H_8S_8)6n,n(C_4Au_4Br_8I_8)$ $2n(AuBr_2)n(C_2I_4)n(Br)$	$[AuX_2]^-$	a =34.278 b =25.412 c =7.954	α =90.00 β =93.27 γ =90.00	C2/m	148
$0.75(C_{12}H_{10}O_2S_6Se_2)1.25$ $C_{12}H_{10}O_2S_6Se_2)0.75(AuI_2)$	$[AuX_2]^-$	a =6.814 b =9.197 c =16.491	α =94.49 β =96.45 γ =109.71	P-1	149
$(C_{14}H_{12}S_{12})[AuI_2]$	$[AuX_2]^-$	a =12.745 b =13.641 c =9.410	α =107.39 β =104.54 γ =100.08	P-1	150
$(C_{12}H_{14}N_2)n,n[Au_2I_4]$	$[AuX_2]^-$	a =12.617 b =12.617 c =6.753	α =90.00 β =90.00 γ =90.00	P42/mnm	151
$(C_{12}H_8S_{10})_2[AuI_2]$	$[AuX_2]^-$	a =18.599 b =8.028 c =13.712	α =90.00 β =107.61 γ =90.00	P21/c	152
$(C_{10}H_8S_6Se_2)_2[AuI_2]$	$[AuX_2]^-$	a =34.094 b =20.268 c =9.928	α =90.00 β =90.00 γ =90.00		153
$(C_9H_{18}N_3O_3)[Au_3I_2]$	$[AuX_2]^-$	a =9.309 b =13.597 c =14.899	α =90.00 β =101.26 γ =90.00	P21/c	154
$(C_9H_{18}N_3O_3)[Au_3I_4]$	$[AuX_2]^-$	a =7.404 b =9.278 c =16.331	α =80.77 β =78.68 γ =81.85	P-1	155
$(C_9H_{18}N_3O_3C_1H_2Cl_2)[Au_3I_6]$	$[AuX_2]^-$	a =14.762 b =8.723 c =22.278	α =90.00 β =91.58 γ =90.00	P21/c	156
$(C_7H_4S_6)_2[AuI_2]$	$[AuX_2]^-$	a =10.797 b =7.789 c =28.991	α =90.00 β =90.00 γ =90.00	Pbnm	157
$(C_8H_6S_6)_2[AuI_2]$	$[AuX_2]^-$	a =12.473 b =7.238 c =29.650	α =90.00 β =90.00 γ =90.00	F222	158
$(C_{10}H_8S_4Se_4)_2[AuI_2]$	$[AuX_2]^-$	a =7.614 b =8.341 c =15.538	α =77.56 β =98.31 γ =112.71	P-1	159
$(C_6H_{19}O_2P_2)[AuI_2]$	$[AuX_2]^-$	a =16.623 b =8.173 c =6.228	α =90.00 β =89.81 γ =90.00	12/m	160

Table 3. (cont.)

$(Tl_6Au_2I_{10})n$	$[AuX_2]^-$	a =10.569 b =10.569 c =13.431	α =90.00 β =90.00 γ =90.00	P-62c	173
$(Cs_2Au^{I}Au^{III}Cl_6)$	$[AuX_2]^-$	a =7.49 b =7.49 c =10.87	α =90.00 β =90.00 γ =90.00	I4mmm	174
$(Cs_2Au^{I}Au^{III}Cl_6)$	$[AuX_2]^-$	a =7.495 b =7.495 c =10.880	α =90.00 β =90.00 γ =90.00	I4mmm	175
$(Cs_2Au^{I}Au^{III}Cl_6)$	$[AuX_2]^-$	a =7.05 b =7.05 c =10.23	α =90.00 β =90.00 γ =90.00	P4/mmm	176
$(Rb_2Au^{I}Au^{III}Br_6)$	$[AuX_2]^-$	a =8.520 b =7.243 c =11.210	α = β =101.24 γ =	I2/m	177
$(Rb_2Au^{I}Au^{III}Cl_8)$	$[AuX_2]^-$	a =12.02 b =7.522 c =18.29	α = β =97.62 γ =	C2/c	178
$(K_2Au^{I}Au^{III}I_6)$	$[AuX_2]^-$	a =7.283 b =9.259 c =11.587	α = β =93.0 γ =	P21/n	179
$(Rb_2AgAu_2{}^{I}Au^{III}I_8)$	$[AuX_2]^-$	a =13.324 b =7.480 c =21.029	α = β =101.08 γ =	C2/c	180
$(Au^{III}(dtc)_2)[Au^{I}Br_2]$	$[AuX_2]^-$	a =22.38 b =15.80 c =8.11	α = β =98.2 γ =	C2/c	181
$(Au^{III}(dmg)_2)[AuCl_2)$	$[AuX_2]^-$	a =11.52 b =10.59 c =6.52	α =90 β =90 γ =90	Pnm	182
$(Au^{I}{}_2Au^{III}{}_2Cl_8)$	$[AuX_2]^-$	a =7.015 b =6.830 c =6.684	α =94.4 β =107.5 γ =88.4	P-1	183
$[AuCl_2]_3(Au^{III}(terpy)Cl_2)[Au^{III}Cl_4]$	$[AuX_2]^-$	a =9.703 b =15.351 c =7.813	α =92.05 β =106.58 γ =107.102	P-1	184
$(Au_2(tmb)Cl_2)$	$[AuX_2]^-$	a =12.5848 b =19.2179 c =6.5452	α =90 β =90 γ =90	Pna2(1)	185
$(C_6H_{13}N_3PI_3Au_2)$	$[AuX_2]^-$	a =15.453 b =11.050 c =9.113	α =90 β =90 γ =90	Pnma	186

CHAPTER II

CRYSTALLOGRAPHY

Solid substances containing a high degree of internal atomic and molecular order can be examined by measuring the pattern of diffracted radiation. The incident radiation should have a wavelength on the order of the atomic distances (~0.5 to 3.0 Å) to determine the internal atomic structure in three dimensions. The intensities of the diffracted radiation can be mathematically correlated to the type and position of atoms within the crystal lattice. Knowledge of structural details reveals significant information such as composition, connectivity, conformation, bond distances and angles, chirality, and electronic density distribution about the atoms.[187]

The smallest representative volume within the lattice is called a unit cell, characterized by the cell edge dimensions (a, b, and c) and the angles between them (α, β, and γ). A unit cell may be classified according to its geometry as belonging to one of seven primitive, or fourteen centered crystal systems. The symmetry of a motif within the unit cell may be explained by combinations of face or body centered positions with the symmetry operations (identity, center of symmetry, rotation axes, inversion axes, and mirror plane) that give rise to thirty two crystallographic point groups. Translational symmetry relating the internal structural components (screw axes and glide planes) combined with the point groups lead to two hundred and thirty possible symmetry arrangements within the unit cell, referred to as space groups.

Bragg's Law defines the geometrical conditions necessary for diffraction to take place when objects in the unit cell are viewed as a series of *hkl* indexed planes separated by a distance, d, that is on the order of the incident radiation wavelength, λ, at an angle of θ to the incident radiation (**n** is the diffraction order).[188]

$$n\lambda = 2d_{(hkl)} \sin\theta \qquad (1)$$

When these conditions are met, radiation leaving the surface members of the set of planes in the diffracting material undergoes positive re-enforcement to produce maximum intensity in the diffracted energy. The Bragg condition depends upon θ, which is the defined angle of incidence and of diffraction for each diffraction maxima produced. Friedel's Law states that diffraction effects are essentially centrosymmetric; for each reflection, *hkl,* there is an identical reflection, $\overline{hkl}$. The combination of this centrosymmetric character applied to the point groups reduces the options to 11 centrosymmetric *Laue* groups.[189]

The raw intensity information collected in the diffraction experiment contains information that allows determination of the molecular structure of the crystal, in addition to background radiation that is produced by the metal target of the X-ray tube. The intensity peak is corrected to remove background radiation by careful measurements with a scanning scintillation counter on the left (I_{lbg}) and right (I_{rbg}) side of the intensity peak, then subtracting these from the measured intensity, I_{raw} :

$$I_{int} = (I_{raw} - I_{lbg} - I_{rbg}) \text{ x Scan speed} \qquad (2)$$

The error associated with the intensity measurement is given by:

$$\sigma I_{int} = (I_{raw} - I_{lbg} - I_{rbg})^{1/2} \text{ x Scan speed} \qquad (3)$$

where σI_{int} is the standard deviation of the integrated intensity. The integrated intensity is observed when the intensity is statistically significant:

$$I_{int} > 2\sigma I_{int} \tag{4}$$

Several geometrical effects attenuate the raw intensity. If the specimen is rotated through the diffraction angle at a constant angular rate, ω, then data collected at higher 2θ angles is in optimum diffraction geometry (at constant ω) for a smaller amount of time than data collected at smaller angles. The Lorentz (L) correction to reduce this effect by incrementing the intensity by an amount equal to that lost is given by:

$$L = (\sin 2\theta)^{-1} \tag{5}$$

The incident beam from the monochromator of the X-ray source is non-polarized. When the atoms in the Bragg plane of the unit cell diffract this incident radiation, the perpendicular electric vector component of the incident beam is diminished in intensity. The parallel component is propagated with un-diminished efficiency. At higher angles of diffraction, the perpendicular component of the diffracted intensity decreases as 2θ increases, until the diffracted intensity is reduced by 50%. Polarization effects can be corrected by combining the parallel component with a corrected perpendicular component in the following relationship:

$$I_{\parallel} = K\, I_o/2 \tag{6}$$

The total scattered intensity becomes:

$$I = I_{\parallel} + I_{\perp} = KI_o\,(1+\cos^2 2\theta)/2 \tag{7}$$

Where $(1+\cos^2 2\theta)/2$ is the polarization factor, p, which is dependant only upon the angular geometry, I_o is the incident intensity, and K is the diffraction constant for the plane spacing in the crystal.

The Lorentz and polarization factors are combined in a single Lorentz-polarization factor trigonometric correction:

$$Lp = (1 + \cos^2 2\theta)(2\sin 2\theta)^{-1} \tag{8}$$

The crystal attenuates the incident radiation as the atoms remove a portion of the incident intensity. This absorption (A) depends on the atomic composition of the crystal, the path length of the radiation through the crystal, and the wavelength of the incident radiation.

$$A = (V^{-1}) \int e^{-\mu L}\, dv \tag{9}$$

Where V is the unit cell volume, μ is the linear absorption coefficient (absorption per mm of material) and L is the path length, in mm.

During data collection, some crystalline materials decompose as a result of exposure to air or the energy of the radiation. A correction can be applied to the data collected by monitoring the relative intensity of several check reflections, sampled at regular intervals during collection. This correction may be applied by evaluating the average intensity (I_{ave}) at the end of every 97 data collected to the original intensity (I_{orig}) for the check reflection:

$$D = I_{orig} / I_{ave} \tag{10}$$

Thus, the final corrected form of the measured intensity, I_{corr}, is given by:

$$I_{corr} = I_{int}\, (Lp)^{-1} A^{-1} D \tag{11}$$

The overall scattering by all the atoms within the crystal unit cell is expressed by the structure factor, F_{hkl}. This description is the vector resultant of radiation scattered in the direction of the (h,k,l) reflection from n atoms within the unit cell, and with a phase of

α_{hkl} . Each atom type in the unit cell has a scattering factor, *f*, associated with the energy scattered by it, and dependent upon the atomic size and electron density[190] :

$$F_{hkl} = \sum_{j}^{n} f_j \, e^{2\pi i(hxj + kyj + lzj)} \tag{12}$$

The variables x_j, y_j, and z_j are positional parameters of the jth atom in the unit cell. Since the Euler relation, $e^{i\alpha} = \cos\alpha + i\sin\alpha$, then $\mathbf{c}_j\, e^{i\alpha j} = \mathbf{A}_j + i\mathbf{B}_j$ for mutually orthogonal vectors (where $\mathbf{A}_j$ and $\mathbf{B}_j$ represent the real and the imaginary projection components of the vector, $\mathbf{c}_j$). The scattering factor (12) describes the projection of the scattered vector from atom_{hkl} on the x and y axes, and can be expressed in complex form:

$$F_{hkl} = A_{hkl} + i\, B_{hkl} \tag{13}$$

The relationship $A_{(hkl)} = \sum_{j}^{n} f_j \cos\alpha_j$ and $B_{(hkl)} = \sum_{j}^{n} f_j \sin\alpha_j$, indicates that:

$$A_{hkl} = \sum_{j}^{n} f_j \cos 2\pi\, i(hx_j + ky_j + lz_j) \tag{14}$$

and

$$B_{hkl} = \sum_{j}^{n} f_j \sin 2\pi\, i(hx_j + ky_j + lz_j) \tag{15}$$

A helpful reduction utilizing the phase angle, α_{hkl}, with (13) is

$$F_{hkl} = |\, F_{hkl} \,|\; e^{i\alpha}{}_{(hkl)} \tag{16}$$

where

$$|\, F_{hkl} \,| = (A_{hkl}{}^2 + i\, B_{hkl}{}^2)^{1/2} \tag{17}$$

is the amplitude of the scattered wave. This amplitude is an important quantity that is proportional to the square root of the corrected intensity:

$$|F_{hkl}| = K_s (I_{corr})^{1/2} \tag{18}$$

where K_s is the scale factor of the data set. The data reduction process results in the conversion of collected intensities (I_{hkl}) to F_{hkl} values. Corrected intensity data converted in this fashion is referred to as the observed structure factor, F_{obs}. The standard deviation of this converted value is determined by :

$$\sigma F = 1/2K(Lp)^{1/2} [C + C_{bgr} + C_{bgl} + (0.01C_{pk})^2] / (C - C_{bgr} - C_{bgl})^{1/2} \tag{19}$$

where C_{pk} (peak count) = $C - C_{bgr} - C_{bgl}$. Background counts on the right and left of the peak count is C_{bgr} and C_{bgl}, and C is the total peak count.

In order to obtain a three dimensional description of a periodic distribution of particulate matter, the information in the scattered radiation must be de-convoluted in a Fourier synthesis. In X-ray crystallography, this structure factor transforms to give the density of electrons at any point, x,y,z, within the unit cell.

$$\rho (xyz) = V^{-1} \sum_h \sum_k \sum_l \; F(hkl)^{[-2\pi i(hx + ky + lz)} \tag{20}$$

The density of electrons at hkl (0,0,0) produces an intensity representative of all the scattering electrons in the unit cell, so that the structure factor is written $|F(000)|$. Friedel's Law indicates that for a structure factor at hkl, there should be a structure factor that has equal A and B magnitudes at $\overline{hkl}$. From (14) and (15) it is apparent that terms involving cosine will maintain an identical term sign ($\cos -x = \cos x$), but that with the sine function will become negative. If $\Phi = 2\pi(hx + ky + lz)$ when substituted into (11) gives :

$$|F| = A \cos \Phi + B \sin \Phi - i(A \sin \Phi - B \cos \Phi) \qquad (21)$$

and the $i(A \sin \Phi - B \cos \Phi)$ terms cancel for each pair of reflections *hkl* and $\overline{hkl}$. Thus, half of the values vanish. The remaining terms are summed over only half of the reflections, and in complex form, (20) becomes:

$$\rho\,(xyz) = |F(000)|V^{-1} + 2V^{-1} \sum_{h>0} \sum_{k} \sum_{l} |F| \cos(\Phi - \alpha) \qquad (22)$$

where $|F(000)|$ is the intensity for the total scattering electrons in the unit cell, and the factor of 2 is present since only half of the reflections are summed. If $|F|$ and α (the phase angle) are known, then the ρ values can be computed for each x,y, and z, and the plot will give rise to a three dimensional electron density map from which the structure can be deduced. Only the amplitude of the structure factor is obtained from the intensity data. The phase angle of each vector is not part of the information collected and α must be derived. This is referred to as the "phase problem" in crystallography, and requires an approximation by the formation of a trial structure or by a purely analytical technique where α can be calculated.

For small molecule analysis, there are two methods of deriving the phases for a structure. *Direct methods* have the objective of determining enough correct phases from observed data to deduce the correct structure. This is a technique which depends on the resulting electron density map to have maxima at the correct location of atoms, and that the density map may have no negative portions (there is no "negative electron density"). This reduces the difficulty of determining phases, since they are constrained to be non-negative. Therefore, calculation of the map, which is dominated by high intensity data, is attempted using only the largest structure factors. For structures which have a center of symmetry at the origin, the phase angle will be 0 or π so that $\cos \alpha$ is +1 or −1, and $\sin \alpha = 0$. Then the $|F|$ is + or -. Thus, the phase of a significant number of reflections are determined.

The structure factors must be normalized to the observed values, in shells of 10° θ, before producing an electron density map. The following normalization technique produces structure factor information that is independent of $\sin \theta/\lambda$:

$$|E_{hkl}| = |F_{hkl}| (\varepsilon \sum_j f_j^2 (h,k,l))^{-1/2} \qquad (23)$$

where ε is an integer constant associated with the crystal class and deviations of specific groups of intensities from expected values. If the structure lacks symmetry, the intensities are nearer the mean value of the intensities than those for a centrosymmetric system:

$|E| = (\sqrt{\pi})/2 = 0.866$ for non-centrosymmetric systems

$|E| = (\sqrt{2\pi}) = 0.798$ for centrosymmetric systems

The normalized structure factors are utilized to map the positions of atoms in the structure.

Unitary structure factors , U, are also useful in phase sign determination, following the Harker-Kasper inequalities method:

$$U^2_{hkl} \leq 1/2 \pm 1/2 |U_{2h,2k,2l}| \qquad (24)$$

Where $U = F_{hkl}/F_{000}$. This initial method provides a determination of the phase sign of a strong reflection in terms of its magnitude with respect to other strong reflections in the data set. The unknown in this expression is $|U_{2h,2k,2l}|$. U^2 must be positive, therefore the determined value of $|U_{2h,2k,2l}|$ must lead to a positive solution to satisfy (24).

After several phases have been assigned, the Sayer expression allows determination of the relationship between these phase angles:

$$\text{Sign}(h,k,l) \approx \text{sign}(h',k',l') \times \text{sign}(h-h',k-k',l-l') \qquad (25)$$

where sign(h,k,l) is $F_{hkl}/|F_{hkl}|$ and is positive or negative, and (h,k,l), (h',k',l') and (h-h',k-k',l-l') are triplets of strong observed reflections. This relationship indicates that reflections having indices related to a particular strong reflection should have the same sign as that reflection. The probability of a correct sign determined by this method is evaluated by the following expression:

$$P = \tfrac{1}{2} + \tfrac{1}{2}\tanh[\{\sigma_3\sigma_2^{-3/2}\}|E(h,k,l)E(h',k',l')E(h-h',k-k',l-l')|] \qquad (26)$$

where $\sigma_k = \sum_{j}^{N} n_j^k$ and n_j is the scattering power of the jth atom.

The determination of phases for non-centrosymmetric systems is achieved by the tangent formula, since they are not restricted to 0 or π values :

$$\tan[\alpha] = \frac{\sum_{h'} |E(h',k',l')E(h-h',k-k'l-l')| \sin(\alpha(h',k',l') + \alpha(h-h',k-k',l-l'))}{\sum_{h'} |E(h',k',l')E(h-h',k-k'l-l')| \cos(\alpha(h',k',l') + \alpha(h-h',k-k',l-l'))} \quad 27$$

where α is the phase angle for the structure factor at hkl.

The *Patterson method* of structure solution is useful if atoms of atomic number greater than 16 are present in the structure. This method utilizes a Fourier synthesis that includes $|F_{hkl}|^2$ and the indices of each reflection so that phase angles are not required to form a structural map. The Patterson function is defined by;

$$P(uvw) = \frac{1}{V}\sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(hu + kv + lw) \qquad (28)$$

where u,v,w represents a vector terminus in the Patterson map arising from a direction vector between two heavy atoms in the unit cell. This notation implies the presence of two electron densities at (x_1,y_1,z_1) and (x_2,y_2,z_2) such that the relative vector coordinates are $u=x_2-x_1$, $v=y_2-y_1$, $w=z_2-z_1$. The solution of the vector value includes radial and angular information, and can be related to the positions of other atoms in the structure by vectors that form triangular sets. If the symmetry of the cell includes translations, mirrors, or rotation axes then Patterson peaks are seen as lines or planes, called "Harker lines" or "Harker planes". If the cell is centrosymmetric, then the x,y,z and the $\overline{x,y,z}$ positions generate a Patterson vector with a 2x,2y,2z magnitude from which the x,y,z positions can be directly determined. Only heavy atom positions can be determined by the Patterson method, and their location is the basis for the initial structure refinement.

After a number of phases have been determined (by direct or Patterson methods), a trial structure can be identified from the electron density map and phased structure factors can be calculated (F_{calc}). The magnitudes of the calculated structure factors are compared with the observed structure factors (F_{obs}). Least squares refinement modifies the positional parameters of the atoms in the model to improve the "fit" of the model. By finding the difference between the observed structure factors and the calculated ones (difference Fourier map, $|F_{obs}|$ - $|F_{calc}|$) the refinement allows the location of atomic positions not accounted for in the initial model.

Initial refinement of a structure assumes atoms are points of electron density unperturbed from spherical shape by temperature and are therefore isotropic in librations about the axis passing through the center of the intensity peak. At an angle of 0, the atoms within the unit cell scatter as a function of the number of electrons present. For any other angle scattering ability decreases as the apparent center of mass of the electrons is distorted, and the incident waves intercept the electrons in a less efficient fashion. Scattering by an individual atom in terms of wavelength and angle is described by the scattering factor, f, and is determined by the function:

$$f_0 = \int a^{\frac{-B\sin^2\theta^2}{\lambda}} \qquad (29)$$

where the constant a is related to the atomic number of a stationary atom, and B is the Debye temperature factor. This expression, when evaluated for a specific atomic type, results in the analytical expression:

$$f = f_0 \exp(-B_{iso}\sin^2 \theta^2/\lambda) \qquad (30)$$

where f_0 is the scattering factor of a stationary atom. B_{iso} is the Debye isotropic thermal parameter:

$$B_{iso} = 8\pi^2 \langle u \rangle^2 \qquad (31)$$

where $\langle u\rangle^2$ is the mean-square amplitude of the atomic vibration. This function is valid for isotropic treatment, but a more realistic representation of atomic volume is described by the analytic function:

$$\exp[-(b_{11}h^2 + b_{22}h^2 + b_{33}h^2 + b_{12}hk + b_{13}hl + b_{23}kl)] \qquad (32)$$

where the six thermal parameters, b_{ij}, are anisotropic displacement parameters. This calculation provides a probability volume that is ellipsoidal in shape, and that is proportional to the probability estimate (normally 50%) and is utilized to graphically evaluate the structure.

The least squares refinement allows the calculation of an agreement factor:

$$R_f = \frac{\sum \left|\, |Fobs| - |Fcalc| \,\right|}{\sum |Fobs|} \qquad (33)$$

which is referred to as the residual factor. As the atomic positions, including the complete location of all non-hydrogen atoms in the model approach those in the crystal (observed data), R_f diminishes.

When all of the atoms in the model are present, hydrogen atoms (if present) are generated in ideal positions, unless visible in a Fourier difference map. An approximate weighting scheme that accounts for systematic errors (except librations) can be applied:

$$w(h,k,l) = \frac{1}{\sigma^2[F_{obs}(h,k,l)]} \qquad (34)$$

where w(h,k,l) is the weighting factor, and σ is the standard deviation.

Another check on the progress of structural refinement is the goodness of fit,GOF:

$$GOF = \left[\frac{\sum w(|F_{obs}| - |F_{calc}|)^2}{n - m} \right] \tag{35}$$

where n is the number of refinement parameters and m is the number of observed reflections. When the calculated model correctly resembles the structure that produced the reflections, the value is about 1. Practically, crystals are imperfect as a result of internal dislocations of unit cells (mosaic disorder) and diffraction equipment does not produce purely monochromatic radiation. This extinction further attenuates the incident radiation in the experiment and can be corrected after most of the refinement steps are completed. Structural refinement is assumed complete when the R_f is between about 3% to 6% with reasonable bond distances and angles, and the GOF is approximately 1.

Modern computational tools, including IBM PC style computers, allow rapid and successful structural analysis by processing the large calculations necessary, very rapidly. Solution and refinement software is widely available, and obtainable for modest, or no cost for use on common computer equipment. In addition, modern X-ray diffractometer equipment relies on computerized data collection software to obtain the large number of data necessary, in an automatic mode. The software supplied for this purpose includes a software management package that provides the solution and refinement processes, and graphical visualization engines. The XSCANS[191] data collection package provides software that searches for and indexes collected reflections, determines unit cell parameters and Laue symmetry, operates intensity data collection, and the reduction of data providing files readable by solution and refinement software. Included is data preparation (XPREP) for solution, and a graphical engine (XP) for evaluating the structure solution and at various stages of refinement. Also included is software for absorption corrections (XEMP). A solution and refinement package that includes powerful direct and Patterson methods (SHELXS) and least squares refinement (SHELXL) is SHELX-98, written by George Sheldrick, for small- and macromolecular structural work on the IBM PC.[192]

CHAPTER III

LUMINESCENCE

Luminescence is the emission of photons from a substance that has undergone excitation of electrons by the absorption of energy. The energy absorption process determines the type of photoluminescence.[193-196] Methods of producing luminescence in molecules include: chemiluminescence (excitation by chemical reaction), bioluminescence (excitation by biological processes), electroluminescence (excitation by electrical energy), radioluminescence (excitation by radio frequency energy), and sonoluminescence (excitation by sound wave energy).

The quantized transitions of excited electrons are determined by selection rules that describe the states of the electrons in their new energy state. For atoms, four quantum numbers are required to specify the state of the electrons. For small diatomic molecules the addition of two symmetry properties is required. For complex non-linear polyatomic species, the total electron spin quantum number, **S**, alone is required. The values of **S** are derived from the sum of the spin moments of the electrons: for a two electron orbital this becomes values of $\mathbf{S} = s_1 + s_2, s_1 + s_2 - 1, \ldots, |s_1 - s_2|$ where s_1 and s_2 are the spin values of the two electrons. The quantized magnitude of the total spin vector for a molecule, **S,** is: $[S\ (S+1)]^{1/2}\hbar$ so that the possible orientations, called the multiplicity, is given by $\mathbf{M} = 2S + 1$. If $\mathbf{S} = 0$, then $\mathbf{M} = 1$. The unitary value represents the spin alignment of electrons called a singlet state. If electrons are unpaired, then a triplet state exists (**M** = 3). Upon excitation, if the spin orientation remains unity, the excited state remains a singlet. If the spin changes upon excitation, the triplet state exists.

Types of photoluminescence can also be defined by the rate at which emission occurs after excitation. The ground state electrons that gain energy by photon absorption arrive in the excited state and then begin to give up the energy they absorbed through several processes, ultimately as an emitted photon at a characteristic wavelength. The rate at which this emission occurs differentiates fluorescence from phosphorescence. Fluorescence is a long-lived radiative process where the emission wavelength is longer than the wavelength of the exciting radiation (Figure 1). This shift in wavelength is called Stokes Shift, and is a result of non-radiative processes within the molecule that diminish the energy available upon emission, although there are increased exceptions to this rule as species become more complex. The wavelength is longer because electrons are decaying from lower excited states than initially reached by excitation.

Photoluminescence is not observed at all in the infrared where strong mechanical coupling provides an excellent vibrational mechanism to reduce the energy of absorption completely. Since emission is one of several mechanisms employed by substances to achieve thermodynamic equilibrium after excitation, a dependence upon temperature exists such that increases in sample temperature favor vibrational losses that reduce the probability of emission. This internal conversion of electronic energy to vibrational energy occurs when the lower vibrational levels of a higher electronic state are close in energy to higher vibrational levels of a lower electronic state. The energy transfer occurs between these near-resonance coupled excited states rather than an excited and ground state, as there is no overlap of energy between the HOMO (highest occupied molecular orbital) and excited states. After the transfer of this energy to vibrational states, the energy rapidly dissipates to the ground state energy. Consequently, cooling the material reduces vibrational mechanisms that decrease the probability of emission.

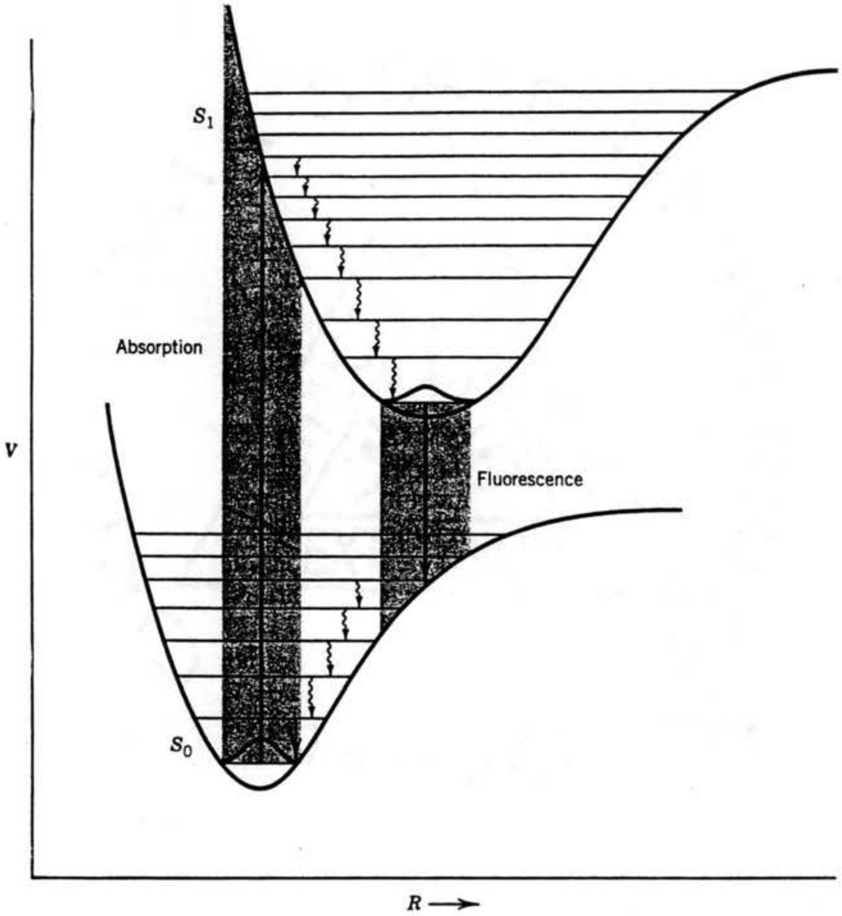


Figure 1. Fluorescence Electronic Mechanism Diagram

(Image from Alberty,R.A., *Physical Chemistry* 3rd ed. Wiley, Pub. **2001**)

The emission lifetime in fluorescence is approximately 10^{-8} seconds, while that of phosphorescence (Figure 2) is on the order of minutes to hr as a result of intersystem crossover, or triplet state electronic transitions from singlet states ($S_1 \rightarrow T_1$) . Since the change in multiplicity for internal crossover is forbidden, the decay process ($T_1 \rightarrow S_0 +$

hv) is slow. Fluorescence decay rates depend directly on the rate at which electrons return to the ground state after excitation, and in the case of phosphorescence, the rate at which triplet state electrons reverse spin in order to return to the ground state orientation.

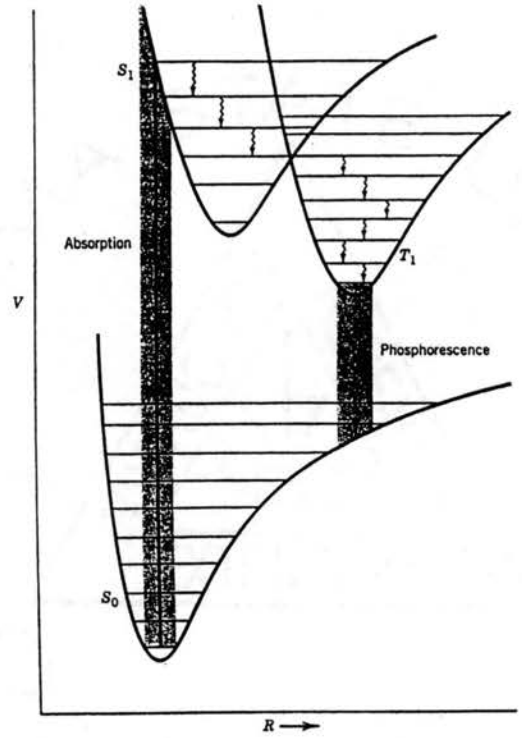


Figure 2. Phosphorescence Electronic Mechanism

(Image from Alberty,R.A., *Physical Chemistry* 3rd ed. Wiley, Pub. **2001**)

SYMMETRY

Electronic transitions involve interaction between the electrons of the molecule in combinations of orbitals and the electric vector component of electromagnetic radiation. Selection rules depend upon the symmetries of the ground state, the excited state, and an operator for the type of transition involved. Orbitals can be described by their symmetry properties, and the configurations representing the occupancy of the orbitals give rise to energy states that are also described by their symmetry properties. Selection rules for non-forbidden transitions depend solely upon the symmetry properties of the orbital wave functions and are determined from electric dipole selection rules. As a consequence, the magnitude of the emission of a fluorophore is proportional to the square of the electronic transition moment integral[98], $R_e=\int \psi_{el}\ \mu\ \psi_{el}^*\ d\tau$, where ψ_{el} and ψ_{el}^* are the electronic wave functions for the ground and excited electronic states, respectively, and μ is the electric dipole moment operator. Analytical evaluation of this integral would require well-understood wave functions for each transition, but the application of symmetry diminishes much of the necessary calculation needed for evaluation. For an allowed electronic transition $|\,\mathbf{R_e}\,| \neq 0$, and the symmetry requirement is $\Gamma(\psi_{el}) \times \Gamma(\mu) \times \Gamma(\psi_{el}^*) = A$ where A is the totally symmetric representation for the point group of the species and $\Gamma(\psi_{el})$, $\Gamma(\mu)$, and $\Gamma(\psi_{el}^*)$ are the symmetry representations for the ground state wave function, the electric dipole moment operator, and the excited state wave function, respectively. The calculation of the total vector $\mathbf{R_e}$ requires integration of the volume of space occupied to evaluate the resulting electric dipole translation vectors along the three axis system, T_x, T_y and T_z:

$$R_{ex}=\int \psi_{el}\ \mu_x\ \psi_{el}^*\ d\tau \qquad (1)$$

$$R_{ey}=\int \psi_{el}\ \mu_y\ \psi_{el}^*\ d\tau \qquad (2)$$

$$R_{ez}=\int \psi_{el}\ \mu_z\ \psi_{el}^*\ d\tau \qquad (3)$$

And since

$$|\,R_e\,|^2 = (R_{e,x})^2 + (R_{e,y})^2 + (R_{e,z})^2 \qquad (4)$$

electronic transitions are allowed if any of R_{ex}, R_{ey}, or R_{ez} is non-zero. Then for an allowed transition, the symmetry requirements are:

$$\Gamma(\psi_{el}) \times \Gamma(T_x) \times \Gamma(\psi_{el}^*) = A \quad (5)$$

$$\Gamma(\psi_{el}) \times \Gamma(T_y) \times \Gamma(\psi_{el}^*) = A \quad (6)$$

$$\Gamma(\psi_{el}) \times \Gamma(T_z) \times \Gamma(\psi_{el}^*) = A \quad (7)$$

If the product of all terms are identical in symmetry (all equal A), then the product of any two symmetry species in the system is also A, and the total transition vector symmetry reduces to $\Gamma(\psi_{el}) \times \Gamma(\psi_{el}^*) = \Gamma(T_x)$ and/or $\Gamma(T_y)$ and/or $\Gamma(T_z)$. In the case of transitions between degenerate orbitals, the symmetry set is contained in the total vector, and a reduction in terms occurs.

This result produces the following symmetry rules:

1) For a centrosymmetrical molecule, all wave functions are *gerade*, g, or *ungerade*, u (even or odd parity, respectively). For a pair of electrons with a wave function of A_g symmetry (gerade, even) the HOMO they inhabit is also A_g since $A_g \times A_g = A_g$. The centrosymmetric molecule contains an inversion center and the electric moment operator in the integral for the excited state necessarily becomes ungerade, and the orbital, which will contain the excited electrons, must be A_u so that the integrand will maintain gerade symmetry : g x u x u = g. This leads to the selection rule for centrosymmetric systems that transitions g → u and u → g are allowed, but g → g and u → u are forbidden.

2) Transitions between states of different multiplicity are forbidden as a result of orthogonal spin functions, α and β (+1/2 and –1/2).

3) Transitions in molecules without a center of symmetry depend upon the symmetry of the initial and final states, so that transitions from HOMO to LUMO (lowest unoccupied molecular orbital) are not forbidden.[197]

MOLECULAR CHARGE DISTRIBUTIONS

The Born-Oppenheimer approximation of the total electronic wavefunction for an n electron molecule is given by:

$$\rho_{el}(r) = -ne\int \Psi^{*}\Psi dr_2 dr_3 ....dr_n \quad (8)$$

where the integration is over all but one electron coordinate.

The charge distribution in molecules is discussed by the molecular wave function: the total electronic wave function gives the *electron charge distribution.* By multiplying the wave function integral of a molecular species by the charge of an electron and the number of electrons, the resulting expression describes the electron charge distribution.

For a linear molecule, the charge distribution is given by the multipole expansion of the electric potential:

$$\Theta(r) = \frac{q}{(4\pi\varepsilon_o)r} + \frac{p\cos\theta}{4\pi\varepsilon_o r^2} + \frac{\Theta(3\cos^2\theta - 1)}{2(4\pi\varepsilon_o)r^3} + ... \text{ higher order terms,} \quad (9)$$

where the first term is the charge (total), the second term is the dipole, the third is the quadrupole, and higher terms describe electron charge distributions of higher order, such as octupole and etc.

$$q = \int \rho(r')d\mathbf{r}' = \text{ the net charge} \quad (10)$$

$$p = \int \rho(r')r\cos\theta d\mathbf{r}' = \text{ the dipole moment} \quad (11)$$

$$\Theta = \int \rho(r')r''^2 (\frac{3\cos^2\theta - 1}{2})d\mathbf{r}' = \text{the quadrupole moment} \quad (12)$$

In (11) and (12), θ is the angle of the vector pointing to the point r from the molecule and the z-axis through the molecule.[198] The field gradient ($\frac{\partial V^2}{\partial^2 z}$) at nucleus A, q^A, in a molecule is related to the electronic wave function by (12) so that the effect of a quadrupole interaction on a nucleus by the electrons surrounding it can be evaluated in terms of orbital interactions. The symmetry of an s orbital causes the quadrupole interaction to be zero, as there is no net field gradient in the spherical environment. For p and d orbitals, where asymmetry exists, the effects on the field gradient are given by

$$e^2 Qq_{mol} = [(1 - s + d - i (1 - s - d)] e^2 Qq_{atom} \qquad (13)$$

where e^2Qq_{atom} is the quadrupole coupling constant for a particular atom, s is the fraction of s character employed in a bond with its neighbor, d is the fraction of d orbital character in the bond, and i is the fraction of ionic character. As the amount of ionic character increases, the electronic environment approaches spherical symmetry and $e^2 Qq_{mol}$ decreases. Hybridization of the p-orbital with an s orbital also decreases $e^2 Qq_{mol}$ as does mixing the s orbital with the p orbital (more spherical) since the field gradient decreases. If the atom under investigation is electropositive, i changes sign. For a molecule A-B, $\Psi^0 = c\psi_a + d\,\psi_b$ and $i = c^2 - d^2$ so that the coefficients derived from evaluation of the electronic wavefunction give the contributions to the orbitals from each bonding atom. In a covalent molecule, d orbital contribution to bonding increases the field gradient.[199] The field gradient is a positive term at the nucleus of a metal atom, and the quadrupole coupling constant decreases (negative field gradient) with increasing σ donor strength of the ligands in linear complexes.[200] The opposite effects are predicted in the case of s-p hybridization. The mixing of d and s orbitals also increase the field gradient in a positive direction.[201]

There is a specific interaction between incident electromagnetic radiation and the electric dipole of the molecule when excitation occurs that is described by the dipole moment operator.[202] The magnitude of the absorption is dependant upon this interaction as becomes apparent below in (14).

Quadrupole interactions are dependant upon symmetry constraints and geometric alignment. Quadrupole terms vanish in the presence of tetrahedral and octahedral symmetries, or in some three-fold and higher symmetries. Linear arrangements allow only one of the five possible independent components of quadrupole interactions. These quadrupole terms become important in molecules where a significant quadrupole moment exists in combination with symmetry conditions that allow strong coupling within the molecule[203], and alter the ligand field splitting constant in some symmetry allowed molecules.[204]

LUMINESCENCE

Luminescence studies are performed with a spectrofluorometer utilizing multiple beam optics for correcting perturbations and attenuation by the sample from the incident exciting radiation during measurements. The basic components are the excitation source, a monochromator to select the radiation wavelength, a sample container or cell, a detection monochromator, and detector. The spectrofluorometer is equipped with two radiation sources, typically a low-pressure xenon lamp for visible to mid-ultraviolet radiation, and a mercury arc lamp for shorter wavelength vacuum ultraviolet radiation. Monochromators serve to select the excitation wavelength desired within a narrow bandwidth, and to select the fluorescence wavelength maxima entering the detector. The xenon lamp presents a reasonably smooth background that is easily compensated for in the twin beam instrument, and the mercury arc lamp which has several large maxima in the source background radiation superimposed on the baseline of the spectrum. Careful adjustments of the monochromator are required for vacuum UV excitation with the mercury arc lamp.

The emission radiation from the sample passes through slits to the emission monochromator. The detector PMT (photomultiplier tube) is placed at 90^{0} with respect to the exciting source to diminish detection of scattered light. The detected radiation is sent to a difference amplifier, where the output voltage from the reference beam provides a I/I_0 measurement. In some varieties of instrument, a single measurement of background is subtracted from the PMT output to correct for sample and system perturbation of the fluorescence emission.

The detector is normally a PMT that has a high gain and broad spectral sensitivity that is required for the detection of low intensity fluorescence emission. The output is sent to a computer software package that displays emission characteristics such as intensity, counts per second, wavelength of the maxima, etc.

Information about the energy levels of molecules may be obtained by careful examination of luminescence. In combination with *Ab-initio* techniques, an understanding of electronic excited states, transition energies, and bonding characteristics can be realized.

Modern computational methods allow the evaluation of the electric and magnetic dipole vector values for possible transitions in a molecule. The presence of a dipole suggests an allowed transition, while a determination of the dimensionless *oscillator strength* (14) predicts the magnitude of the energy of excited electrons in the transitions responsible for fluorescence. Comparison of the emission maxima measured for a molecule can be compared with the predicted values to help understand the electronic states responsible for the absorption and emission process.

$$f = \frac{8\pi^2 m_e \nu}{3he^2}\left|\int \Psi^* \mu \Psi d\tau\right| \quad \text{where } \mu = -\mathbf{er} \qquad (14)$$

The Hamiltonian operator for a wave function may be determined and evaluated, but the Schrödinger equation for the wave function is not solvable for molecules since the term that evaluates the repulsions of electrons from those of neighboring atoms cannot be separated from the rest of the function. Approximations of the behavior of electrons in molecular environments have been developed that combines two principles that apply generally, and are computationally feasible. The Hartree-Fock[205] approximation (15) determines the repulsions of electrons by estimating the potential energy that exists as a sum of contributions from all of the electrons. The wave equation then becomes solvable.

$$H \approx -\frac{\hbar}{2me}\sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi\varepsilon_o r_i} + \sum_i V(r_i) \qquad (15)$$

The set of solutions obtained from this function can be used to form a potential energy surface for a molecule giving the best energy fit, and the wave functions that result from this process are called the molecular orbitals for the species. The resulting potential energy evaluation is based on the *Born-Oppenhiemer approximation* where the positions of the nuclei are rigid in space, and the electronic wave functions describe the electrons as centrally located about the nucleus. This does not allow for evaluation of the bonding character of the electronic wave function about the nuclei. The Hartree-Fock approximation can be made to include diffuse wave functions for orbitals that allow a separation of the outer electron wave functions from those of core electrons about each nucleus. These Gaussian functions produce a set of orbitals for the atoms called the *self-*

consistent field approximation (HF-SCF) (16) of the spherical potential for each electron's movement. This potential is determined from contributions by all the surrounding electrons.

$$H^{eff}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{A}^{nuclei}\frac{Z_A}{r_{1A}} + \sum_{j}^{N/2}[2\hat{J}_j(1) - \hat{K}_j(1)] \qquad (16)$$

The first two terms of (16) represent the kinetic energy operator of the electron, and the attraction between one electron and the nuclei of the molecule (core Hamiltonian), similar to equation (15). The next term contains two functions: $\hat{J}(1)$ is called the coulomb operator that accounts for the smearing out effect of electronic potential as a result of two electrons in an orbital, and the last term is the exchange operator used to correlate the spin orientation of the two electrons.

Determining a realistic geometry is computer-time expensive, and various techniques are utilized to eliminate as much computation time as possible. Many geometry configurations require the writing of hundreds of thousands of integrals in order to approximate the geometry of the species. A significant savings in time, and an improvement in geometry approximation, is obtained through the utilization of accurately determined structures from X-ray diffraction studies. A reduction in computational overhead arises when *single point* calculations can be performed that eliminate the need for geometry optimization. The computational requirement is then for evaluation of outer sphere electronic behavior, resulting in less costly approximations of the wave functions for the molecular system in the ground and in the excited states.

As molecular size and complexity increase, the approximation of separate instantaneous electronic motion within an orbital becomes more important. The difficulty arises from the HF-SCF computation, which does not correlate electron trajectories well. Consider two electrons in an orbital. Since there is repulsion between them, it is energetically favorable for one electron to be far from the nucleus when the other is near it. The calculated approximation is poor in terms of the evaluation of instantaneous motions of an electron due to the presence of another electron. A *Configuration Interaction* (CI) technique, that considers a number of excited states by evaluating them with the HF ground state wave function rather than a diffuse potential arising from the collective set of electrons, improves the approximation of energy for the excited state configuration. The expansion coefficients for the wave functions of the excited states are varied in the calculation until energy minima are reached. Since the excited configurations have a large percentage of their probability density far away from the nuclei, convergence is slow, and only electrons from the HOMO to the first allowed LUMO are considered in detail. A less elaborate technique for excited state configuration determinations may be used initially, with more excited states, to determine the correct orbital configurations needed for more careful examination. The result of careful analysis of these excited states leads to an understanding of the fundamental processes and energies for similar systems that share the characteristic fluorescence properties in this study.

CHAPTER IV

EXPERIMENTAL

Materials used in this study were commercial, reagent-grade products used without further purification. Solvents used were acetone, 95% ethyl alcohol, dichloromethane, and de-ionized water. Alkali and alkaline earth halides were dissolved in minimum amounts of water or added directly to the metal halides in acetone. Crystalline products were stored in room air until utilized for characterization.

SYNTHESIS:

(I) [Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$I$_4$)

A 1.00 mmol (0.220 g) portion of silver iodide was mixed with 10 mL of a 5.00 mmol (1.30 g) aqueous solution of cesium iodide in a 50-mL round-bottomed flask. Acetone (30 mL) was added and the resulting mixture stirred until homogeneous. To the light yellow solution, 2.00 mmol (0.626 g) of dicyclohexano-18-crown-6 was added and the mixture heated under reflux for two hr. The clear solution was gravity filtered and allowed to stand. Within 2 hr, clusters of small clear, prismatic rod-shaped crystals formed.

(II) [Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$Br$_4$)

A 1.00 mmol (0.280 g) portion of silver bromide as mixed with 10 mL of a 5.00 mmol (1.370 g) aqueous solution of cesium bromide in a 50-mL round-bottomed flask. Acetone

(30 mL) was added and the mixture stirred until homogeneous. To the light yellow solution, 2.00 mmol (0.626 g) of dicyclohexano-18-crown-6 was added and the mixture refluxed for 2 hr. The clear solution was gravity filtered and allowed to stand. Within 24 hr, small, transparent prism shaped and square flat plate shaped crystals formed along the bottom surface.

(III) [Sr(benzo-15-crown-5)$_2$](Ag$_2$I$_4$)

A 1.00 mmol (0.220 g) portion of silver iodide was mixed with 5 mL of a 5.00 mmol (0.680 g) aqueous solution of strontium iodide in a 50-mL round-bottomed flask and 30 mL of acetone added with stirring until all solids dissolved. To the clear solution, 1.50 mmol (0.402 g) of benzo-15-crown-5 was added and the mixture heated under reflux for 13 hr. The milky white solution was gravity filtered and allowed to stand. Within 2 days, clusters of small flat rhombic crystals formed.

(IV) [Rb(benzo-15-crown-5)$_2$]$_2$(Ag$_2$I$_4$)

A 2.00 mmol (0.440 g) portion of silver iodide was mixed with 5 mL of a saturated RbI aqueous solution in a 50-mL round-bottomed flask along with 40 mL of acetone and stirred until homogeneous. To the light yellow solution, 2.00 mmol (0.536 g) of benzo-15-crown-5 was added and the mixture heated under reflux for 3 hr. The clear solution was gravity filtered and within 24 hr, small hexagonal rod-shaped crystals formed.

(V) $[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2Br_4)$

A 1.00 mmol (0.220 g) portion of silver bromide was mixed with 10 mL of a saturated aqueous solution of RbI in a 50-mL round-bottomed flask. An additional 20 mL of acetone was added and stirring was continued until the mixture was homogeneous. To the light yellow solution, 3.00 mmol (0.784 g) of benzo-15-crown-5 was added and the mixture was heated under reflux for 3 hr. The clear solution was gravity filtered, and within 24 hr, colorless rhombohedral crystals were observed.

(VI) $[K(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2I_4)$

A 2.00 mmol (0.440 g) portion of silver iodide was mixed with 5.0 mL of an aqueous saturated KI solution in a 50-mL round-bottomed flask with an additional 40 mL of acetone and stirred until the mixture was homogeneous. To the light yellow solution, 2.00 mmol (0.500 g) of dibenzo-18-crown-6 was added and the mixture was heated under reflux for 12 hr. The clear solution was gravity filtered and allowed to stand. Within 24 hr, small rod-shaped colorless crystals formed.

(VII) $[K(dicyclohexano\text{-}18\text{-}crown\text{-}6)(C_3H_6O)(H_2O)]_2(Ag_2I_4)$

A 1.00 mmol (0.220 g) portion of silver iodide was mixed with 5.0 mL of a saturated aqueous solution of KI in a 50-mL round-bottomed flask. Acetone (40 mL) was added and the mixture was stirred until homogeneous. To the light yellow solution, 2.00 mmol (0.550 g) of dicyclohexano-18-crown-6 was added and the mixture was heated under reflux for 24 hr. The clear solution was gravity filtered and allowed to stand. Within 24 hr, small colorless plates formed.

(VIII) [Na(benzo-18-crown-6)(H_2O)]$_2$(Ag_2I_4)

A 1.00 mmol (0.220 g) portion of silver iodide was mixed with 5.0 mL of an aqueous saturated NaI solution in a 50-mL round-bottomed flask. Acetone (20 mL) was added and stirred until the mixture was homogeneous. To the resulting light yellow solution, 2.00 mmol (0.536 g) of benzo-18-crown-6 was added and the mixture was heated under reflux for 18 hr. The clear solution was gravity filtered and allowed to stand. Within 24 hr colorless rhombohedral crystals formed.

(IX) [Cs(benzo-15-crown-5)](Ag_3I_4)$_n$

A 1.00 mmol (0.220 g) portion of silver iodide was mixed with 10.0 mL of an aqueous solution of CsI in a 50-mL round-bottomed flask. Acetone (20 mL) was added and the mixture was stirred until homogeneous. To the clear solution, 2.00 mmol (0.626 g) of benzo-18-crown-6 was added and the mixture was heated under reflux for 2 hr. The clear solution was gravity filtered and allowed to stand. Within 5 days needle-like crystals formed.

(X) [Ba(benzo-15-crown-5)$_2$]$_2$(Ag_4I_8)

A 1.00 mmol (0.220 g) portion of silver iodide was mixed with 1.0 mmol $BaI_2 \cdot 2H_2O$ (0.427 g) in a 50-mL round-bottomed flask along with 25 mL of acetone and was stirred until homogeneous. To the light yellow solution, 2.00 mmol (0.536 g) of benzo-15-crown-5 was added and the mixture was heated under reflux for 5 hr. The clear solution was gravity filtered and allowed to stand. Within 4 days, colorless, small plates and slender rod crystals formed.

(XI) [Cs(18-crown-6)](Ag_2I_3)$_n$

A 2.00 mmol (0.440 g) portion of silver iodide was mixed with 5.0 mL of aqueous CsI in a 50-mL round-bottomed flask. Acetone (20 mL) was added and the mixture stirred until homogeneous. To the clear solution, 2.00 mmol (0.523 g) of 18-crown-6 was added and the mixture was heated under reflux for 18 hr. The clear solution was gravity filtered and allowed to stand. Within 3 days rod-like crystals, and after five days, square crystals formed. Both types of crystal were colorless.

(XII) [K(benzo-18-crown-6)](AuI_2)

A 2.00 mmol (0.648 g) portion of gold iodide was mixed with 5.0 mL of a saturated aqueous solution of KI in a 50-mL round-bottomed flask. A 20 mL portion of acetone was added and the mixture stirred until homogeneous. To the clear orange solution, 2.00 mmol (0.626 g) of benzo-18-crown-6 was added and the mixture was heated under reflux for 18 hr. The clear yellow-gold solution was gravity filtered and allowed to stand. Within 5 days orange needle-like crystals formed.

(XIII) [K(benzo-15-crown-5)$_2$](AuI_2)

A 1.00 mmol (0.320 g) portion of gold iodide and 1.00 mmol of silver iodide (0.220 g) was mixed with 5.0 mL of a saturated aqueous solution of KI in a 50-mL round-bottomed flask. A 30 mL portion of acetone was added and the mixture stirred until homogeneous. To the clear solution, 2.00 mmol (0.540 g) of benzo-15-crown-5 was added and the mixture was heated under reflux for 24 hr. The clear amber solution was gravity filtered and within 24 hr brown prismatic rods formed.

(XIV) [Cs(dicyclohexano-18-crown-6)](AuI_2)

A 1.00 mmol (0.324 g) portion of gold iodide was mixed with 0.520g of CsI in 5.0 mL of water. This was mixed in a 50-mL round-bottomed flask with 20 mL of acetone and stirred until homogeneous. To the clear solution, 2.00 mmol (0.626 g) of dicyclohexano18-crown-6 was added and the mixture was heated under reflux for 10 hr. The clear colorless solution was gravity filtered. Within three days rod-like crystals, and after 5 days, prismatic crystals formed.

(XV) [Cs(benzo-15-crown-5)$_2$](AuI_2)

A 1.00 mmol (0.320 g) portion of gold iodide and 1.00 mmol of cesium iodide (0.260 g) in 3.0 mL of 95% ethanol was mixed in a 50-mL round-bottomed flask with 30 mL of acetone and the mixture stirred until homogeneous. To the dark yellow solution, 1 mmol (0.270 g) of benzo-15-crown-5 was added and the mixture was heated under reflux for 18 hr. The clear yellow solution was gravity filtered and allowed to stand. Within 24 hr large, orange rhombic crystals formed.

(XVI) [Rb(benzo-15-crown-5)$_2$](AuI_2)

A 1.00 mmol (0.325 g) portion of gold iodide was mixed with 10 mL of a saturated aqueous solution of RbI in a 50-mL round-bottomed flask. A 20 mL portion of acetone was added and the mixture stirred until homogeneous. To the light yellow solution, 3 mmol (0.804 g) of benzo-15-crown-5 was added and the mixture was heated under reflux for 18 hr. The clear solution was gravity filtered and allowed to stand. Within 2 days clear, prismatic rod crystals formed.

(XVII) $(Ag_4I_8)(P(Ph)_2Me)_4$

A 2.00 mmol portion of silver iodide (0.440 g) was mixed with 2.00 mmol of tri-*m*-tolylphosphine (0.550g) in 100 mL of CH_2Cl_2 and heated under reflux for 24 hr. The clear solution was gravity filtered allowed to evaporate to dryness from a 50-mL beaker. After 3 days, large cubic crystals formed.

(XVIII) $(Ag_4I_8)(P(m\text{-tolyl})_3)_4$

A 2.00 mmol portion of silver iodide (0.440 g) was mixed with 2.00 mmol of tri-*m*-tolylphosphine (0.550g) in 40 mL of CH_2Cl_2 (re-distilled) and was heated under reflux for 24 hr. The clear solution was gravity filtered and allowed to evaporate to dryness. After 5 days, large clear cubic crystals formed.

(XIX) $(Ag_4I_8(P(p\text{-tolyl})_3)_4)$

A 2.00 mmol portion of silver iodide (0.440 g) was mixed with 2.00 mmol of tri-*p*-tolylphosphine (0.550g) in 40 mL of CH_2Cl_3 and was heated under reflux for 24 hr. The clear solution was gravity filtered and set aside to evaporate to dryness. After 3 days, colorless cubic crystals formed .

(XX) $(Ag_2I_2)(P(Ph)_2Me)_4$

A 2.00 mmol portion of silver iodide (0.440 g) was mixed with 2.00 mmol of bis(diphenylphosphino)methane (0.769g) in 40 mL of 95% methanol and was heated under reflux for 24 hr. The clear solution was gravity filtered and set aside to evaporate to dryness. A gelatinous product was then re-dissolved in ether and set aside to recrystallize. Large, colorless flat crystals formed after 2 days.

(XXI) $(Ag_2I_2(PPh(Me)_2)_4)_2$

Recrystallization of compound **XX** in $CHCl_3$ produced a fine powder. This powder was then dissolved in acetonitrile and, upon standing, produced a gelatinous material. This was dissolved in ether, and crystallization upon standing produced plate-like colorless transparent crystals.

(XXII) $(AgI(P(m\text{-tolyl})_3)_3)$

XVIII was dissolved in ether with heating. Large transparent square crystals formed upon standing for 2 days.

(XXIII) $[K(\text{dicyclohexano-18-crown-6})(H_2O)_2]Br$

A 1.00 mmol (0.280 g) portion of silver bromide was mixed with 5.0 mL a saturated aqueous solution of KBr in a 50-mL round-bottomed flask along with 20 mL of acetone and stirred until homogeneous. To the light yellow solution, 2.00 mmol (0.550 g) of dicyclohexano-18-crown-6 was added and the mixture was heated under reflux for 18 hr. The clear solution was gravity filtered and allowed to stand. Within 24 hr, small flat plates and rhombic shaped crystals formed.

(XXIV) $[Ba(\text{benzo-15-crown-5})](I_2)$

A 1.00 mmol (0.285 g) portion of silver bromide was mixed with 10 mL of an aqueous saturated solution of $BaBr_2$ in a 50-mL round-bottomed flask. A 20 mL portion of acetone was added and the mixture was stirred until homogeneous. To the light yellow solution, 2.00 mmol (0.540 g) of benzo-15-crown-5 was added, and the mixture was heated under reflux for 2 hr. The clear solution was gravity filtered and allowed to stand. Within 24 hr prism shaped crystals formed.

(XXV) [Mg(18-crown-6)(H_2O)$_6$](I)$_2$

A 1.00 mmol portion of MgI_2 (0.278 g) was mixed with 2.00 mmol of silver iodide (0.440 g) in a 50-mL round-bottomed flask with a 30 mL portion of acetone The mixture was stirred until homogeneous. 2.00 mmol (0.552 g) of 18-crown-6 crown ether was dissolved in this solution and heated under reflux for 24 hr. The resulting dark yellow liquid was gravity filtered and allowed to stand. After 24 hr, yellow cubic and plate-like crystals formed.

(XXVI) [Sr(benzo-15-crown-5)$_2$ (H_2O)](I_2)

A 2.00 mmol (0.440 g) portion of silver iodide was mixed with 5.0 mL of a 5.00 mmol (0.680 g) solution of strontium iodide in a 50-mL round-bottomed flask. Acetone (30 mL) was added and the mixture stirred until homogeneous. To the clear solution, 2.00 mmol (0.540 g) of benzo-15-crown-5 crown ether was added, and the mixture was heated under reflux for 13 hr. The solution was gravity filtered into an open beaker and allowed to stand. Within 2 days, clusters of small flat rhombic crystals formed.

(XXVII) [Sr(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$)$_2$

A 2.00 mmol (0.440 g) portion of silver iodide and 1.00 mmol (0.190 g) of copper iodide was mixed with 5.0 mL of a 5.00 mmol (0.680 g) solution of strontium iodide in a 50-mL round-bottomed flask. Acetone (30 mL) wa added and the mixture stirred until homogeneous. To the clear solution, 2.00 mmol (0.536 g) of benzo-15-crown-5 crown ether was added whereupon the solution became milky white. The mixture was heated under reflux for 24 hr. The solution was gravity filtered and allowed to stand. Within 2 days, clusters of small flat rhombic crystals formed.

(XXVIII) [K(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$)

A 1.00 mmol (0.220 g) portion of silver iodide and 1.00 mmol (0.190 g) of copper iodide was mixed with a saturated aqueous solution of KI (dropwise until clear) in a 50-mL round-bottomed flask. Acetone (40 mL) was added and the mixture was stirred until homogeneous. To the light yellow solution, 2.00 mmol (0.536 g) of Benzo-15-crown-5 was added and the mixture was heated under reflux for 24 hr. The clear solution was gravity filtered and allowed to stand. Within 24 hr, small hexagonal rod-shaped crystals formed along the bottom surface.

CRYSTALLOGRAPHY

Crystals of suitable size (< 0.2 mm in all dimensions) of regular form were chosen for X-ray crystallographic diffraction studies. These crystals were mounted on glass fibers cemented to brass supports and fixed to a goniometer. An automated Siemans P4 four-circle diffractometer integrated with a 486DX PC was used for data collection. The diffractometer was equipped with a molybdenum target source for X-rays of 0.71073 Å wavelength (weighted average of $K_{\alpha 1}$ and $K_{\alpha 2}$ maxima) and the source was operated at 50 KV and 30 mA. Unit cell dimensions were determined using centered angles from 25-50 independent intense reflections and refined by a least-squares method using the data collection software, XSCANS.[206] The data were collected at room temperature using a variable scan rate and a θ-2θ scan mode with a scan range of 0.6° below and above the initial 2θ value. The limit of 2θ is normally 60°, or the observed diffraction limit of the sample. Backgrounds were measured at the ends of the scan range for a combined time equal to the total scan time. The intensities of three standard check reflections were measured after each 97 data to monitor sample decomposition. The collected data were corrected for Lorentz, polarization, decomposition, and background effects. Redundant data and symmetry forbidden data were removed from the data set, and data were reduced with a profile fitting technique.

Direct methods (SHELXS) utilizing observed reflections ($F \geq 4.0\ \sigma F$) localized non-hydrogen positions in most cases.[207] When direct methods failed, heavy atom positions were determined utilizing Patterson methods. Successive refinement and difference Fourier cycles then allowed the location of the remaining non-hydrogen atoms. Refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms and the scale factor was accomplished with SHELXL (refinement based on F^2) until convergence.[208] The International Tables for Crystallography provided scattering factors.[209] Hydrogen atom positions were calculated using idealized geometry and a fixed C-H distance of 0.97 Å. An extinction correction and a weighting scheme was applied in the last steps of the refinement..The weighting was based on counting statistics and was equal to $\left(w = \frac{1}{\sigma^2 F + |g| F^2} \right)$. Final refinement led to the agreement factor, $R_{w.}$

FLUORESCENCE

Crystalline samples used for luminescence studies were ground to a fine powder and applied to a double-sideded tape surface of a non-emitting 0.5 x 1.5 cm cardboard. The samples, cooled for low temperature studies, were attached to a 0.5 x 2.5 cm quartz vessel containing liquid nitrogen.

The emission spectra of all samples were measured in a Fluorolog FL3-11 spectrofluorometer utilizing a R928P photomultiplier tube as the detector, and a Xenon lamp as the source of UV radiation, shown in Figure 3.

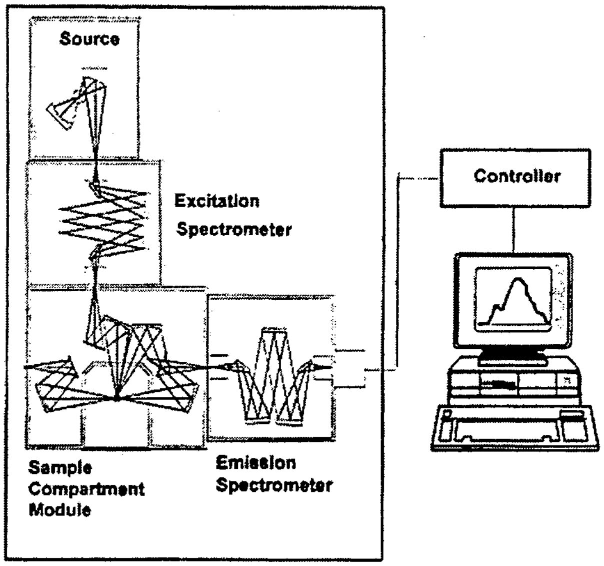


Figure 3 . Block Diagram of the Fluorolog 3

The spectrum of each sample was measured at low temperature with an excitation wavelength of 250 or 300 nm using monochromator slit widths of 2.5 nm, and integration intervals of 0.1 s. A background and low temperature blank spectrum was determined for data treatment. Spectra of pure metal halides and crown ethers were compared with the spectra of samples to eliminate the possibility of spectral defects arising from unreacted materials. None were observed in any sample spectrum. All were positioned at a 45^{o} front surface angle with respect to excitation and detector windows (90^{o} collection angle) to eliminate reflection of source radiation. Data were corrected for background and recorded as a spectrum with relative intensity plotted against wavelength, in nm.

CHAPTER V

RESULTS AND CONCLUSIONS

Synthetic efforts produced 26 compounds previously unreported. These compounds fall into four main groups with two further miscellaneous groups : i) 8 rhombohedral $[Ag_2X_4]^{2-}$ silver(I) halide-crown ether adducts, ii) 5 linear gold(I) -crown ether adducts ($[AuI_2]^-$), iii) 3 polymeric silver(I) iodide structures ($[Ag_3I_4]^-$, $[Ag_4I_8]^{4-}$, $[Ag_5I_6]^-$) with crown ethers, iv) 4 crown ether encapsulated cations with halide counter ions, v) 1 tetrahedral, 2 rhombohedral and 3 tetrameric silver(I) iodide phosphines, and vi) 2 rhombohedral $[Cu_2I_4]^{2-}$copper(I) iodide crown ether adducts (re-preparations). Selected crystallographic data for the structural work are given in Table 4, while complete results are listed in Tables 12 through 156. Projection views of crystallographic results are given in Figures 16 through 48. Emission spectra for two compounds of group i (**II, V**), one compound in group iii (**X**), and both compounds of group vi are given in Figures 17, 22, 28, 46 and 48, respectively. Results of *ab-initio* computations are given in Tables 6 and 10, and graphical results in Figures 4-13.

TETRAIODODIARGENTATES

Eight new compounds were synthesized containing an anionic tetraiodoargentate moiety $[Ag_2I_4]^{2-}$ in which two bridging iodides connect two trigonal planar silver atoms, each having a terminal iodide ligand. All of these rhombic structures are planar, with minor distortions of the terminal ligand angles with respect to the plane of the rhomb.

Table 4. Synthesized Compounds

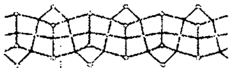
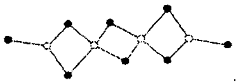
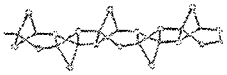
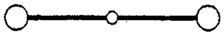
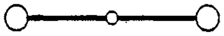
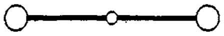
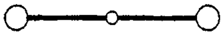
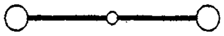
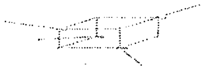
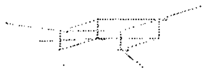
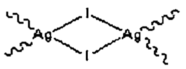
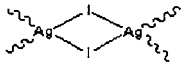
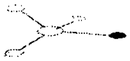
Structure	Compound	Motif Type	Unit Cell Size	Cell Angles.	Space Group	Sample #
	[Cs(DCH-18-crown-6)]$_2$(Ag$_2$I$_4$)	$[Ag_2X_4]^{2-}$	a =12.69 b =8.705 c =25.08	α = β =95.28 γ =	P2(1)/c	I
	[Cs(DCH-18-crown-6)]$_2$(Ag$_2$Br$_4$)	$[Ag_2X_4]^{2-}$	a =12.581 b =8.492 c=24.477	α = β =95.0 γ =	P2(1)/c	II
	[Sr(benzo-15-crown-5)$_2$](Ag$_2$I$_4$)	$[Ag_2X_4]^{2-}$	a =12.016 b =12.523 c =13.202	α = β =91.47 γ =	P2(1)/c	III
	[Rb(benzo-15-crown-5)$_2$](Ag$_2$I$_4$)	$[Ag_2X_4]^{2-}$	a =12.314 b =12.436 c =12.600	α =102.96 β =94.73 γ =110.15	P-1	IV
	[Rb(benzo-15-crown-5)$_2$](Ag$_2$Br$_4$)	$\{Ag_2X_4]^{2-}$	a =12.023 b =12.486 c =12.986	α =106.13 β =91.07 γ =111.42	P-1	V
	[K(benzo-15-crown-5)$_2$](Ag$_2$I$_4$)	$[Ag_2X_4]^{2-}$	a =12.331 b =12.452 c =18.044	α =103.32 β =95.33 γ =111.11	P-1	VI
	[K(DCH-18-crown-6)(C$_3$H$_6$O)(H$_2$O)] (Ag$_2$I$_4$)	$[Ag_2X_4]^{2-}$	a =14.216 b =17.910 c =12.111	α = β =91.98 γ =	C2/m	VII
	[Na(benzo-18-crown-6)(H$_2$O)]$_2$ (Ag$_2$I$_4$)	$[Ag_2X_4]^{2-}$	a =9.316 b =9.691 c =12.880	α =91.94 β =95.17 γ =100.61	P-1	VIII
	[Cs(benzo-15-crown-5)](Ag$_3$I$_4$)	$[Ag_3X_4]^{-}$	a =13.385 b =26.26 c =8.33	α = β =106.11 γ =	P2(1)/c	IX
	[Ba(benzo-15-crown-5)$_2$](Ag$_4$I$_8$)	$[Ag_4X_8]^{4-}$	a =13.372 b =11.714 c =25.622	α = β =102.46 γ =	P2(1)/c	X
	[Cs(18-crown-6)](Ag$_2$I$_3$)	$[Ag_5X_6]^{-}$	a =25.965 b =11.449 c =18.873	α = β =120.30 γ =	C2/c	XI
	[K(benzo-18-crown-6)](AuI$_2$)	$[AuX_2]$	a =17.058 b =15.457 c =8.831	α =90 β =90 γ =90	Pna2(1)	XII
	[K(benzo-15-crown-5)$_2$](AuI$_2$)	$[AuX_2]$	a =19.483 b =13.061 c =15.421	α = β =116.63 γ =	C2/c	XIII
	[Cs(DCH-18-crown-6)](AuI$_2$)	$[AuX_2]$	a =8.486 b =14.258 c =22.716	α =90 β =90 γ =90	P212121	XIV
	[Cs(benzo-15-crown-5)$_2$](AuI$_2$)$_2$	$[AuX_2]$	a =11.93 b =13.07 c =13.32	α =96.38 β =116.0 γ =103.43	P-1	XV
	[Rb(benzo-15-crown-5)$_2$](AuI$_2$)$_2$	$[AuX_2]$	a =11.838 b =13.02 c =13.164	α =97.79 β =115.36 γ =102.95	P-1	XVI

Table 4. Synthesized Compounds (cont.)

Structure	Compound	Motif Type	Unit cell, A size	Cell Angles	Space Group	sample #
	$(Ag_4I_8(P(m\text{-tolyl})_3)_4)$	$[Ag_4X_8]$	a =13.576 b =18.010 c =12.368	α =90 β =90 γ =90	$P2_12_12_1$	XVII
	$(Ag_4I_8(P(p\text{-tolyl})_3)_4)$	$[Ag_4X_8]$	a =28.128 b =28.128 c =28.128	α =109.45 β =109.45 γ =109.45	R3c	XVIII
	$(Ag_4I_8(P(p\text{-tolyl})_3)_4)$	$[Ag_4X_8]$	a =20.486 b =20.486 c =20.486	α =50.31 β =50.31 γ =50.31	R-3	XIX
	$(Ag_2I_2)(P(Ph)_2Me)_4$	$[Ag_2X_2]^-$	a =10.375 b =14.220 c =18.585	α =83.37 β =83.90 γ =79.44	P-1	XX
	$(Ag_2I_2(PPh(Me)_2)_4)$	$[Ag_2X_2]^-$	a =10.379 b =12.210 c =18.104	α =103.22 β =91.58 γ =114.49	P-1	XXI
	$(AgI(P(m\text{-tolyl})_3)_3)$	$[AgX]$	a =20.34 b =22.92 c =24.64	α =90 β =90 γ =90	Pbca	XXII
	$[K(DCH\text{-}18\text{-crown-}6)(H_2O)_2]Br$		a =6.890 b =10.283 c =10.293	α =109.83 β =106.99 γ =99.76	P-1	XXIII
	$[Ba(benzo\text{-}15\text{-crown-}5)](I_2)$		a =9.846 b =10.899 c =17.350	α = β =105.38 γ =	P2(1)/c	XXIV
	$[Mg(18\text{-crown-}6)(H_2O)_6](I)_2$		a =10.322 b =13.692 c =18.044	α =90 β =90 γ =90	Pnma	XXV
	$[Sr(benzo\text{-}15\text{-crown-}5)_2(H_2O)_2](I_2)$		a =9.829 b =10.567 c =17.287	α = β =106.01 γ =	P2(1)/c	XXVI
	$[Sr(benzo\text{-}15\text{-crown-}5)_2]_2(Cu_2I_4)$	(Cu_2X_4)	a =33.238 b =20.584 c =22.291	α = β =131.49 γ =	C2/c	XXVII
	$[K(benzo\text{-}15\text{-crown-}5)_2]_2(Cu_2I_4)$	(Cu_2X_4)	a =12.303 b =12.450 c =12.660	α =103.58 β =95.23 γ =111.19	P-1	XXVIII

The symmetry of these structures places them in two categories. Seven of the eight complexes (structures **I-VI** and **VIII**, cf. Table 4) have an inversion center at the center of the anionic moiety and one (structure **VII**) exists with a mirror in the plane of the rhomb and a two-fold rotation axis passing through the center of the rhomb and perpendicular to the mirror plane.

The compounds in the first group, i, have Ag-Ag distances that vary from 3.094 Å to 3.69 Å. Complexes **I** and **II** have a Ag-Ag distance of 3.094 and 3.325 Å, respectively.

For the compounds **I, II**, and **VIII**, this distance is within the sum of the van der Waals radii and may be interactive.[210] Terminal Ag-iodide distances range from 2.496 Å to 2.687 Å, and are shorter than the corresponding bridging Ag-X distances, which range from 2.645 Å to 2.830 Å. The bridging iodide has one longer and one shorter distance to the Ag centers. All terminal Ag-I distances are identical except in [K(dicyclohexano-18-crown-6)$(C_3H_6O)(H_2O)]_2(Ag_2I_4)$ **(VII)**, which has equal distances for terminal and equal distances and angles for both bridging ligand-metal bonds. This species exhibits the shortest Ag-Ag contact (2.955 Å), as well as a long bridging Ag-I distance (2.808 Å) and the smallest bridging I-Ag-I angle. This is the only product in this group to include solvent molecules within the crystal structure. No close-contacts to any atoms of the rhombs are present within group i.

Two of the structures (**I** and **II**) that crystallize in the $P2_1/c$ spacegroup are isostructural with a previously reported $[Cu_2I_4]^{2-}$ moiety.[24] Structure **II** has bromine ligands, and shows a larger bridging angle of 76.71° than the corresponding structure **I** bridging iodide angle of 67.31°. Structure **II** shows an emission maximum at 490 nm with

Table 5. Selected Structural Data for Iodoargentates

Compound	Space Group	Sample #	symm H-M/Sch.	close contacts Å	radius of cation	Ag-X-Ag (o) X-Ag-X angs.	Ag-X term. Å	Ag-X bridg Å	Ag-Ag Å
$[Cs(DCH\text{-}18\text{-}crown\text{-}6)]_2(Ag_2I_4)$	P2(1)/c	I			Cs	67.31			3.094
			C_i	I2--Cs 3.962	1.67	126.41	2.696	2.804	
			C^5_{2h}			120.88	2.696	2.779	
$[Cs(DCH\text{-}18\text{-}crown\text{-}6)]_2(Ag_2Br_4)$	P2(1)/c	II			Cs	76.71			3.3252
			C_i	Br2--Cs 3.6206	1.67	123.96	2.5367	2.6451	
			C^5_{2h}			132.74	2.5367	2.7131	
$[Sr(Benzo\text{-}15\text{-}crown\text{-}5)_2](Ag_2I_4)$	P2(1)/c	III			Sr	75.66			3.469
			C_i		1.18	127.77	2.684	2.826	
			C^5_{2h}			127.89	2.684	2.83	
$[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2\ (Ag_2I_4)$	P-1	IV			Rb	82.22			3.681
			C_i		1.52	134.66	2.643	2.777	
						127.54	2.643	2.821	
$[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2\ (Ag_2Br_4)$	P-1	V			Rb	84.54			3.568
			C_i		1.52	130.33	2.496	2.66	
						134.17	2.496	2.646	
$[K(benzo\text{-}15\text{-}crown\text{-}5)_2]_2\ (Ag_2I_4)$	P-1	VI			K	82.31			3.69
			C_i		1.38	127.82	2.644	2.828	
						134.46	2.644	2.777	
$[K(DCH\text{-}18\text{-}crown\text{-}6)(C_3H_6O)(H_2O)]_2\ (Ag_2I_4)$	C2/m	VII			K	63.49			2.955
			2/m		1.38	121.74	2.687	2.808	
			C^3_{2h}			121.74	2.687	2.808	
$[Na(benzo\text{-}18\text{-}crown\text{-}6)(H_2O)]_2\ (Ag_2I_4)$	P-1	VIII			Na	68.22			3.13
			C_i	I1-O(H_2O) 3.602	1.02	125.1	2.687	2.808	
						122.49	2.687	2.773	
$[Cs(benzo\text{-}15\text{-}crown\text{-}5)](Ag_3I_4)_n$	P2(1)/c	IX			Cs	61.74			3.338
			C_i		1.67	105.38		2.972	3.029
			C^5_{2h}			91.13		2.931	3.093
$[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2]_2\ (Ag_4I_8)$	P2(1)/c	X			Ba	70.38		2.742	3.354
			C_i		1.35	51.57		3.06	2.802
			C^5_{2h}			59.1			
$[Cs(18\text{-}crown\text{-}6)](Ag_2I_3)_n$	C2/c	XI			Cs	59.38		3.147	2.817
			2/m		1.67	55.86		3.046	2.967
			C^6_{2h}					2.853	3.2

300 nm UV excitation, while structure **I** (having iodide ligands) exhibits no emission under these conditions. The previously reported copper(I) species[24] that is isostructural with (**I**), has an emission maximum at 422 nm, and has a metal-metal distance of 2.790(3) Å, which is within the sum of the van der Waals radius of the copper metal centers.

Compounds **IV** ($[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2I_4)$) and **VI** ($[K(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2I_4)$) are isostructural with **XXVIII** ($[K(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Cu_2I_4)$, a copper(I) iodide complex having $[Cu_2I_4]^{2-}$ geometry, previously reported.[24] All three structures have bridging iodine ligands subtending a similar angle, and both terminal iodine ligand distances are equal for each cluster. This is consistent with the complexes forming in similar chemical environments; the cations have radii of 1.86 Å for Rb and 1.78 Å for K. Both are encapsulated in the same crown ether cavity. The copper(I) complex has an emission maximum at 475 nm, identical with that of the previously reported copper(I) complex.[24] The two silver(I) iodide complexes have no emission characteristics within the wavelength range of this study.

Complexes **IV** and **V** crystallized in the centrosymmetric space group $P\bar{1}$ and have similar stoichiometries with rubidium cations encapsulated in a benzo-15-crown-5 crown ether. The ligand in compound **V** is bromine, and terminal ligand-metal bond distances are shorter for the bromine version due to the decreased covalent radius of bromine. The Ag-Br-Ag bridging angle is larger (84.54° versus 82.22°) and bridging ligand-metal distances shorter, in **V** than in the iodide version (**IV**), similar to these structural differences in complexes **I** and **II**. The Ag-Ag distances in **IV** and **V** are 3.681 Å and 3.568 Å, respectively. Complex **V** exhibits emission at 305 nm with excitation at 250 nm at low temperature (100 K). Complex **IV** exhibits no emission characteristics. There are no close metal-metal contacts in either structure (Table 5). Complex **II** crystallizes in the $P2_1/c$ space group, has a similar stoichiometry as **I** , and a shorter contact distance with the encapsulated Cs cation than **I.** This complex is a bromide with a similar anionic fragment stoichiometry as **V**, but with terminal ligands distorted away from the center of symmetry in the rhomb, and bent away from planarity with it. Complex **II** has longer terminal ligand-metal distances than **V**, as well as longer bridging ligand-metal distances. The metal-metal distance in **II** is much shorter than that found in **V** (3.325 Å vs 3.568 Å), and the emission spectrum of **II** has a maximum at 496 nm under identical conditions as for structure **V**.

Ab initio calculations were performed using the Gaussian 98 software package for the tetraiodates with the LANL1DZ basis set that utilizes Gaussian type orbitals (GTO) to represent the non-valent core electrons for elements from Na to Bi.[211] The X-ray crystallographic determination of the solid-state geometry allows the use of a *Hartree-Fock* (HF) *single point* calculation method to eliminate computer calculations normally required to optimize geometry from first principles. A Z-matrix for each complex was constructed from the crystallographic data to serve as input for the Gaussian program. Since all of these structures are centrosymmetric, a central dummy position was placed at the center of symmetry and the Z-matrix vectors determined from this point. A final calculation involved the electron correlation interaction method (CI) where trajectories for one and two electron transitions were optimized. Evaluation of the relative absorption energy for the transitions was performed using the CI results. A natural orbital population bond order (NBO) analysis was performed to determine the location of charge density in the ground-state molecule. From the NBO results, the electronic notation for each atom, the orbital population, and the mixing or hybridization of each ground-state orbital was evaluated.[212,213,214] This analysis evaluates electron population about atomic centers based on bonding environments, where each bond is attributed electronic density considering the wavefunctions of electrons about the nucleus of the center, and which do not transform as symmetry elements of the molecule but remain essentially localized on atomic centers. The NBO is constructed from the diagonalized density matrix of the atom, and has angular symmetry based on the electronic structure of individual atoms in the molecule. This creates an orthonormal set of orbitals which are optimal for each atom in the bonded state, and the elimination of interatomic overlap produces a realistic assignment of charge to each atomic center. In addition, the analysis gives an estimate of hybridization, or a percent contribution of electrons in specific atomic orbitals to a particular bond. This differs from the arbitrary atomic charge and electron density based on local charges of the atoms (Mullikin populations).

Each anion has two silver (10 x 2) and four iodine (8 x 4) valence electron's involved in the calculations, for a total of 52 electrons in each anion. The calculations determined, in part, the energy involved in the transition from the highest occupied molecular orbital (HOMO) to the lowest allowed unoccupied molecular orbital (LUMO). Transitions of electrons in centrosymmetric species must follow symmetry rules for allowed and forbidden transition levels. In the case of silver(I) iodide centrosymmetric systems in this study, the *gerade* ↔ *ungerade* transition requirement produces symmetry allowed transitions of electrons from the B_u symmetry HOMO → LUMO + 2, +4, +5 levels and higher, having B_g and A_g symmetry. The silver(I) bromide systems have a HOMO with A_u symmetry, and allowed transitions are from HOMO → LUMO +2, +4, +5 levels and above, having A_g symmetry. Table 6 lists electronic orbital contributions for transitions which have large oscillator strengths and are more probable, and also the ground state hybridization from the NBO analysis.

Table 6. Electronic Orbital Contributions of Selected Complexes

(I) [Cs(Dicyclohexano-18-crown-6)]$_2$(Ag$_2$I$_4$)

	HOMO 26	LUMO+2 (29)	LUMO+5 (32)
Ag1 and Ag2	ground	excited	excited
Au-->Ag	**f = 0.2358**		
d_{z^2}	0.21364		
d_{yz}	-0.11582		
5s			-0.67811
5py		-0.13216	
6py		1.43098	
5pz			
Bridge Iodine			
5pz	0.24811		-0.12706
6pz	0.25965		
5s		-0.00741	0.12486
5px		0.01414	-0.2805
Terminal Iodine			
5s			0.39231
5pz	0.23975		
6pz	0.24861		
5py		-0.05836	
6py		-0.27344	
5px			0.13707

Ground State
Electronic structure
Ag (1) [Kr] $5s^{0.31}\ 4d^{9.98}\ 5p^{0.01}\ 6p^{0.02}$
$I_{bridg.}$ (2)[Kr] $5s^{1.95}\ 5p^{5.85}$
$I_{term.}$ (6) [Kr] $5s^{1.97}\ 5p^{5.90}$

(II) [Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$Br$_4$)

	HOMO 26	LUMO+2 (29)	LUMO+5 (32)
Ag1	ground	excited	excited
Au-->Ag	**f = 0.4377**		
$d_{x^2-y^2}$	-0.28676		
3pz		1.6419	
4pz		-1.32711	
3px			1.13874
4px			0.32218
Bridge bromine			
3py	0.1898		
4py	0.21699		
3px			0.35071
2s		0.16863	-0.35777

Table 6. (cont.)

Terminal bromine			
3px	0.28032		
4px	0.30378		
3py			
4py		0.07814	
2s			-0.35687

Ground State

Electronic structure

Ag (1) [Kr] $5s^{0.33}\ 4d^{9.92}\ 5p^{0.06}\ 6p^{0.02}$

$Br_{bridg.}$ (2)[Ar] $4s^{1.96}\ 4p^{5.85}\ 5p^{0.02}$

$Br_{term.}$ (6) [Ar] $4s^{1.96}\ 4p^{5.81} 5p^{0.02}$

Emission Maximum = 496 nm

(V) $[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2Br_4)$

	HOMO 26	LUMO+2 (29)	LUMO+5 (32)
Ag1	ground	excited	excited
Au-->Ag	**f =0.3945**		
d_{z^2}	0.01483		0.05929
d_{yz}	0.29588		
3py		-0.16528	
4py		1.25977	
3pz			0.44054
4pz			1.1364
Bridge Bromine			
3px	0.26992		
4px	0.29196		-0.22608
3py		0.00238	
4py		0.00523	
Terminal Bromine			
2s			-0.3377
3px	0.16733		
4px	0.19146		
3py		-0.06083	
4py		-0.20429	
3pz			-0.10423

Table 6 (cont.)

Ground State
Electronic Structure
Ag(1) [Kr] $5s^{0.26}\ 4d^{9.98}\ 5p^{0.02}\ 6p^{0.01}$
$\mathrm{Br_{bridge}}$ [Ar] $4s^{1.96}\ 4p^{5.88}$
$\mathrm{Br_{term}}$ [Ar] $4s^{1.97}\ 4p^{5.90}$
Emission Maximum = 305 nm

(X) $[\mathrm{Ba(benzo\text{-}15\text{-}crown\text{-}5)_2}](\mathrm{Ag_4I_8})$

	HOMO 52	LUMO+1 (54)	LUMO+2 (55)
Ag1 (distorted)	ground	excited	excited
Au-->Ag	**f = 0.75920**		
d_{xz}	-0.09937		
d_{yz}	-0.08977		
2s		-0.84812	0.61965
3px		-1.10157	-0.37569
4py			-0.38848
3pz			-0.45093
Bridge Iodine			
3px	0.18859		
4px	0.20628		
3py			-0.10848
Terminal Iodine			
2s		-0.27174	-0.26105
3px	0.08836		
4px	0.09747	0.14583	
3pz			-0.10848
Ag6 (4 coordinate)			
d_{z^2}	0.1036		
d_{yz}	0.16696		
3s		1.14707	0.39379
3py		-0.71296	1.22357
4py		-0.46189	0.82385
Bridge Iodine			
3px	0.18859		
4px	0.20628		-0.10848

Ground State

Electronic Structure

Ag1 [Kr] $5s^{0.28}\ 4d^{9.99}\ 5p^{0.01}\ 6p^{0.01}$

$\mathrm{I_{bridge}}$ [Kr] $5s^{1.96}\ 5p^{5.93}$

$\mathrm{I_{term}}$ [Kr] $5s^{1.95}\ 5p^{5.89}$

Ag6 [Kr] $5s^{0.28}\ 4d^{9.99}\ 5p^{0.02}\ 6p^{0.01}$

$\mathrm{I_{bridge}}$ [Kr] $5s^{1.94}\ 5p^{5.87}$

Emission Maximum = 309 nm

Table 6. (cont.)

(XIII) [K(benzo-15-crown-5)$_2$](AuI$_2$)

	HOMO 13	LUMO 14
Au	ground	excited
PIU-->PIG	**f =.0000**	
$5d_{yz}$		-0.35433
$6d_{yz}$		-0.06728
6Py	0.05502	
7Py	0.0434	
Iodine		
5Py	0.36547	
6Py	0.36556	
5Px		0.35262
6Px		0.39545

Ground State

Electronic structure

Au [Xe] $6s^{0.75}$ $5d^{9.83}$ $6p^{0.07}$ $6d^{0.07}$ $7p^{0.01}$
I [Kr] $5s^{1.94}$ $5p^{5.69}$ $6p^{0.02}$

No Emission

(XXVIII) [K(benzo-15-crown-5)$_2$]$_2$ (Cu$_2$I$_4$)

	HOMO 26	LUMO+2 (29)	LUMO+5 (32)
Cu1	ground	excited	excited
Au-->Ag		**f = 0.3414**	
d_{z^2}	0.16199		.0.2205
d_{xy}	-0.11319		-0.11604
3Py		-0.13906	
4Py		1.59869	
3pz			-0.12729
Bridge Iodine			
3pz	0.25938		0.24562
4pz	0.27213		0.24162
2s		0.00183	
4px		-0.00451	
Terminal Iodine			
3pz	0.24848		0.25727
4pz	0.25629		0.25061
3py		-0.05738	
4py		-0.29449	

Table 6. (cont.)

Ground State
Electronic Structure
Cu (1) [Ar] $4s^{0.40}\,3d^{9.85}4p^{0.06}\,4d^{0.11}5p^{0.02}$
$I_{bridg.}$(2) [Kr] $5s^{1.93}5p^{5.78}6p^{0.01}$
I_{term} (6) [Kr] $5s^{1.95}5p^{5.86}6p^{0.01}$
Emission Maximum = 450 nm

Analysis of *ab initio* calculations for the species in this study predicts the electronic behavior of the compounds producing the emission properties. The correlated interaction calculation predicts optimal transition symmetries for electrons which may not coincide with all symmetry allowed transitions. The Einstein population ratio for the transitions are determined and results in an oscillator strength (f). This number determines the probability of an excited state resulting from a particular series of one or two electron transitions. If a particular transition is associated with a small or zero oscillator strength, the probability of the excited state orbital being populated is zero. Oscillator values are listed in Table 10. In the excited states of the copper(I) and silver(I) species, certain symmetry allowed states are ignored as a result of a zero magnitude oscillator strength. In the instance of the copper and silver rhomb structures, LUMO + 4 has a zero oscillator strength, and is not discussed further. Orbital notations given are for the Gaussian type basis functions used to approximate wavefunctions from the LANL1DZ basis set. Ground state configuration with large coefficients are the location of electronic density in molecular bonding. Excited state MO's are considered populated if the oscillator strength is significant.

As a representative distorted centrosymmetric silver(I) iodide complex, structure **I** can be characterized in the ground and first excited state with a graphical representation of the molecular orbitals determined from the coefficients of the atomic contributions from *ab initio* calcualtions. The molecular orbital graph (Figure 4) indicates the location of electron density in the HOMO for the metal centers as $d_z{}^2$ and d_{yz} type orbitals mixed with p_z -like orbitals on both bridging and terminal iodine ligands. This corresponds well with the NBO calculated electronic structure that indicates ground state electron density donated to metal-ligand bonding from the metal centers is about 96% s, 2.2% p, and 1% d in origin. The terminal ligand bonds have a 26.2% s and 73.8% p character. The total bonding between the terminal ligand and metal is 6.63% metal based and 93.3 % ligand based. The bridging ligand also bonds with the metal having a 68.3% s and 31.68% p character. The excited state, LUMO + 2 (orbital 29), shows a transfer of electronic density to largely p_y orbitals centered over the metal atom-terminal ligand bond, while p_y orbitals centered over the terminal ligands remain. The orbital contribution to the metal center has increased and evolved into a p_y wavefunction while the wavefunction at the bridging ligand is very small. This suggests a transfer of electron density to the metal centers. Individual MO contributions are listed in Table 6.

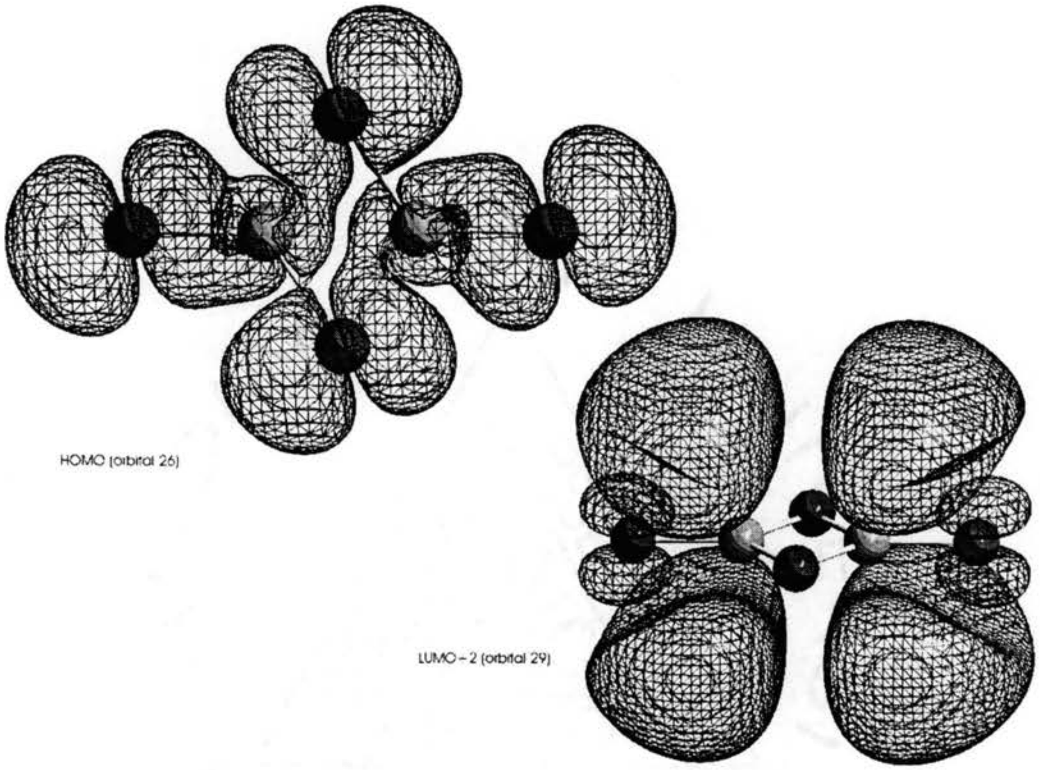
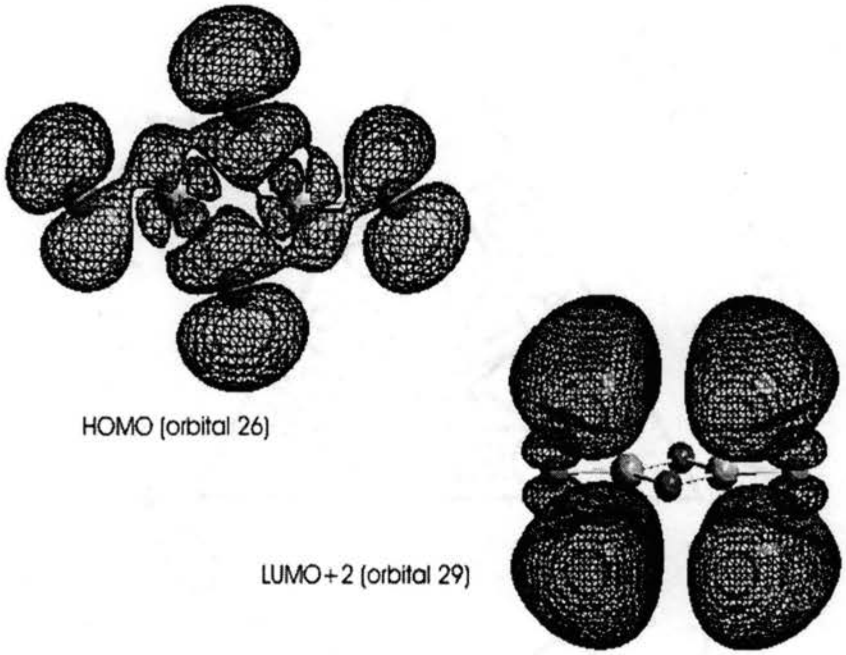


Figure 4. Graphical representation of the molecular orbital contributions in the ground and the first excited state for (**I**).

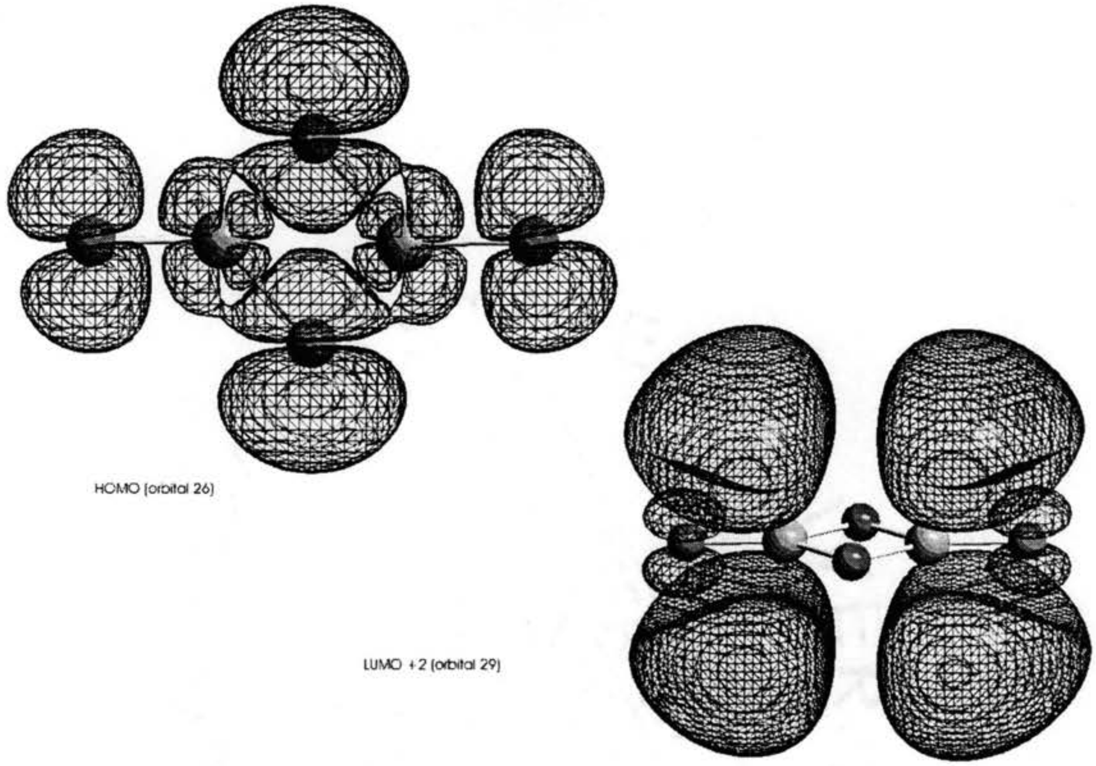
The disilver(I) tetrabromides are structures **II** and **V.** A graphical representation in the ground and excited states is given in Figures 5 and 6. The analysis of the wavefunctions for **II** indicates the ground state density configuration of the metal centers as 96.57% s, 2.37% p and 1.07% d in nature. The metal contributes 5.86% of the electron density to the metal-ligand bonds while the bromine ligands donate 94.14%.

The terminal ligand has an electronic character that is 24.06% s and 75.94% p while the bridging ligand is 74.64% s and 25.36% p.


HOMO (orbital 26)

LUMO+2 (orbital 29)

Figure 5. Graphical representation of the molecular orbital contributions in the ground and the first excited state for (**II**)


HOMO (orbital 26)

LUMO + 2 (orbital 29)

Figure 6. Graphical representation of the molecular orbital contributions in the ground and the first excited state for (**V**)

The molecular orbital graph of **V** indicates the wavefunction for ground state electron density of the metal centers as d_z^2 and d_{yz} like , while the bridging and terminal ligand bromine has electrons located principally in p_x type orbitals. The calculated NBO ground state electronic configuration predicts most of the metal electron bonding is from the s and p orbitals, with a small amount contributed by the d orbitals. The metal center bonding is 96.6% s, 2.15% p, and 1.26% d in character. The metal contributes 6.63% of the bonding while the terminal and bridging ligands contribute the remainder. The terminal ligand has an electronic character that is 24.2% s and 75.8% p while the bridging one is 61.3% s and 38.7% p. The excited state LUMO + 2 (orbital 29) indicates that the electron density is located in p_y type orbitals over the metal-terminal ligand bond. The metal centers also may have electron density in p_y orbitals. The terminal ligands have a wavefunction remaining as p_y orbitals. This suggests a ligand to metal transfer of electronic density in the excited state.

TETRAIODODICUPRATES

Two rhombohedral tetraiododicuprate anions were synthesized that have been previously reported. The structures conform to the crystallographic space group and have similar physical properties as determined by Nurtaeva et al.[24] A graphical representation of the electronic characteristics and NBO analysis are given in the discussion section of this chapter. The crystallographic data are listed in Table 4 for synthesized complexes, and orbital contributions are shown graphically in Figures 6 and 7.

For comparison purposes, a MO and NBO analysis of copper(I) tetraiodate complex (**IV** from reference 24) is shown in Figure 7. This complex is isostructural with the silver iodide complex, **I**, and displays a similar ligand orbital axis orientation in the ground state. The ground state metal center has a d_{z^2} and d_{yz} type orbital system mixing with p_z -like terminal and bridging iodine ligand orbitals. The NBO analysis predicts ground state electronic density donated from the metal center that is 97.4% s , 1.7% p, and less than 1% d in character. The terminal ligand has a bond character of 31.7% s and 68.2% p while the bridging ligand is 62.7% s and 37.3% p. The excited state wavefunction is centered over the metal-terminal ligand bond and has contributions from the bridging ligands to form p_y orbitals with no residual electron density on the bridging ligands, and a diminished amount that remains on the terminal ligand in a p_y orbital. This suggests that the transfer of electron density in the excited state is from the ligands to the

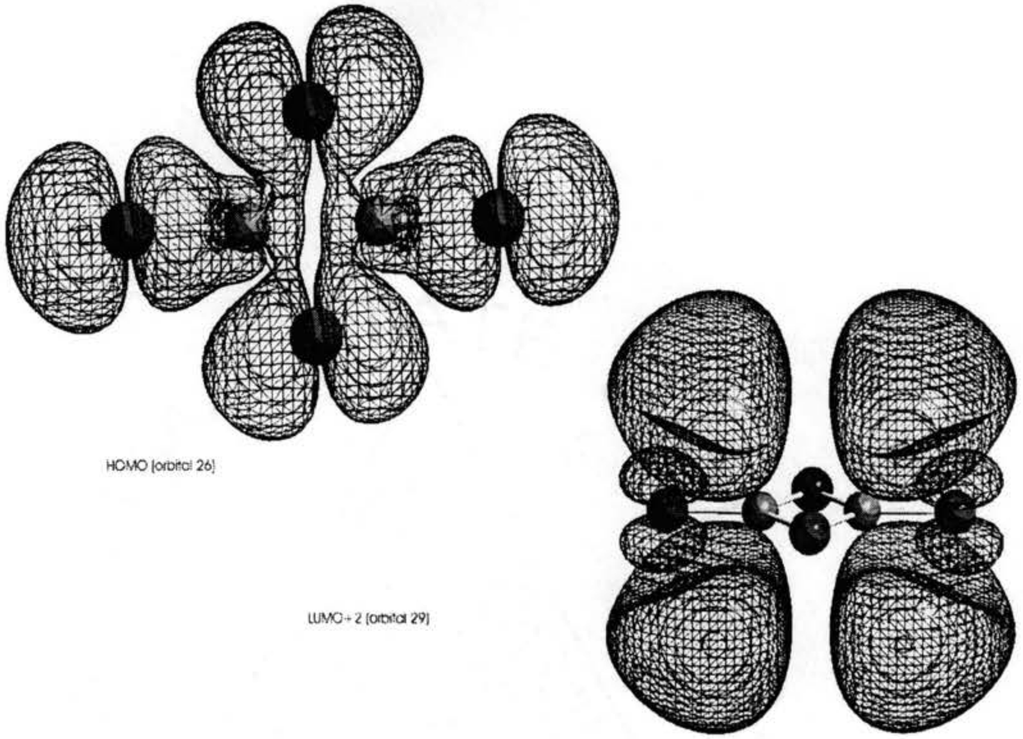
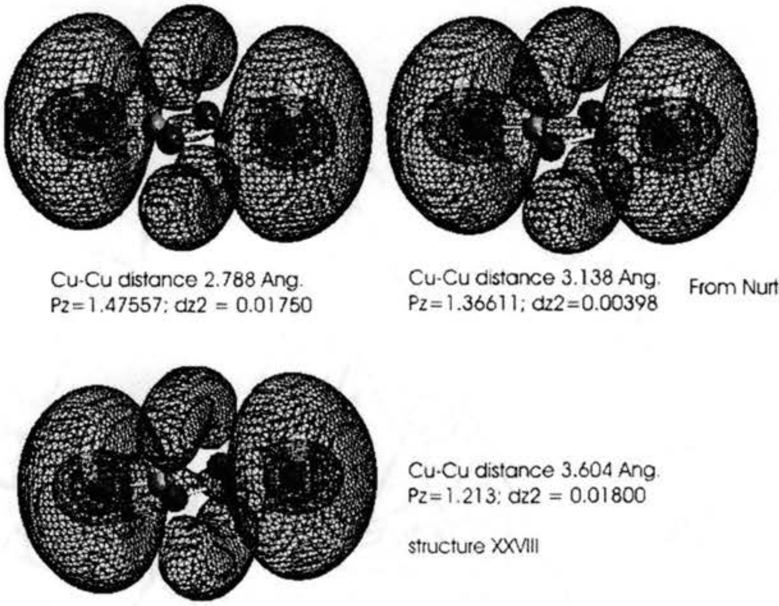


Figure 7 Graphical representations of the molecular orbital contributions in the ground and excited states for reference 24 $Cu_2I_4^{2-}$ anion

metal centers, similar to that of structure **I**. The excited states above the first symmetry allowed LUMO represent different orbital mixing, and as a result, the fifth excited state (orbital 32) shows significant metal-metal overlap (from CI analysis) in an orbital made from metal p_z and d_z^2 wavefunctions. This metallophilic bonding is present in all of the copper species evaluated with up to a metal-metal distance of 3.604 Å (Figure 7). The increasing distance between the metal centers reduces the magnitude of the contributions to this orbital configuration, as seen in Figure 8 for 2.788 Å (IV ref 24), 3.318 Å (VI ref 24) and 3.604 Å (**XXVIII**, this study). In addition, the amount of contributions to the d_z^2 and p_z orbitals increases in this excited state (Table 6). This result supports previously reported evidence of metal-metal interactions in copper compounds that have close metal-metal distances.[120,121,215]



Cu-Cu distance 2.788 Ang.
Pz=1.47557; dz2 = 0.01750

Cu-Cu distance 3.138 Ang.
Pz=1.36611; dz2=0.00398

From Nurtaeva et al.

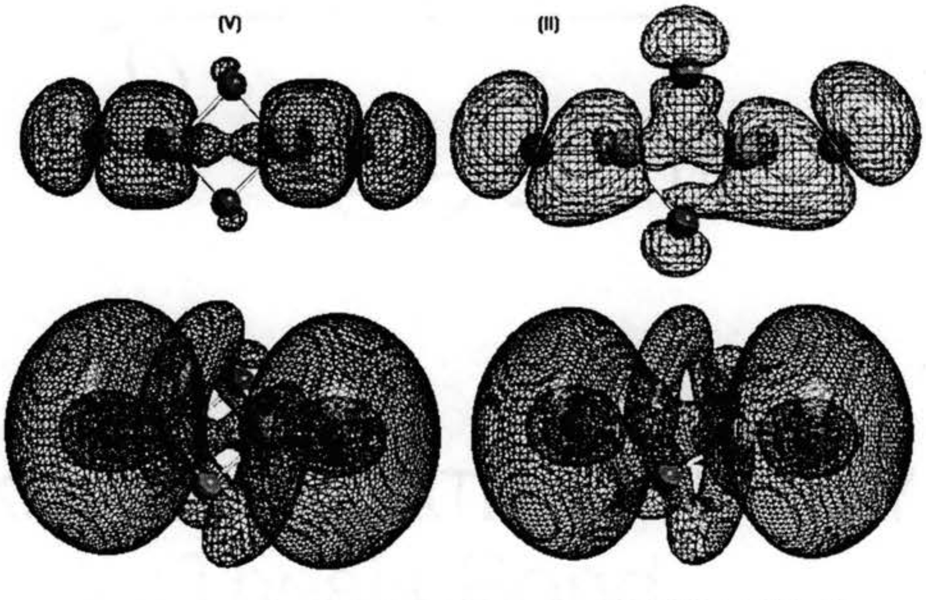
Cu-Cu distance 3.604 Ang.
Pz=1.213; dz2 = 0.01800

structure XXVIII

Figure 8. Metal-metal contacts in copper(I)

The shape of the orbital between the metals becomes narrowed with increasing metal-metal distance, until an hour-glass shaped volume is apparent at 3.604 Å. A similar computation for an idealized structure having a metal-metal distance of 3.680 Å shows no orbital overlap between the metal centers. There does not seem to be a correlation between emission energy and metal-metal distance, but it is significant to note that this interaction does not exist for any of the silver(I) tetraiodates, even when the metal-metal distance is much closer (**VII**, 2.955 Å), and none of these centrosymmetric silver(I) tetraiodate species have an emission profile between 320 nm and 770 nm.

A possible explanation for emission in the disilvertetrabromides can be found in the examination of CI calculations that predict transition probabilities. A wavefunction that bridges the two silver centers within the rhomb has a high oscillator strength associated with a transition to a higher, excited state wavefunction that also has significant overlap between the metal centers. Since the oscillator strength for this transition is high, the probability that it is populated upon excitation suggests that this overlap may be responsible for the ability of these silver complexes to luminesce. The silver complexes synthesized with iodine ligands do not show this metal-metal overlapping wavefunction in the ground state, or in any excited state. The presence of this overlap in the disilver tetrabromides, which is similar to that seen in the copper complexes, may provide a mechanism that allows emission that is not present in the iodine analogues. A graph of the wavefunctions for these electronic states in **V** and **II** is shown in Figure 9.



DisilverTetrabromide Ground and Excited States for (V) and (II) [HOMO-6 to LUMO+5]

Figure 9. HOMO-6 (orbital 20, top) to LUMO + 5 (orbital 32, bottom) of [Rb(Benzo-15-crown-5)$_2$]$_2$(Ag$_2$Br$_4$) **(V)**, [Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$Br$_4$) **(II)**

POLYMERIC SILVER IODATES

Two of the silver(I) iodate complexes synthesized are polymeric and built up from from four coordinate silver centers. A third polymeric species has both three and four coordinate silver centers. Structure (**IX**), [Cs(benzo-15-crown-5)](Ag_3I_4), is a polymeric double strand of edge sharing Ag_2I_4 rhombs having neighboring Ag edge atoms bridged by an additional iodide ligand (Figure 10). This structural polymer has been reported previously as chloride, bromide and iodide argentates with tetraphenyl phosphine, tetramethyl amines and tetrabutyl arsine counter ions.[85,102-104] Reported here is the form with Cesium benzo-15-crown-5 crown ether as the cation complex (Fig. 27). The structural details of this complex do not vary significantly from those reported for the other Ag_3I_4 polymers.[85] The metal-metal distances in this polymer range from 3.338(2) Å to 3.029(2) Å which is not within the van der Waals radii of the metals and is thus not a close contact. The Ag-I distances range from 2.770(17) Å to 2.9723(18) Å.

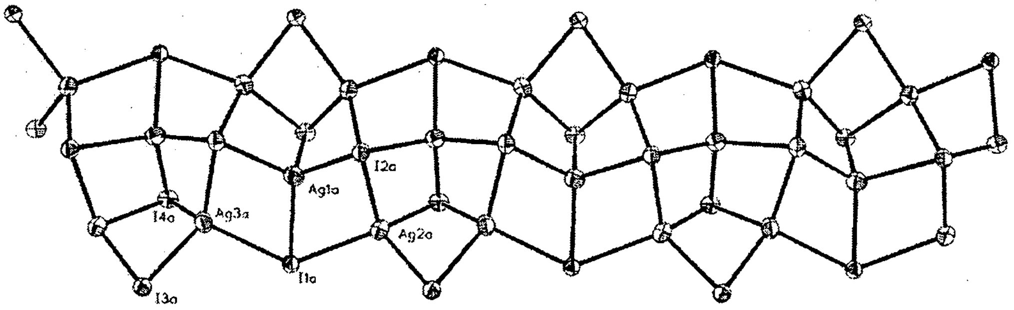


Figure 10 . [Cs(benzo-15-crown-5)](Ag_3I_4) (**IX**) Polymer Fragment

The second polymeric structure, [Cs(18-crown-6)](Ag_2I_3) (**XI**) (Figure 11.), is a previously unknown single ribbon of edge sharing Ag_2I_4 rhombs. The two Ag atoms of every other rhomb are bridged by an additional iodide ligand. These iodide atoms project a backbone structure in an *up up, down down* repetition. Examples of the copper analogue of this complex have been known since 1981,[41] with *up down, up down, up up, and up up down down* repetition. Three examples of the copper complex have been synthesized in this laboratory[24]. Metal–metal distances in this silver(I) polymer range from 2.817(2) Å to 3.200(4) Å while metal ligand bond lengths range from 2.712(2) Å to 3.147(3) Å.

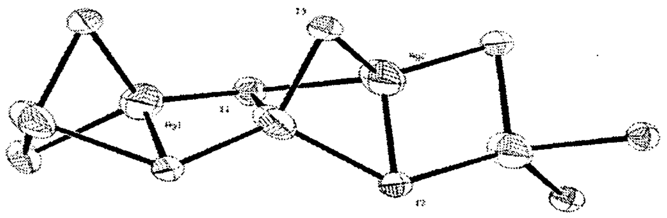


Figure 11. Cs(18-crown-6)](Ag_2I_3) **(XI)** Polymer Fragment

The third structure, [Ba(benzo-15-crown-5)$_2$](Ag_4I_8) **(X)** (Figure 12.) is a pair of four coordinate Ag centers bridged by two iodine ligands forming a rhomb containing a center of symmetry. Each silver metal is attached, via two further bridging iodide atoms, to a three-coordinate silver center having a terminal iodide. The bond distances to the bridging halides in the center rhomb are 3.059(3) Å and 2.742(2) Å while in the monomeric rhombic silver complexes the bridging distance is from 2.606(2) Å to 2.808(2) Å. The terminal iodide ligand bond length is 2.663(3) Å compared to a range of 2.606(1) Å to 2.690(2) Å observed in the monomer species. The Ag_4X_8 complex is reported [85,86] with tetraphenyl phosphonium and tetraphenyl arsonium counter ions as Ag_4Cl_4 or Ag_4Br_4. This is the first report of Ag_4I_4. The metal-metal contact distances in the previously reported complexes are much longer than those found in structure **X** (2.967(4) Å).

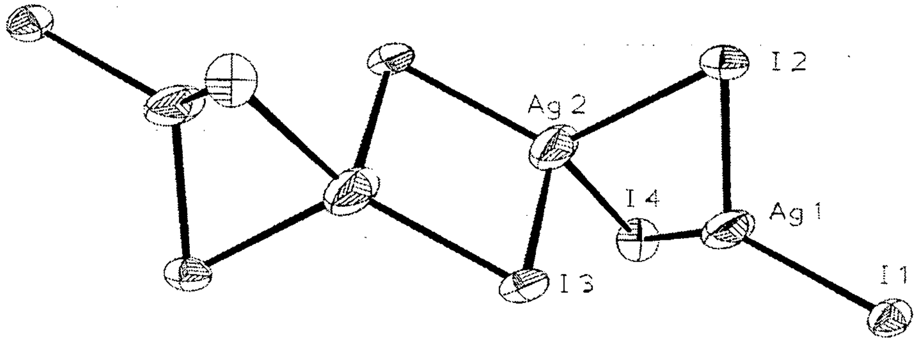


Figure 11. [Ba(benzo-15-crown-5)$_2$](Ag$_4$I$_8$) (**X**)

There is no emission from either of the first two polymers (**IX** and **XI**) while the third complex has an emission maximum at 309 nm. This is the only silver iodide complex in this study with emission in the visible spectrum. The three coordinate metal center is distorted from planarity and there is a close contact between the four-coordinate and three-coordinate silver metal centers in this structure that is within the van der Waals radius of silver-silver interactions (2.802(2) Å) and that is significantly shorter than others observed in silver complexes. The oscillator strengths for the CI *ab initio* calculated transitions of **X** are significantly larger than for any other silver, copper or gold halide complexes in this study (table 10).

IODOAURATES

Synthesis of gold(I) iodides in this study led to 5 previously unreported structures with an anionic moiety, [AuI$_2$]$^-$, charge balanced in the solid by alkali metal cations encapsulated in benzo-15-crown-5 and dicyclohexano-18-crown-6 macrocycles. The symmetry of these linear two-coordinate gold iodides places them in two categories.

There are two species (**XV** and **XVI**) having an inversion center (C_i) at Au as a result of crystallization in a centrosymmetric space group (cf. Tables 4 and 7), and thus an 180.0° angle at the metal center. In the second category, compound **XIII** crystallizes in the C2/c spacegroup having a two-fold rotation axis perpendicular to a mirror plane producing a center of symmetry (C_{2h}). Compound **XIV** crystallizes C_{2v} symmetry, resulting in an

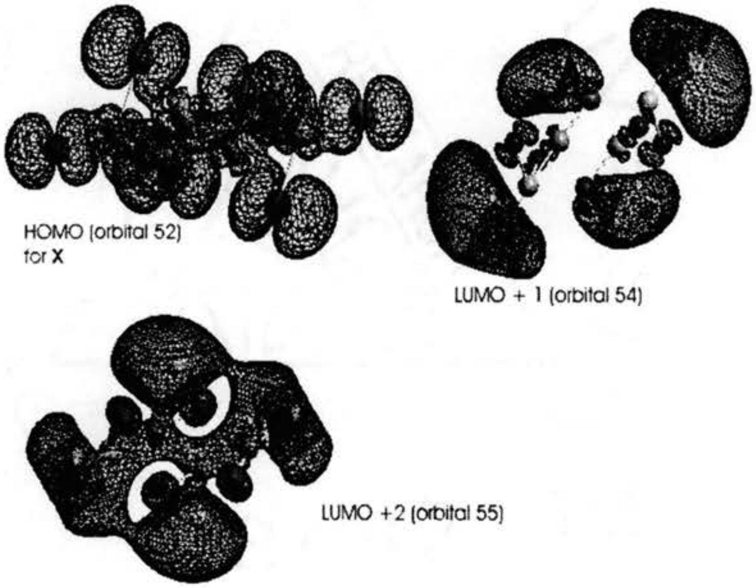


Figure 12. HOMO and LUMO + 1, LUMO + 2 for

$[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2](Ag_4I_8)$ (**X**)

anion with a bond angle of 178.47° at the metal center. A non-linear bond angle (C_{2v}) is present in complex **XII** where crystallization with C_{2v} symmetry at the Au atom results in an angle of 178.45°. All of the anionic moieties maintain equal iodine-gold distances except **XIV**. In this complex, an interaction may exist between the cesium cation and the iodine of the anionic moiety, resulting in a reduction of electron density at this bond and a slightly longer Au-I bond distance to the involved halide. This interaction is a result of a close contact (3.822 Å) that is near the sum of the Cs – I ionic radius (3.73 Å).

Table 7. Selected Structural Data for Iodoaurates

Gold complexes			symm	close contacts	radius of cation	I-Au-I angle	Au-I 1	Au-I 2	Au-Au
[K(benzo-18-crown-6)](AuI$_2$)	Pna2(1)	XII		Å	K		Å	Å	
			C_s	I2--K 3.818	1.38	178.45	2.529	2.53	
			C^9_{2v}	Au1--C14 3.807					
[K(benzo-15-crown-5)$_2$](AuI$_2$)	C2/c	XIII			K				
			C_i		1.38	180	2.517	2.517	
			C^6_{2h}						
[Cs(DCH-18-crown-6)](AuI$_2$)	P212121	XIV			Cs				
			C_s	I2--Cs 3.822	1.67	178.47	2.515	2.523	
			C^9_{2v}						
[Cs(benzo-15-crown-5)$_2$](AuI$_2$)	P-1	XV			Cs				
			C_i	Au2--C15 3.69	1.67	180	2.5179	25179	8.799
			C^6_{2h}	I2--C24 3.889		180	2.5117	2.5117	
[Rb(benzo-15-crown-5)$_2$](AuI$_2$)	P-1	XVI			Rb				
			C_i	Au2--c34 2.5175	1.52	180	2.517	2.517	8.607
			C^6_{2h}			180	2.517	2.517	

There were no emission spectra for any of the gold complexes. *Ab initio* calculations were performed using the Gaussian 98 software package for the AuI$_2^-$ complexes.

Each anion has two iodide (8 x 2) and one gold (10) valence electron sets involved in the calculations, for a total of 26 electrons. In the case of centrosymmetric AuI$_2^-$ systems, the *gerade* ↔ *ungerade* transition requirement produces symmetry allowed transitions of electrons from the Π_g symmetry HOMO → LUMO + 1, +2, and +3 levels and higher having Π_u symmetry (cf. Table 6). The predicted transition excitation energies where the oscillator strength is nearest unity of the symmetric species are significantly larger than the values of the less symmetric anion. The highly symmetric complexes showed no oscillator strengths for the lowest twenty transition states. When compared with their copper counterparts, published elsewhere, the gold complexes also have noticeably higher energies for predicted transitions.[216,23] This is analogous to the silver versus copper complexes. Since there are no close gold-gold metal center contacts in the two coordinate complexes, however, there is no comparison to the close contact characteristics exhibited by both the copper and silver complexes above. A graph of the wavefunctions, determined by *ab initio* calculations, of the gold(I) complex **XIII** in the ground and excited states is given in Figure 13.

Table 8 gives populations of the metal centers and the ligands in the synthesized compounds, and similar complexes with chloride and bromide ligands, re-calculated and presented here for comparison.[201]

Table 8. Gold(I) and Copper(I) Dihalide Electronic Populations

Ground State Atomic Orbital Populations

Metal orbital	*Cu (Cl)*	*Cu(Br)*	*Cu(I)**	*Au(Cl)*	*Au(Br)*	*Au(I)**
s (σ)	0.36126	0.3999	0.3642	0.6522	0.7416	0.6599
p_z (R) (σ)	0.0038	0.00548	0.0090	0.0140	0.0194	0.0090
p_x, p_y(R) (π)	0.0176	0.01345	0.0099	0.0225	0.0309	0.0090
d_z^2 (σ)	1.9266	1.9409	1.9666	1.8101	1.8294	1.9035
d_{xz}, d_{yz} (π)	1.9998	1.9999	1.9999	1.9988	1.9893	1.9985
d_{xy}, $d_{x^2-y^2}$(δ)	1.9999	1.9999	1.9999	1.9999	1.9888	1.9996
(R = Rydberg orbitals)						
Ligand orbital						
s (σ)	1.9687	1.9563	1.9621	1.9549	1.9422	1.9406
p_z (σ)	1.8818	1.8656	1.8648	1.8073	1.7487	1.7683
p_x,p_y (π)	1.9908	1.9930	1.9948	1.9928	1.9830	1.9954

* synthesized in this laboratory

Copper(I) metal halide bonding is largely metal s and p in character with some d_z^2 electron density involved in d-s σ bonds, according to NBO analysis. The ligand donates electron density from both s and p orbitals. The largest contribution from the ligands is the σ bond forming electrons from atomic s and p_z orbitals, which extend along the molecular axis. Figures 12 and 13 show the location of the wavefunction in the ground state to be distributed over the molecule as contributions from p_y and p_x, or p_y and p_z orbitals over the ligands and d_{xz}, d_{yz}, and d_{xy} orbitals over the metal atom. In the excited state, these wavefunctions are largely ligand in nature and centered over the metal atom. This suggests a ligand to metal charge transfer process in the excited state.

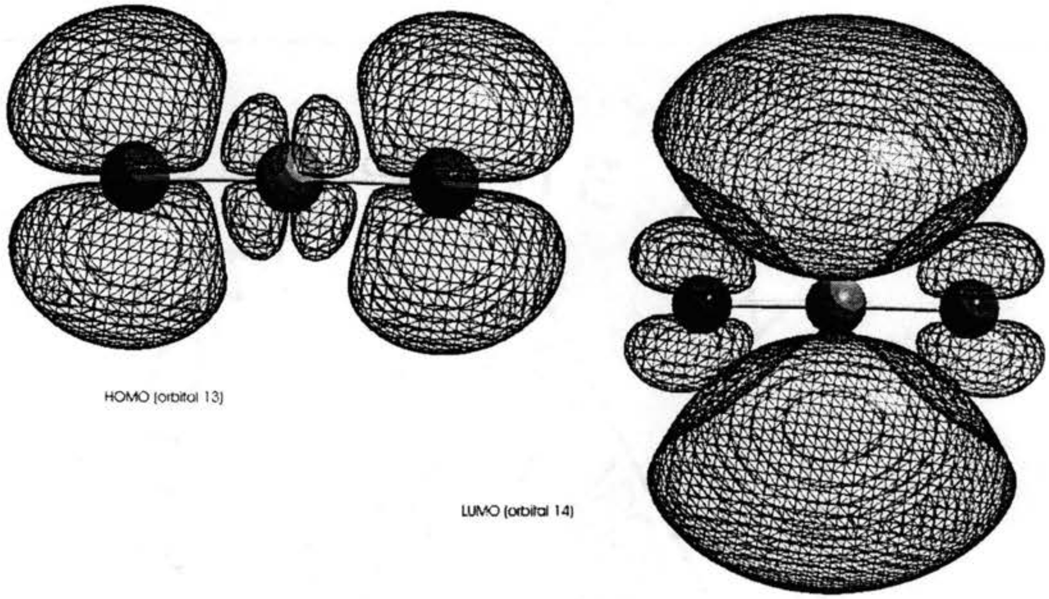


Figure 13. Graphical representation of the molecular orbital contributions in the ground and excited states for structure (**XIII**)

Interestingly, from the NBO data in Table 8, the gold(I) complexes show more contribution to bonding from d_z^2 orbitals (electronic population missing from d_z^2 and contributed to bond), and less from the s and p orbitals (more highly populated in the bonded state), than the copper(I) species in forming sigma bonds. The other orbital populations appear similar in both types of compounds. This is consistent with metallophilic effects in gold compounds that suggest significant d orbital interaction in bonding.[217,218] Relativistic destabilization of d orbitals and a tendency for stronger covalent bonding as a result of greater stability in s and p orbitals (contraction) enhance electronic correlation, and may be more significant factors in the aurophilic tendency that close gold-gold metal centers exhibit.[219,220]

SILVER(I) PHOSPHINE COMPLEXES

Three complexes containing phosphorus, iodine, and silver(I) were synthesized having a cubane structure (**XVII**, **XVIII** and **XIX**) with $Ag_4I_8L_4$ stoichiometry , and two with a rhombic geometry $Ag_2I_2L_2$ stoichiometry (**XX** and **XXI**). All structures were determined by single crystal X-ray crystallography (cf. Table 4). The tolyl-phosphine complexes formed from silver(I) iodide anions showed no emission in the evaluated spectral range, although similar complexes and clusters that include sulfide, selenide, or telluride ions are known to luminesce through a LMCT mechanism.[221] This non-emission is consistent with the quenching effect of electronegative ligands bonded to aromic functional groups.

ALKALI AND ALKALINE EARTH COMPLEXED CROWN ETHERS

Crown ether *host-guest* complexes with alkali and alkaline earth metals were utilized to provide cations without emission properties. A certain number of these crystallized without a coinage metal presence in the crystal. The metal-crown ether chelates are stabilized by the fact that they are hard acid-hard base type complexes having electrostatic interactions between the cation and the oxygen atoms of the crown ether.

This interaction brings about a conformational change in the crown ether and produces stoichiometry that is related to the relative size of the cation and the cavity in the crown ether ring.[222] Increased stability of the crown ether-metal chelate is related to the size of the cavity and the size of the cation. The smaller the difference in the cavity and cation size, the greater the kinetic stability.[223] This stability does not translate directly into effective crystallization, however. Critical factors related to crystallization are the solubility of the complex in the required solvent, and the charge sphere of the anionic species solvated with the crown ether. In the first case, solvation may be difficult for the crown ether in a solvent needed for the anionic species: metal halides may require water solutions of counter ions. Crown ethers are readily soluble in some organic solvents, but quickly reach saturation when significant amounts of water are present.

The charge magnitude of the anion is most readily accommodated when it is +1 or +2. An additional factor is the proximity of the halide ligand to the cation metal, which may try to achieve higher coordination. This can affect the packing in the solid phase and was observed in structures where simple halides were complexed (**XXIV, XXV** and **XXVI**), and in **I** and **II** where close contacts between a halogen ligand and cesium cation approach the van der Waals radius. This may shift electron density from a terminal ligand and cause deviations in the bond length to this ligand. However, this is not observed for **I** and **II**. In **XIV**, a close interaction between the iodine ligand and the cesium cation exists. This gold complex exhibits one bond that is slightly longer than the other (cf. Table 7) where the closer iodine has an Au-I bond length of 2.523(4) Å and the other one has a shorter Au-I bond distance of 2.515(4) Å. In addition, the bond angle is distorted from 180° to 178.47° changing the molecular symmetry from D_∞ to D_2. Another longer contact (3.818(4) Å) between cation and halide occurs in **XII**, however the Au-I bond lengths are the same, within the error of measurement. The bond angle is distorted from 180° to 178.45°, in a similar fashion as in **XIV**, resulting in a change of molecular symmetry from D_{∞} to C_{2v}.

Two general types of crown ethers were used in synthesis for this study: larger radius crown ethers having 6 oxygen atoms (dicyclohexano-18-crown-6, benzo-18-crown-6, and 18-crown-6) and smaller, 5 oxygen ring (benzo-15-crown-5) crown ethers with Cs, Ba, K, Na, Rb, and Sr were used to serve as cations for anionic copper, silver and gold halides. Table 9 shows the metal to oxygen plane distances, as well as the coordination number and stoichiometry for the crown ether moieties. The stoichiometry, distances and charge ratios observed in this study are similar to those reported in the literature.

Table 9. Selected Crystallographic Data for Crown Ethers

Sample	symm	Metal:CE	Coord. number	Å M-O dist.	cation-oxy plane	radius of cation
I	(C_i) C^5_{2h}	1:1	6	3.04(1) - 3.32(1)	1.3795	Cs 1.67
II	(C_i) C^5_{2h}	1:1	7	3.04(3)- 3.30(4)	1.428	Cs 1.67
III	(C_i) C^5_{2h}	1:2	10	2.676(7) - 2.776(7)	1.4454 1.4454	Sr 1.18
IV	(C_i)	1:2	10	2.92(2) - 3.08(2)	1.8572 1.8394	K 1.38
V	(C_i)	1:2	10	2.88(2) - 3.13(3)	1.847 1.8375	Rb 1.52
VI	(C_i)	1:2	10	2.745(5) - 3.021(4)	1.7414 1.7327	K 1.38
VII	(2/m) C^3_{2h}	1:1	8	2.723(7) - 2.98(5)	0.8692	K 1.38
VIII	(C_i)	1:1	7	2.293(7) - 2.931(7)	0.3866	Na 1.02
IX	(C_i) C^5_{2h}	1:1	5	3.01(1) - 3.21(1)	1.5167	Cs 1.67
X	(C_i) C^5_{2h}	1:2	10	2.765(2) 2.895(2)	1.6657 1.6486	Ba 1.35
XI	(2/m) C^6_{2h}	1:1	6	3.069(2) 3.220(2)	0.3199	Cs 1.67
XII	(C_s) C^9_{2v}	1:1	6	2.733(1) - 2.810(1)	0.2135	K 1.38

Table 9. Selected Crystallographic Data for Crown Ethers (cont.)

Sample	symm	Metal:CE	Coord. number	Å M-O dist.	cation-oxy plane	radius of cation
XIII	(C_i) C^6_{2h}	1:2	10	2.790(7) - 2.986(6)	0.17237 0.17237	K 1.38
XIV	C_s C^9_{2v}	1:1	7	2.98(3) - 3.22(3)	1.2927	Cs 1.67
XV	(C_i) C^6_{2h}	1:2	10	3.003(6) - 3.205(6)	2.0328 2.1096	Cs 1.67
XVI	(C_i) C^6_{2h}	1:2	10	2.784(8) - 3.240(8)	1.8879 1.8446	Rb 1.52
XXIII	(C_i)	1:1	8	2.696H2O 2.696(4) - 2.928(3)	0	K 1.38
XXIV	(C_i) C^5_{2h}	1:1	10	2.801(8) - 2.856(7)	1.563	Ba 1.35
XXV	D^{16}_{2h}	1:1	6	2.074(8) 2.029(5)	4.482	Mg 1.03
XXVI	(C_i) C^5_{2h}	1:2	10	2.680(6) - 2740(6)	1.426	Sr 1.18
XXVII	(C_i) C^6_{2h}	1:2	10	2.67(2) - 2.78(2)	1.4514 1.4674	K 1.38
XXVIII	(C_i)	1:2	10	2.74(1) - 2.98(1)	1.8866 1.7261	K 1.38

DISCUSSION

Examination of the calculated relative electronic transition energies for all transitions with oscillator strengths (f) nearest to unity (probability of a transition) show trends that are of interest (Table 10). For the centrosymmetric systems, the frontier energies required for a transition tend to be higher values while those for lower symmetry systems are appreciably lower. Additionally, complexes that exhibit close metal-metal contacts have an increased number of high probability transitions, and several emit within the visible emission wavelength range monitored in this study. Silver iodide complexes exhibit higher excitation energies when compared with similar copper complexes. Bromide ligands (**II**, **V**) result in silver complexes that emit within the visible wavelengths, but attempts to find a similar correlation between energy and symmetry, as with copper(I) complexes, fails. Structures having symmetry distortions that reduce the overall symmetry (**XI**) of the anion and produce close metal-metal contacts also produce emission, even in the case of iodide ligands (**X**) that otherwise show no emission.

Table 10. Experimental Emission Wavelength, and Oscillator Strength

Structure	Excitation energy,eV	Symm H-M	Emission nm	Symm molecule	Oscillator Strength
Copper(I) [reference 24]					
$Cu_2I_4^{2-}$	6.06	$P2_1/c$	422	C_{2h}	0.3265
$Cu_2I_4^{2-}$	5.95	C2/m	479	C_{2h}	0.3199
$Cu_2I_4^{2-}$	5.78	$P2_1/c$	675	C_1	0.2391
Silver(I) [this work]					
$[Cs(DCH\text{-}18\text{-}crown\text{-}6)]_2(Ag_2I_4)$(I)	5.78	$P2_1/c$	0	C_{2h}	0.5945
$[Cs(DCH\text{-}18\text{-}crown\text{-}6)]_2(Ag_2Br_4)$(II)	6.35	$P2_1/c$	496	C_i	0.4377
$[Rb(benzo15\text{-}crown\text{-}5)_2]_2(Ag_2Br_4)$(V)	5.65	$P\bar{1}$	305	C_{2h}	0.3942
$[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2]_2$ (Ag_4I_8)(X)	5.75	$P2_1/c$	309	C_i	0.7592
Gold(I) [this work]					
$[K(benzo\text{-}18\text{-}crown\text{-}6)](AuI_2)$	5.65	$Pna2_1$	0	C_{2h}	0.2726
$[K(benzo\text{-}15\text{-}crown\text{-}5)_2](AuI_2)$(XIII)	5.91	C2/c	0	C_{2v}	0.2077
CuI_2^- *[reference 216]*	4.09	$P2_1/n$	490	C_{2h}	0.341

In the example of structure **X**, the distortion of the iodine-silver angles reduces symmetry constraints which may decrease the orbital energy associated with a distorted three-coordinate geometry between the bridging ligand and the metal center.[224] This is supported by the presence of luminescence in this silver(I) iodide that is not present for any other silver iodide fragment studied. In addition, the bond lengths for bridging iodide ligands are similar to those found in the other silver iodide complexes, but much smaller ligand-metal-ligand angles are found in **X** (51.57° vs 105.38 in **IX**) while the bridging distances vary more widely than seen in the other complexes (2.72 Å to 3.06 Å).

The orbit-lattice interaction (vibronic coupling) between atoms in a molecular structure with a significant quadrupole moment can lead to dissipation of excitation energy before photon emission can occur.[225,226] This is a breakdown of the Born-Oppenheimer approximation and results in the loss of symmetry-related selection rules. The copper(I) and silver(I) structures containing bromide or chloride ligands have small quadrupole moments and may experience emission, in part, as a result of a lower probability of vibronic coupling, and effects in the ordering of energy in the frontier orbitals. The presence of the strong quadrupole in iodine leads to the conclusion that energy dissipating interactions are present and result in non-emission. Table 11 lists the quadrupole moments for the synthesized species, and several calculated ideal species, in this study.

Table 11. Quadrupole Moments of Synthesized and Ideal Anions

		molecular	**(Debye-Angst.)**					
Motif	**Structure**	**symm**	**xx**	**yy**	**zz**	**xy**	**xz**	**yz**
Ag_3I_4	**(X)**	C_i	-541.2	-331.17	-458.33	7.1339	-163.954	4.281
Ag_2I_4	**ref 215 (Ag_2I_4)**	D_{2h}	-137.394	-162.868	-250.226	0	0	0
Ag_2I_4	**(I)**	C_{2h}	-162.897	-137.367	-250.102	-0.0325	1.9351	0.4786
Cu_2I_4	**Idealized**	D_{2h}	-132.233	-150.408	-243.458	0	0	0
Cu_2I_4	**ref 24 Cu_2I_4**	C_{2h}	-153.257	-131.869	-235.542	-0.0035	-0.4254	-0.1358
Ag_2Br_4	**(V)**	C_{2h}	-126.108	-99.5638	-219.8920	-0.0401	-2.4034	-2.0067
Cu_2I_4	**ref 24 Cu_2I_4**	(I+2 fold)	-139.894	-224.81	-114.259	-0.3311	0	0
AuI_2	**ref 215**	D_{2h}	-65.2353	-68.0155	-97.086	0.1636	0	0
AuI_2	**(XII)**	C_{2v}	-96.2929	-68.5033	-65.3399	-0.408	0	0
$AuBr_2$	**ref 215**	D_{2h}	-54.6261	-56.0371	-81.916	0.0322	0	0
$AuCl_2$	**ref 215**	D_{2h}	-47.0018	-47.6563	-73.9363	-0.0428	0	0
CuI_2	**ref 25**	D_{2h}	-61.8744	-65.0037	-87.5149	-0.0454	0	0
CuI_2	**ref 25***	C_{2v}	-64.99	-61.9126	-87.4966	0.2763	0	0
$CuBr_2$	**ref 215**	D_{2h}	-49.3325	-51.1236	-74.6288	-0.0429	0	0
$CuBr_2$	**ref 215 ****	D_{2h}	-48.1001	-49.8516	-78.112	0.2802	0	0
$CuCl_2$	**ref 215**	D_{2h}	-42.8469	-42.8469	-67.4484	0	0	0

(dipole moments are zero for the listed structures. * one bond shortened by 0 .003 Å. ** different bond lengths than previous structure.)

The energies of the frontier orbitals determined by CI *ab initio* computations increase systematically (Figures 14 and 15) with increasing nuclear quadrupole and ligand quadrupole, and luminescence is less probable (smaller f) and shorter in wavelength. The emission characteristics of copper(I) halide anions reflect the lower frontier energy of the smaller metal and availability of s and p orbitals that dominate the luminescence behavior,[200] while gold halide bonding produces both a higher frontier energy and a large quadrupole interaction (particularly with iodine) that increases the energy difference of the ground and excited state (Figure 15). Clearly, this trend suggests the second order effects of the quadrupole moment are important in quenching the luminescence in gold(I) iodides. The configuration and magnitude of the quadrupole in the molecular structure is given as a result of the multipole expansion of the molecular charge. The zz vector component in Table 9 for the dihalo aurates shows a trend that parallels the energy calculation results for excitation energies. The zz vector magnitude increases with increasing quadrupole of the metal and ligand, as expected. Two interesting results are observed. The magnitude of the molecular quadrupole and molecular symmetry for the idealized AuI_2 species having D_{2h} symmetry, and the synthesized one from this study (**XII**) having C_{2v} symmetry, is diminished significantly with lowered symmetry. The decreasing magnitude associated with smaller ligand quadrupole is expected. The decrease observed in this series, however, is greater in magnitude than that observed in ligand quadrupole changes in the rest of the complexes. There is associated with this lowered symmetry, a significant drop in magnitude of the predicted absorption energy for the (singlet) excitation states (longer wavelengths). For the copper(I) linear complexes, the same altered symmetry conditions do not reflect a significant decrease in the molecular quadrupole, but rather, the expected decrease associated with ligands having smaller quadrupole moments. The zz vector magnitude is a reflection of electron density orthogonal to the z vector axis, where bond formation of the terminal ligands is located. If a larger interaction occurs, the magnitude of the molecular quadrupole would be more perturbed than seen in the copper(I) environment where a smaller quadrupole distortion of electron density occurs in the bonding along the z axis. This is a reflection of the intensity of the quadrupole effect as a function of radius. The dipole and charge interactions are a function of the inverse radius squared. The quadrupole is inversely related to the radius cubed. Since the interactions are very local, more reduction in molecular quadrupole effects are seen when bond distances are shorter. Deviations along the bonding axis (lowered symmetry) would then result in more dramatic changes in overall quadrupole size. The reduced symmetry species does have a lower predicted excitation energy.

One example of a silver(I) iodide (**X**), showed emission at 309 nm, as a result of a distortion of the three-coordinate silver metal center, allowing ligand s and p orbitals to mix with metal s and p orbitals in a way that diminished the effect of quenching. The loss of symmetry negates the quadrupole effects which also reduces vibronic coupling. The terminal ligand bond length of this complex is very similar to the symmetrical bridging ligand bond distances in other three-coordinate silver iodide complexes. This example has a predicted transition oscillator strength that is large (0.7592) since a partially ionic species is expected to have f values on the order of 0.1500 to 0.5000.[227] This interaction obviously overcomes vibronic quenching, even from a high quadrupole moment complex (**X**), where the vactor zz = -458.32. In addition, this complex displays no dipole, which would otherwise destroy the quadrupole effect, suggesting that the real interaction of the quadrupole is destroyed by reduction of symmetry along the z axis. The silver(I) tetrabromides have an emission maximum (496 nm for **II**, and 305 nm for **V**) within the measured spectrum at a typical excitation of 250 nm, but only at low temperature (~100 K). This suggests that vibronic coupling effects are a significant factor in the non-emission of the undistorted silver compounds. Since the quadrupole moment for the bromide containing complex is less than half the magnitude of the iodide containing complex, a decrease in vibronic coupling results in more probable emission. Structure **II** (C_i) is lower energy emission than structure **V** (C_{2h}) as a result of the distorted 3-coordinate angles from the terminal ligand, as in **X,** which allows different wavefunction mixing with bridging ligand s and p orbitals. This can also be observed in the large difference in terminal ligand bond lengths in structures **II** and **V** (2.496 vs 2.537). Since the local quadrupole effect is eliminated by the lack of symmetry, the distortion of the bromide orbital surface is no longer perturbed along the zz vector by the quadrupole (90^o to the Z axis), the electron density of the bromide orbital extends further toward the metal resulting in more similar terminal and bridging bond distances.

Copper(I) tetraiodates do not follow this trend of quenched emission, even with the significant quadrupole of the complexes. The large quadrupole associated with the copper(I) tetraiodates may also be a result of significant d orbital interaction when metal centers are close, since this phenomenon increases the quadrupole in complexes with significant covalent bonding.[199] The copper(I) species emit at room temperature, indicating that vibronic coupling is not a significant factor in the energy absorption and emission process. This also suggests that the vibronic coupling associated with the large molecular quadrupole, is defeated by a faster mechanism. It is interesting to note that the presence of a metal-metal interaction in symmetry allowed excited states are present in these copper(I) tetraiodates which emit well at higher temperatures. The silver(I) tetraiodate complexes, under identical conditions, do not emit, and also have evidence of very little metal-metal interaction (Table 6). Consequently, emission appears to be strongly related to the molecular quadrupole in high symmetry metal(I) tetraiodates, and to the presence of metal-ligand non-symmetrical distortions or a metal-metal interaction.

The results of CI *ab initio* calculations for ideal and distorted anions of all metals in this study indicate an increasing probability, and lower excitation energy, for an excited population with reduced symmetry (Table 10). This is supported by experimental spectroscopic results that coincide with the trend of low symmetry species having significant absorption probability at lower emission energies, and higher symmetry species that have larger excitation energy.

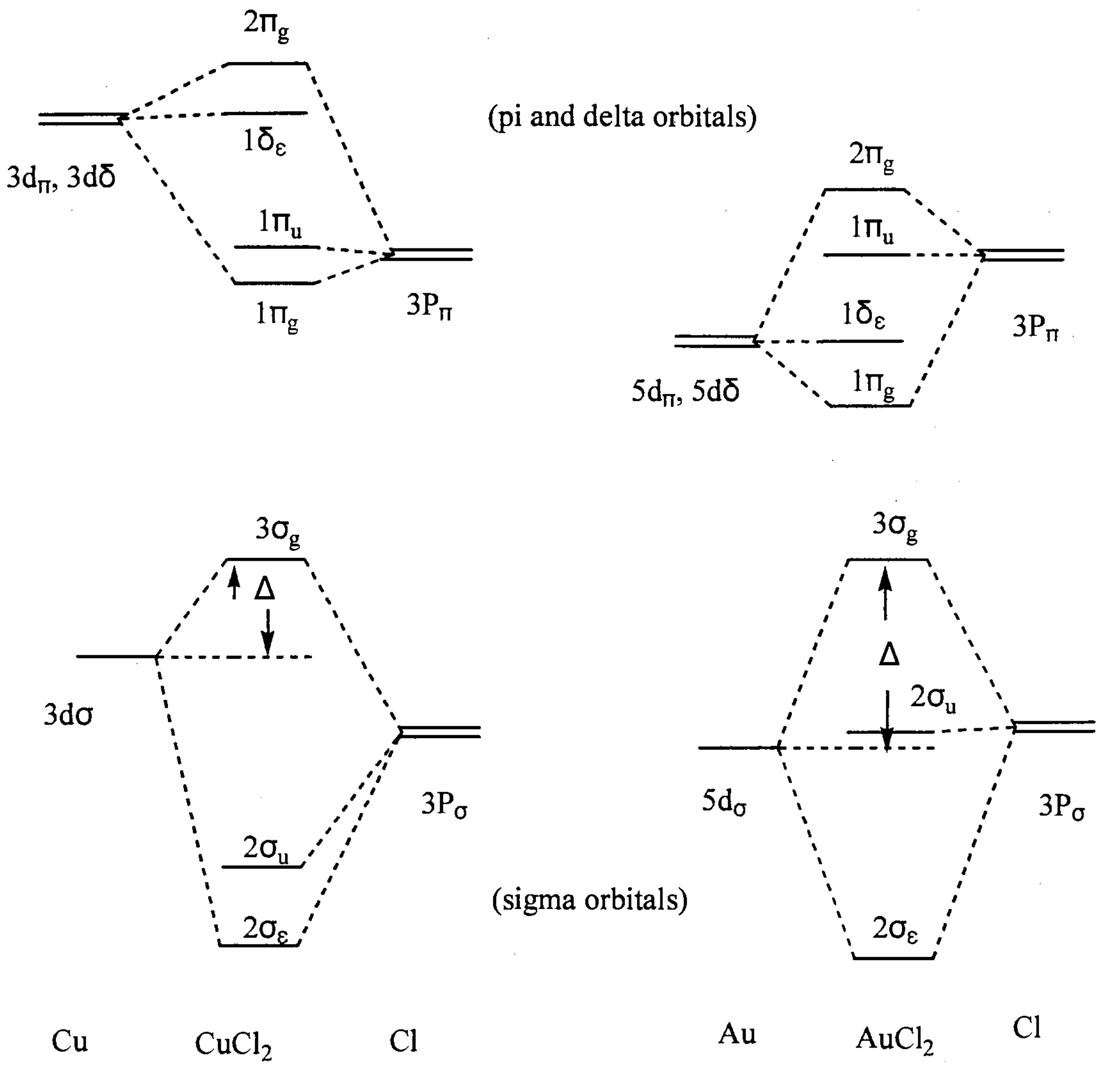


Figure 14. Orbital diagram of MX_2^- species showing relative frontier energies (Adapted from ref. 200).

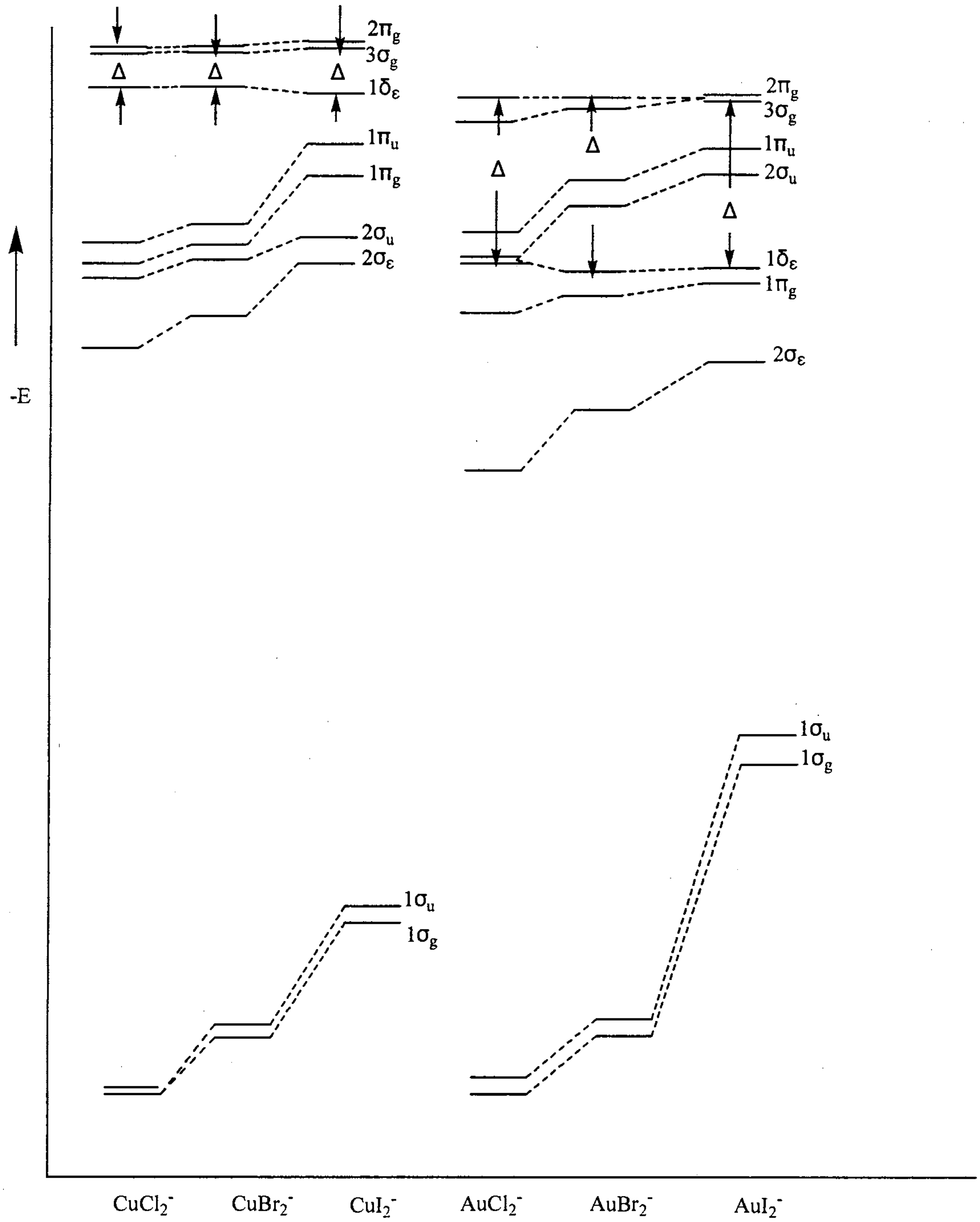


Figure 15. Molecular energy levels of MX_2^- species indicating relative frontier energy (Adapted from ref. 200)

A large frontier energy increase is observed with the combination of linear gold(I) and iodine (cf. Fig. 15). All synthesized gold(I) iodide structures are non-emitting, and multiple metal centers in the unit cell are not within metal-metal contact distance.

The large quadrupole, in the case of iodine ligands with gold, produces a change in the order of molecular orbital energy levels in the frontier orbital region, resulting in an increase in orbital energy.[200]

CONCLUSIONS

Silver(I) complexes, when isostructural with copper complexes, have very different emission characteristics. Quadrupole induced interactions (vibronic coupling) due to iodine ligands appear to be a factor in the lack of emission in silver(I) complexes. Low temperature dependence for emission is also significant for the silver(I) bromides, which also have smaller molecular quadrupole moments. This coincident requirement for low temperature in order to observe emission is a reflection of vibrational losses. The energy requirements of the halide ligand, and the distortion of the coordination angles in bonding, are observed in the analysis of orbital energies, and are associated strongly with luminescence in each of these complexes. Silver(I) bromides for instance, exhibit evidence of metal-metal interactions and also emit in the visible spectrum, while the silver(I) iodide versions lack this interaction and emission is not observed. Similarly, metal-metal interaction appears to play a role in absorption and emission for copper(I) and gold(I) species[223-228] Finally, the trend found in the increasing molecular quadrupole moments and increasing symmetry of the molecule is similar to the trends observed for emission of the metal halides and the molecular symmetry of the compounds, although a direct relationship between quadrupole moments and emission is not observed.

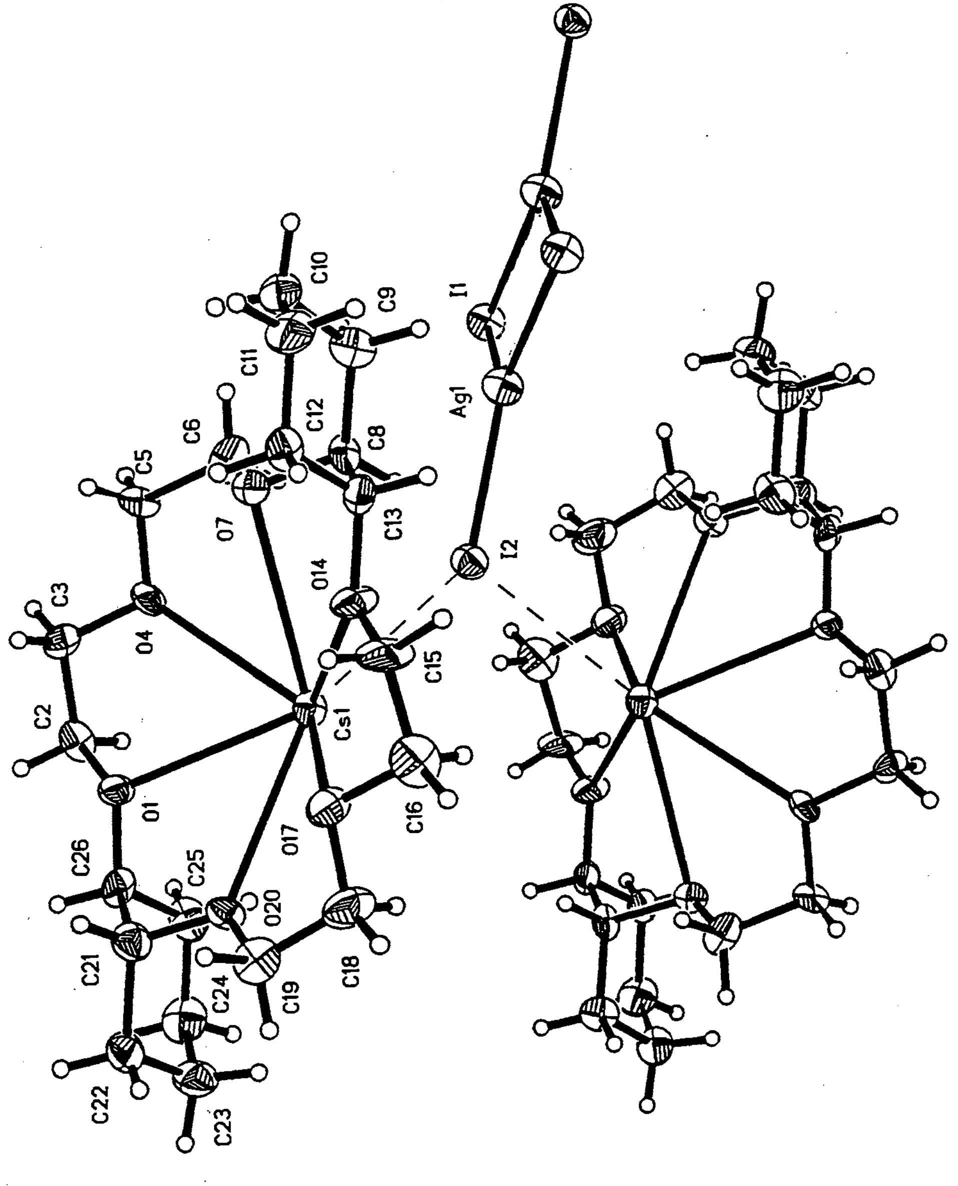


Figure 16. Projection View of $[Cs(dicyclohexano\text{-}18\text{-}crown\text{-}6)]_2(Ag_2I_4)$ **(I)**

Table 12.
Crystal data and structure refinement for $[Cs(dicyclohexano\text{-}18\text{-}crown\text{-}6)]_2(Ag_2I_4)$ (I)

Empirical formula	$C_{40} H_{72} Ag_2 Cs_2 I_4 O_{12}$	
Formula weight	1734.14	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	monoclinic, $P2_1/c$	
Unit cell dimensions	a = 12.690(5) Å	$\alpha = 90^\circ$
	b = 8.705(7) Å	$\beta = 95.28(1)^\circ$
	c = 25.081(11) Å	$\gamma = 90^\circ$
Volume	2759(3) $Å^3$	
Z, Calculated density	2, 2.088 mg/m^3	
Absorption coefficient	4.299 mm^{-1}	
F(000)	1648	
Theta range for data collection	2.18 to 20.39 deg.	
Index ranges	$-12 \le h \le 1$, $-1 \le k \le 8$, $-24 \le l \le 24$	
Reflections collected / unique	3750 / 2715 [R(int) = 0.0927]	
Completeness to $2\theta = 20.39^\circ$	91.4%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2715 / 0 / 271	
Goodness-of-fit on F^2	1.023	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0558, wR2 = 0.0985	
R indices (all data)	R1 = 0.1103, wR2 = 0.1159	
Largest diff. peak and hole	0.677 and -0.882 $Å^{-3}$	

Table 13.
Atomic coordinates (x 10^4) and equivalent isotropic
displacement parameters ($\AA^2$ x 10^3) for
[Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$I$_4$) (I)

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
I(2)	6701(1)	10074(2)	156(1)	49(1)
I(1)	10013(1)	12657(2)	88(1)	54(1)
Ag(1)	8799(1)	9963(2)	64(1)	61(1)
Cs(1)	4750(1)	7998(2)	1070(1)	43(1)
O(1)	3882(9)	927(2)	2098(4)	45(3)
C(2)	4524(13)	10460(2)	2340(7)	45(5)
C(3)	5634(12)	9860(2)	2496(6)	43(5)
O(4)	6094(9)	930(2)	2033(4)	48(4)
C(5)	7169(12)	8860(2)	2152(7)	38(5)
C(6)	760(2)	8120(2)	1676(7)	54(6)
O(7)	7091(9)	667(2)	1563(4)	45(3)
C(8)	7386(14)	5900(2)	1077(6)	42(5)
C(9)	8513(13)	5580(2)	1103(7)	49(5)
C(10)	889(2)	4440(2)	1557(7)	59(6)
C(11)	824(2)	2980(3)	1512(8)	69(7)
C(12)	7070(13)	3320(2)	1473(7)	46(5)
C(13)	6758(14)	4410(2)	1019(7)	48(6)
O(14)	5639(9)	4785(2)	978(5)	51(4)
C(15)	4965(14)	3530(2)	834(8)	69(7)
C(16)	3910(2)	4130(3)	601(8)	70(6)
O(17)	3458(9)	4916(17)	1005(5)	58(4)
C(18)	242(2)	5480(3)	828(9)	79(8)
C(19)	188(2)	6190(2)	1278(8)	52(6)
O(20)	2437(8)	7564(14)	1443(4)	41(3)
C(21)	2137(13)	8280(2)	1933(7)	52(6)
C(22)	939(13)	8690(3)	1894(7)	67(7)
C(23)	661(14)	910(3)	1464(8)	65(6)
C(24)	134(2)	11350(3)	1538(8)	71(7)
C(25)	249()	10890(3)	1585(7)	64(6)
C(26)	2799(14)	9700(2)	2024(7)	44(5)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 14.
Bond lengths [Å] and angles [°] for

[Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$I$_4$) **(I)**

I(2)-Ag(1)	2.696(2)	C(5)-C(6)	1.50(2)
I(2)-Cs(1)^{1}	3.962(2)	O(7)-C(8)	1.47(2)
I(1)-Ag(1)^{2}	2.779(3)	C(8)-C(9)	1.45(2)
I(1)-Ag(1)	2.803(3)	C(8)-C(13)	1.52(2)
Ag(1)-I(1)^{2}	2.779(3)	C(9)-C(10)	1.55(2)
Ag(1)-Ag(1)^{2}	3.094(3)	C(10)-C(11)	1.52(3)
Cs(1)-O(14)	3.032(13)	C(11)-C(12)	1.51(2)
Cs(1)-O(4)	3.044(11)	C(12)-C(13)	1.51(2)
Cs(1)-O(1)	3.100(10)	C(13)-O(14)	1.45(2)
Cs(1)-O(17)	3.140(14)	O(14)-C(15)	1.41(2)
Cs(1)-O(20)	3.184(10)	C(15)-C(16)	1.51(2)
Cs(1)-O(7)	3.319(11)	C(16)-O(17)	1.39(2)
Cs(1)-C(16)	3.69(2)	O(17)-C(18)	1.44(2)
Cs(1)-C(18)	3.69(2)	C(18)-C(19)	1.51(2)
Cs(1)-C(6)	3.78(2)	C(19)-O(20)	1.43(2)
Cs(1)-C(8)	3.80(2)	O(20)-C(21)	1.46(2)
Cs(1)-I(2)	3.824(2)	C(21)-C(26)	1.50(2)
Cs(1)-C(2)	3.87(2)	C(21)-C(22)	1.56(2)
O(1)-C(2)	1.41(2)	C(22)-C(23)	1.53(3)
O(1)-C(26)	1.42(2)	C(23)-C(24)	1.52(3)
C(2)-C(3)	1.52(2)	C(24)-C(25)	1.51(2)
C(3)-O(4)	1.43(2)	C(25)-C(26)	1.54(2)
O(4)-C(5)	1.419(17)		
Ag(1)-I(2)-Cs(1)^{1}	110.65(6)	O(1)-Cs(1)-C(8)	123.1(3)
Ag(1)-I(2)-Cs(1)	135.11(6)	O(17)-Cs(1)-C(8)	92.6(4)
Cs(1)^{1}-I(2)-Cs(1)	112.66(4)	O(20)-Cs(1)-C(8)	140.8(4)
Ag(1)^{2}-I(1)-Ag(1)	67.31(7)	O(7)-Cs(1)-C(8)	22.4(3)
I(2)-Ag(1)-I(1)^{2}	126.40(9)	C(16)-Cs(1)-C(8)	78.1(4)
I(2)-Ag(1)-I(1)	120.89(9)	C(18)-Cs(1)-C(8)	114.0(5)
I(1)^{2}-Ag(1)-I(1)	112.69(7)	C(6)-Cs(1)-C(8)	37.6(4)

Table 14. (continued)
Bond lengths [Å] and angles [°] for
[Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$I$_4$) **(I)**

I(2)-Ag(1)-Ag(1)^2	176.63(12)	O(14)-Cs(1)-I(2)	119.9(2)
I(1)^2-Ag(1)-Ag(1)^2	56.71(7)	O(4)-Cs(1)-I(2)	131.9(2)
I(1)-Ag(1)-Ag(1)^2	55.97(7)	O(1)-Cs(1)-I(2)	109.3(2)
O(14)-Cs(1)-O(4)	102.6(3)	O(17)-Cs(1)-I(2)	97.1(2)
O(14)-Cs(1)-O(1)	123.8(3)	O(20)-Cs(1)-I(2)	84.3(2)
O(4)-Cs(1)-O(1)	54.8(3)	O(7)-Cs(1)-I(2)	143.2(2)
O(14)-Cs(1)-O(17)	53.4(3)	C(16)-Cs(1)-I(2)	92.3(3)
O(4)-Cs(1)-O(17)	127.6(3)	C(18)-Cs(1)-I(2)	79.0(3)
O(1)-Cs(1)-O(17)	97.2(3)	C(6)-Cs(1)-I(2)	132.9(3)
O(14)-Cs(1)-O(20)	105.8(3)	C(8)-Cs(1)-I(2)	124.9(3)
O(4)-Cs(1)-O(20)	106.0(3)	O(14)-Cs(1)-C(2)	129.0(3)
O(1)-Cs(1)-O(20)	52.4(3)	O(4)-Cs(1)-C(2)	38.7(3)
O(17)-Cs(1)-O(20)	54.8(3)	O(1)-Cs(1)-C(2)	19.8(3)
O(14)-Cs(1)-O(7)	51.7(3)	O(17)-Cs(1)-C(2)	115.9(3)
O(4)-Cs(1)-O(7)	54.3(3)	O(20)-Cs(1)-C(2)	71.6(3)
O(1)-Cs(1)-O(7)	100.9(3)	O(7)-Cs(1)-C(2)	91.0(3)
O(17)-Cs(1)-O(7)	99.6(3)	C(16)-Cs(1)-C(2)	136.5(4)
O(20)-Cs(1)-O(7)	131.8(3)	C(18)-Cs(1)-C(2)	110.2(4)
O(14)-Cs(1)-C(16)	40.0(4)	C(6)-Cs(1)-C(2)	78.1(4)
O(4)-Cs(1)-C(16)	135.7(4)	C(8)-Cs(1)-C(2)	113.1(4)
O(1)-Cs(1)-C(16)	118.5(4)	I(2)-Cs(1)-C(2)	110.6(3)
O(17)-Cs(1)-C(16)	21.6(3)	O(14)-Cs(1)-C(6)	73.1(4)
O(20)-Cs(1)-C(16)	74.8(4)	O(4)-Cs(1)-C(6)	39.3(4)
O(7)-Cs(1)-C(16)	91.4(4)	O(1)-Cs(1)-C(6)	93.1(3)
O(14)-Cs(1)-C(18)	74.8(4)	O(17)-Cs(1)-C(6)	121.3(4)
O(4)-Cs(1)-C(18)	137.2(4)	O(20)-Cs(1)-C(6)	139.1(3)
O(1)-Cs(1)-C(18)	90.5(4)	O(7)-Cs(1)-C(6)	22.1(3)
O(17)-Cs(1)-C(18)	22.5(4)	C(16)-Cs(1)-C(6)	113.1(4)
O(20)-Cs(1)-C(18)	39.7(4)	C(18)-Cs(1)-C(6)	143.5(5)
O(7)-Cs(1)-C(18)	122.1(4)	O(14)-Cs(1)-C(8)	39.3(4)
C(16)-Cs(1)-C(18)	37.0(5)	O(4)-Cs(1)-C(8)	75.3(3)
C(2)-O(1)-C(26)	111.9(13)	C(15)-O(14)-C(13)	114.2(14)
C(2)-O(1)-Cs(1)	112.5(9)	C(15)-O(14)-Cs(1)	120.7(9)
C(26)-O(1)-Cs(1)	113.5(9)	C(13)-O(14)-Cs(1)	124.8(11)
O(1)-C(2)-C(3)	109.9(14)	O(14)-C(15)-C(16)	109.2(2)
O(1)-C(2)-Cs(1)	47.7(7)	O(17)-C(16)-C(15)	107.6(2)
C(3)-C(2)-Cs(1)	83.4(9)	O(17)-C(16)-Cs(1)	56.4(10)
O(4)-C(3)-C(2)	110.2(12)	C(15)-C(16)-Cs(1)	88.4(12)
C(5)-O(4)-C(3)	112.1(12)	C(16)-O(17)-C(18)	111.7(15)
C(5)-O(4)-Cs(1)	121.7(9)	C(16)-O(17)-Cs(1)	102.0(11)

Table 14. (continued)
Bond lengths [Å] and angles [°] for

[Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$I$_4$) **(I)**

C(3)-O(4)-Cs(1)	121.9(8)	C(18)-O(17)-Cs(1)	100.7(12)
O(4)-C(5)-C(6)	110.7(14)	O(17)-C(18)-C(19)	112(2)
O(7)-C(6)-C(5)	111(2)	O(17)-C(18)-Cs(1)	56.8(9)
O(7)-C(6)-Cs(1)	60.4(8)	C(19)-C(18)-Cs(1)	92.5(12)
C(5)-C(6)-Cs(1)	86.3(10)	O(20)-C(19)-C(18)	108(2)
C(6)-O(7)-C(8)	115.1(14)	C(19)-O(20)-C(21)	116.1(14)
C(6)-O(7)-Cs(1)	97.5(9)	C(19)-O(20)-Cs(1)	117.4(10)
C(8)-O(7)-Cs(1)	97.9(8)	C(21)-O(20)-Cs(1)	121.1(9)
C(9)-C(8)-O(7)	112.0(14)	O(20)-C(21)-C(26)	107.2(14)
C(9)-C(8)-C(13)	110(2)	O(20)-C(21)-C(22)	112.0(14)
O(7)-C(8)-C(13)	107.2(14)	C(26)-C(21)-C(22)	111(2)
C(9)-C(8)-Cs(1)	162.3(14)	C(23)-C(22)-C(21)	111(2)
O(7)-C(8)-Cs(1)	59.7(7)	C(24)-C(23)-C(22)	113(2)
C(13)-C(8)-Cs(1)	87.5(9)	C(25)-C(24)-C(23)	109(2)
C(8)-C(9)-C(10)	113(2)	C(24)-C(25)-C(26)	115(2)
C(11)-C(10)-C(9)	110.4(2)	O(1)-C(26)-C(21)	109(2)
C(12)-C(11)-C(10)	111(2)	O(1)-C(26)-C(25)	117(2)
C(13)-C(12)-C(11)	111.2(2)	C(21)-C(26)-C(25)	110(2)
O(14)-C(13)-C(12)	112.4(2)	O(1)-C(26)-Cs(1)	46.9(7)
O(14)-C(13)-C(8)	108(2)	C(21)-C(26)-Cs(1)	88.4(10)
C(12)-C(13)-C(8)	111.5(14)	C(25)-C(26)-Cs(1)	87.3(10)

Symmetry transformations used to generate equivalent atoms:
1= -x+1,-y+2,-z 2= -x+2,-y+2,-z

Table 15.
Anisotropic displacement parameters (Å^2 x 10^3) for

[Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$I$_4$) (**I**)

atom	U11	U22	U33	U23	U13	U12
I(2)	48(1)	48(1)	52(1)	6(1)	8(1)	5(1)
I(1)	60(1)	39(1)	63(1)	-1(1)	7(1)	0(1)
Ag(1)	54(1)	63(1)	68(1)	1(1)	11(1)	-1(1)
Cs(1)	49(1)	38(1)	42(1)	-2(1)	4(1)	2(1)
O(1)	34(7)	55(10)	46(7)	-19(7)	1(6)	5(7)
C(2)	59(14)	28(14)	50(12)	-15(11)	17(10)	-11(10)
C(3)	40(11)	38(13)	49(11)	-12(11)	-8(9)	-11(10)
O(4)	41(8)	57(10)	48(7)	-20(7)	13(6)	10(7)
C(5)	36(11)	14(11)	64(13)	-15(10)	8(9)	9(10)
C(6)	70(14)	38(14)	52(12)	8(12)	-7(11)	-11(10)
O(7)	41(7)	46(10)	49(7)	2(7)	4(6)	2(8)
C(8)	63(14)	30(13)	33(11)	0(10)	7(10)	31(13)
C(9)	49(13)	26(13)	72(14)	-11(11)	6(11)	-8(11)
C(10)	67(14)	56(2)	55(13)	8(12)	-1(11)	28(13)
C(11)	72(15)	60(2)	74(14)	-1(14)	-8(12)	30(2)
C(12)	52(12)	40(15)	46(11)	-11(11)	6(9)	-12(12)
C(13)	53(14)	59(16)	31(11)	-5(11)	0(9)	9(13)
O(14)	40(7)	40(10)	71(8)	-20(8)	-12(6)	20(9)
C(15)	40(12)	60(2)	100(2)	-24(14)	-8(12)	34(14)
C(16)	86(2)	42(15)	83(15)	-17(14)	13(14)	-15(14)
O(17)	52(8)	58(10)	61(8)	-21(9)	-9(7)	16(9)
C(18)	52(14)	100(2)	87(2)	-7(2)	-14(13)	-22(15)
C(19)	68(14)	19(13)	69(14)	9(12)	-1(12)	-1(13)
O(20)	35(7)	36(9)	53(7)	-6(7)	11(6)	-14(7)
C(21)	53(13)	50(2)	53(13)	0(12)	9(10)	8(13)
C(22)	57(14)	100(2)	48(12)	-6(14)	10(10)	29(14)
C(23)	46(12)	70(2)	76(14)	-12(15)	6(11)	20(2)
C(24)	84(17)	50(2)	74(15)	12(13)	0(13)	20(2)
C(25)	77(16)	60(2)	59(13)	16(13)	16(12)	25(14)
C(26)	54(13)	40(2)	39(11)	-22(11)	-4(9)	-4(13)

The anisotropic displacement factor exponent takes the form:
$-2 \mathrm{pi}^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

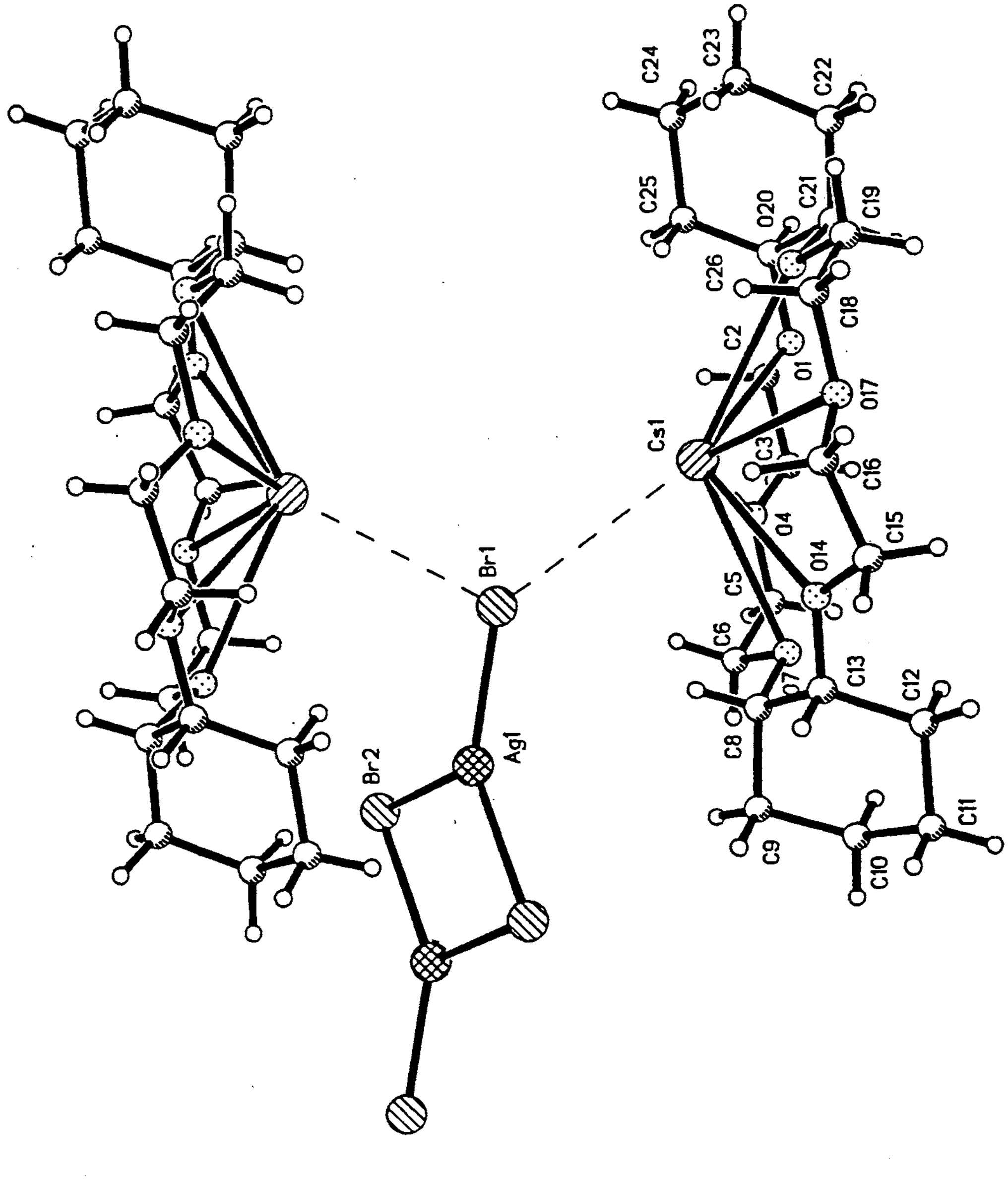


Figure 17. Projection View of [Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$Br$_4$) (II)

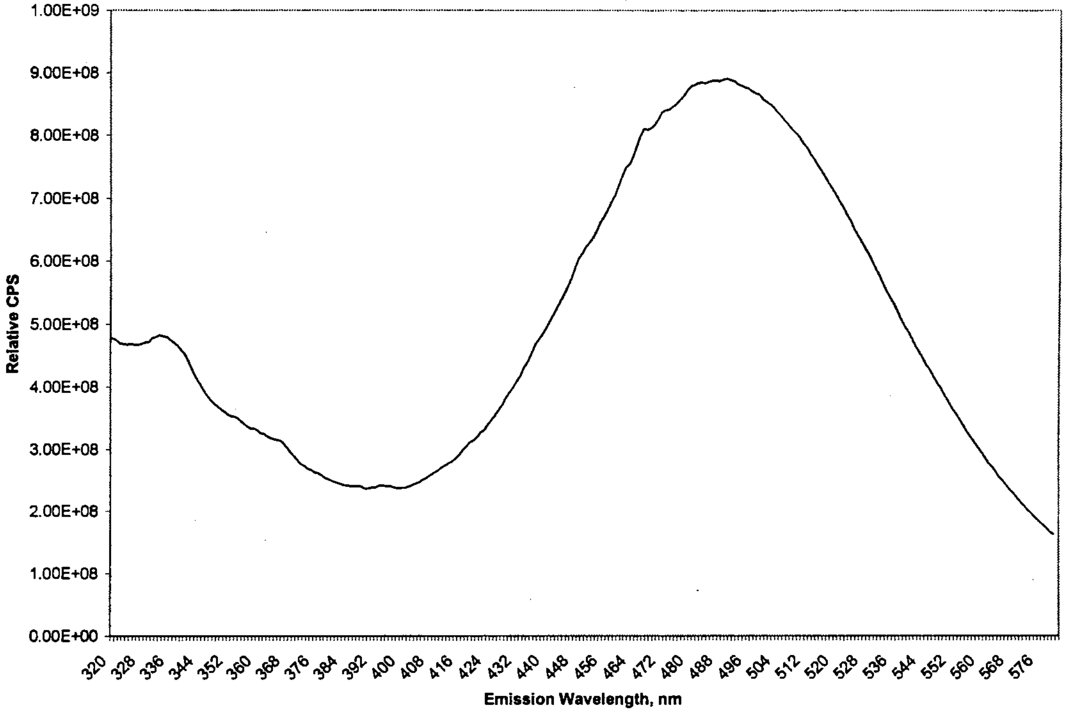


Figure 18. Emission Spectrum of [Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$Br$_4$) **(II)**

Table 16.
Crystal data and structure refinement for
[Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$Br$_4$) **(II)**

Empirical formula	$C_{40} H_{72} Ag_2 Br_4 Cs_2 O_{12}$	
Formula weight	1546.18	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	monoclinic, $P2_1/c$	
Unit cell dimensions	a = 12.476(11) Å	α= 90°
	b = 8.492(6) Å	β = 97.35(8)°
	c = 24.141(12) Å	γ = 90°
Volume	2537(3) Å^3	
Z, Calculated density	2, 1.959 mg/m^3	
Absorption coefficient	5.220 mm^{-1}	
F(000)	1504	
Theta range for data collection	2.21 to 20.81 deg.	
Index ranges	$-1 \leq h \leq 12$, $-1 \leq k \leq 8$, $-24 \leq l \leq 24$	
Reflections collected / unique	3629 / 2640 [R(int) = 0.1560]	
Completeness to $2\theta = 20.81°$	91.0%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2640 / 0 / 263	
Goodness-of-fit on F^2	0.991	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0884, wR2 = 0.1468	
R indices (all data)	R1 = 0.2128, wR2 = 0.1925	
Extinction coefficient	0.0004(4)	
Largest diff. peak and hole	0.740 and -0.807 Å^{-3}	

Table 17.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Cs(dicyclohexano-18-crown-6)]$_2$(Ag_2Br_4) **(II)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Br(1)	6707(4)	10078(9)	158(2)	52(3)
Br(2)	10007(5)	12446(6)	88(2)	60(3)
Ag(1)	8695(3)	9923(8)	60(2)	81(3)
Cs(1)	4744(3)	8052(4)	1007(1)	42(1)
O(1)	3890(3)	9360(5)	2107(13)	60(14)
C(2)	4600(5)	10430(6)	2320(2)	80(3)
C(3)	5730(3)	9980(7)	2480(2)	60(2)
O(4)	6080(2)	9350(5)	2000(12)	80(2)
C(5)	7180(3)	8870(5)	2107(15)	26(15)
C(6)	7570(3)	8160(7)	1600(2)	80(3)
O(7)	7080(3)	6690(5)	1514(13)	72(14)
C(8)	7370(5)	5830(5)	1020(2)	60(3)
C(9)	8590(4)	5620(9)	1040(2)	180(5)
C(10)	8900(5)	4550(7)	1530(2)	90(3)
C(11)	8310(4)	2840(5)	1490(2)	90(3)
C(12)	7110(3)	3280(6)	1456(15)	40(2)
C(13)	6760(3)	4370(6)	990(2)	60(2)
O(14)	5640(2)	4620(4)	920(12)	45(11)
C(15)	4840(4)	3330(6)	800(2)	60(2)
C(16)	3800(3)	4080(5)	610(2)	50(2)
O(17)	3330(3)	4950(4)	950(11)	60(13)
C(18)	2210(4)	5440(7)	830(2)	110(3)
C(19)	1820(4)	6210(6)	1280(2)	60(2)
O(20)	2420(2)	7620(4)	1402(14)	56(13)
C(21)	2160(6)	8300(8)	1930(2)	110(3)
C(22)	1030(5)	8670(6)	1910(2)	110(3)
C(23)	640(4)	9710(6)	1460(2)	50(2)
C(24)	1280(6)	11310(6)	1490(2)	100(3)
C(25)	2470(3)	10910(5)	1580(2)	22(15)
C(26)	2840(5)	9920(9)	2020(2)	80(2)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 18.
Bond lengths [Å] and angles [°] for
[Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$Br$_4$) **(II)**

Br(1)-Ag(1)	2.537(6)	Ag(1)-Br(1)-Cs(1)^1	112.5(2)
Br(1)-Cs(1)^1	3.621(6)	Ag(1)-Br(1)-Cs(1)	136.4(3)
Br(1)-Cs(1)	3.784(6)	Cs(1)^1-Br(1)-Cs(1)	109.06(13)
Br(2)-Ag(1)^2	2.645(8)	Ag(1)^2-Br(2)-Ag(1)	76.7(2)
Br(2)-Ag(1)	2.713(8)	Br(1)-Ag(1)-Br(2)^2	132.7(3)
Ag(1)-Br(2)^2	2.645(8)	Br(1)-Ag(1)-Br(2)	124.0(3)
Ag(1)-Ag(1)^2	3.325(8)	Br(2)^2-Ag(1)-Br(2)	103.3(2)
Cs(1)-O(4)	3.04(3)	Br(1)-Ag(1)-Ag(1)^2	174.7(4)
Cs(1)-O(14)	3.16(3)	Br(2)^2-Ag(1)-Ag(1)^2	52.6(2)
Cs(1)-O(20)	3.18(3)	Br(2)-Ag(1)-Ag(1)^2	50.72(19)
Cs(1)-O(1)	3.19(3)	O(4)-Cs(1)-O(14)	102.5(9)
Cs(1)-O(17)	3.19(3)	O(4)-Cs(1)-O(20)	104.9(8)
Cs(1)-O(7)	3.30(4)	O(14)-Cs(1)-O(20)	104.8(8)
Cs(1)-Br(1)^1	3.621(6)	O(4)-Cs(1)-O(1)	53.2(8)
Cs(1)-C(16)	3.70(5)	O(14)-Cs(1)-O(1)	122.2(8)
Cs(1)-C(6)	3.72(4)	O(20)-Cs(1)-O(1)	53.0(10)
Cs(1)-C(8)	3.81(6)	O(4)-Cs(1)-O(17)	127.2(9)
Cs(1)-C(2)	3.82(5)	O(14)-Cs(1)-O(17)	55.0(8)
O(1)-C(2)	1.35(5)	O(20)-Cs(1)-O(17)	52.5(7)
O(1)-C(26)	1.40(7)	O(1)-Cs(1)-O(17)	95.8(9)
C(2)-C(3)	1.50(6)	O(4)-Cs(1)-O(7)	54.3(9)
C(3)-O(4)	1.40(4)	O(14)-Cs(1)-O(7)	52.2(9)
O(4)-C(5)	1.45(4)	O(20)-Cs(1)-O(7)	131.0(8)
C(5)-C(6)	1.50(5)	O(1)-Cs(1)-O(7)	99.3(8)
C(6)-O(7)	1.41(6)	O(17)-Cs(1)-O(7)	101.5(10)
O(7)-C(8)	1.48(5)	O(4)-Cs(1)-Br(1)^1	132.4(7)
C(8)-C(13)	1.46(6)	O(14)-Cs(1)-Br(1)^1	121.0(5)
C(8)-C(9)	1.55(7)	O(20)-Cs(1)-Br(1)^1	83.0(6)
C(9)-C(10)	1.53(7)	O(1)-Cs(1)-Br(1)^1	109.0(6)
C(10)-C(11)	1.63(6)	O(17)-Cs(1)-Br(1)^1	95.2(7)
C(11)-C(12)	1.55(6)	O(7)-Cs(1)-Br(1)^1	145.4(6)
C(12)-C(13)	1.52(6)	O(4)-Cs(1)-C(16)	133.4(10)
C(13)-O(14)	1.42(4)	O(14)-Cs(1)-C(16)	40.3(7)
O(14)-C(15)	1.51(5)	O(20)-Cs(1)-C(16)	72.0(8)
C(15)-C(16)	1.49(5)	O(1)-Cs(1)-C(16)	115.0(11)
C(16)-O(17)	1.31(4)	O(17)-Cs(1)-C(16)	20.2(6)
O(17)-C(18)	1.47(5)	O(7)-Cs(1)-C(16)	91.7(8)
C(18)-C(19)	1.41(6)	Br(1)^1-Cs(1)-C(16)	93.9(6)
C(19)-O(20)	1.44(5)	O(4)-Cs(1)-C(6)	40.3(8)
O(20)-C(21)	1.47(5)	O(14)-Cs(1)-C(6)	73.5(11)
C(21)-C(22)	1.46(7)	O(20)-Cs(1)-C(6)	139.2(10)

Table 18. (continued)
Bond lengths [Å] and angles [°] for
[Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$Br$_4$) **(II)**

C(21)-C(26)	1.64(9)	O(1)-Cs(1)-C(6)	92.5(9)
C(22)-C(23)	1.46(5)	O(17)-Cs(1)-C(6)	123.4(12)
C(23)-C(24)	1.58(7)	O(7)-Cs(1)-C(6)	22.1(10)
C(24)-C(25)	1.53(7)	Br(1)^1-Cs(1)-C(6)	134.0(10)
C(25)-C(26)	1.43(7)	C(16)-Cs(1)-C(6)	113.5(11)
O(4)-Cs(1)-Br(1)	86.1(6)	C(6)-O(7)-C(8)	115(4)
O(14)-Cs(1)-Br(1)	97.7(5)	C(6)-O(7)-Cs(1)	96(3)
O(20)-Cs(1)-Br(1)	151.9(6)	C(8)-O(7)-Cs(1)	98(3)
O(1)-Cs(1)-Br(1)	126.0(8)	C(13)-C(8)-O(7)	108(4)
O(17)-Cs(1)-Br(1)	138.2(4)	C(13)-C(8)-C(9)	115(5)
O(7)-Cs(1)-Br(1)	76.4(6)	O(7)-C(8)-C(9)	110(4)
Br(1)^1-Cs(1)-Br(1)	70.94(13)	C(13)-C(8)-Cs(1)	89(3)
C(16)-Cs(1)-Br(1)	118.9(7)	O(7)-C(8)-Cs(1)	59(3)
C(6)-Cs(1)-Br(1)	63.6(9)	C(9)-C(8)-Cs(1)	157(4)
O(4)-Cs(1)-C(8)	75.9(9)	C(10)-C(9)-C(8)	106(4)
O(14)-Cs(1)-C(8)	38.9(8)	C(9)-C(10)-C(11)	113(5)
O(20)-Cs(1)-C(8)	139.3(8)	C(12)-C(11)-C(10)	103(4)
O(1)-Cs(1)-C(8)	121.6(8)	C(13)-C(12)-C(11)	114(4)
O(17)-Cs(1)-C(8)	93.8(9)	O(14)-C(13)-C(8)	113(4)
O(7)-Cs(1)-C(8)	22.7(7)	O(14)-C(13)-C(12)	113(4)
Br(1)^1-Cs(1)-C(8)	127.2(6)	C(8)-C(13)-C(12)	111(3)
C(16)-Cs(1)-C(8)	78.6(8)	C(13)-O(14)-C(15)	124(4)
C(6)-Cs(1)-C(8)	37.9(9)	C(13)-O(14)-Cs(1)	119(3)
Br(1)-Cs(1)-C(8)	68.1(6)	C(15)-O(14)-Cs(1)	117(2)
O(4)-Cs(1)-C(2)	36.6(10)	C(16)-C(15)-O(14)	107(4)
O(14)-Cs(1)-C(2)	126.5(10)	O(17)-C(16)-C(15)	119(4)
O(20)-Cs(1)-C(2)	72.2(10)	O(17)-C(16)-Cs(1)	57(2)
O(1)-Cs(1)-C(2)	19.7(9)	C(15)-C(16)-Cs(1)	94(3)
O(17)-Cs(1)-C(2)	114.3(8)	C(16)-O(17)-C(18)	121(4)
O(7)-Cs(1)-C(2)	88.7(11)	C(16)-O(17)-Cs(1)	102(3)
Br(1)^1-Cs(1)-C(2)	111.7(9)	C(18)-O(17)-Cs(1)	107(3)
C(16)-Cs(1)-C(2)	132.3(10)	C(19)-C(18)-O(17)	111(4)
C(6)-Cs(1)-C(2)	76.9(11)	C(19)-C(18)-Cs(1)	89(3)
Br(1)-Cs(1)-C(2)	107.5(7)	O(17)-C(18)-Cs(1)	52(2)
C(8)-Cs(1)-C(2)	111.3(11)	C(18)-C(19)-O(20)	110(4)
C(2)-O(1)-C(26)	114(5)	C(19)-O(20)-C(21)	111(4)
C(2)-O(1)-Cs(1)	108(3)	C(19)-O(20)-Cs(1)	121(2)
C(26)-O(1)-Cs(1)	112(3)	C(21)-O(20)-Cs(1)	120(3)
O(1)-C(2)-C(3)	121(5)	C(22)-C(21)-O(20)	110(5)
O(1)-C(2)-Cs(1)	53(2)	C(22)-C(21)-C(26)	109(5)
C(3)-C(2)-Cs(1)	88(3)	O(20)-C(21)-C(26)	107(5)
O(4)-C(3)-C(2)	104(3)	C(23)-C(22)-C(21)	115(5)

Table 18. (continued)
Bond lengths [Å] and angles [°] for
[Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$Br$_4$) **(II)**

C(3)-O(4)-C(5)	109(3)	C(22)-C(23)-C(24)	111(4)
C(3)-O(4)-Cs(1)	129(2)	C(25)-C(24)-C(23)	108(4)
C(5)-O(4)-Cs(1)	120(3)	C(26)-C(25)-C(24)	119(5)
O(4)-C(5)-C(6)	110(3)	O(1)-C(26)-C(25)	124(5)
O(7)-C(6)-C(5)	108(4)	O(1)-C(26)-C(21)	102(6)
O(7)-C(6)-Cs(1)	62(2)	C(25)-C(26)-C(21)	105(4)
C(5)-C(6)-Cs(1)	88(2)		

Symmetry transformations used to generate equivalent atoms:
1 = -x+1,-y+2,-z   2 = -x+2,-y+2,-z

Table 19.
Anisotropic displacement parameters ($Å^2$ X10^3) for [Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$Br$_4$) **(II)**

atom	U11	U22	U33	U23	U13	U12
Br(1)	42(4)	48(5)	66(4)	-3(4)	14(3)	6(5)
Br(2)	72(5)	38(5)	71(5)	0(4)	11(4)	11(4)
Ag(1)	71(4)	105(5)	69(3)	8(4)	11(3)	4(4)
Cs(1)	48(2)	32(3)	46(2)	-4(2)	2(2)	2(3)
O(1)	50(3)	80(4)	50(2)	0(2)	-30(2)	50(3)
C(2)	130(6)	40(5)	90(5)	-50(4)	50(4)	-140(5)
C(3)	0(3)	110(5)	50(4)	-70(4)	-60(3)	0(4)
O(4)	50(3)	140(5)	40(2)	-20(3)	40(2)	40(3)
C(5)	10(3)	20(4)	30(3)	20(3)	-50(2)	70(3)
C(6)	0(3)	180(8)	60(4)	-120(5)	0(3)	70(5)
O(7)	120(4)	60(3)	40(2)	-30(2)	30(2)	-50(3)
C(8)	180(8)	0(3)	0(3)	-20(3)	10(4)	-110(4)
C(9)	10(3)	320(13)	240(9)	-150(8)	90(5)	-200(6)
C(10)	90(5)	100(7)	80(4)	120(5)	10(4)	50(5)
C(11)	130(6)	20(4)	120(5)	-110(4)	90(4)	-140(5)
C(12)	0(3)	80(5)	40(3)	40(3)	-50(2)	60(4)
C(13)	0(3)	90(6)	60(4)	-40(4)	-60(3)	100(4)
O(14)	20(2)	30(3)	90(3)	10(2)	20(2)	50(2)
C(15)	100(5)	40(5)	50(3)	-10(3)	20(4)	-100(5)
C(16)	0(3)	0(3)	130(5)	40(3)	-10(3)	70(3)
O(17)	80(3)	30(3)	70(2)	-100(2)	80(2)	10(3)
C(18)	0(3)	50(6)	260(8)	-60(5)	-80(4)	30(4)
C(19)	80(5)	40(5)	80(4)	20(4)	100(4)	110(4)
O(20)	90(3)	0(2)	90(3)	10(2)	80(2)	-70(2)
C(21)	160(7)	180(8)	0(3)	-10(4)	10(4)	190(8)
C(22)	210(8)	90(6)	40(4)	0(4)	30(4)	210(6)
C(23)	50(4)	0(4)	90(4)	-40(4)	-30(3)	-20(4)
C(24)	270(10)	40(5)	0(3)	-20(3)	-20(5)	110(6)
C(25)	30(3)	0(3)	20(3)	10(3)	-60(3)	0(3)
C(26)	110(6)	50(6)	80(5)	-30(5)	-50(4)	-50(7)

The anisotropic displacement factor exponent takes the form:
$-2 \, pi^2 \, [\, h^2 \, a^{*2} \, U_{11} + \ldots + 2 \, h \, k \, a^* \, b^* \, U_{12} \,]$

Table 20.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [Cs(dicyclohexano-18-crown-6)]$_2$(Ag$_2$Br$_4$) **(II)**

atom	x	y	z	U(eq)
H(2A)	4287	10896	2626	80
H(2B)	4662	11233	2051	80
H(3A)	5700	9122	2733	80
H(3B)	6166	10795	2650	80
H(5A)	7247	8085	2389	80
H(5B)	7613	9747	2228	80
H(6A)	8336	8095	1629	80
H(6B)	7345	8817	1292	80
H(8A)	7156	6455	707	80
H(9A)	8967	6601	1053	80
H(9B)	8771	5054	726	80
H(10A)	8724	5095	1856	80
H(10B)	9664	4396	1560	80
H(11A)	8517	2199	1801	80
H(11B)	8469	2297	1162	80
H(12A)	6974	3828	1784	80
H(12B)	6689	2336	1439	80
H(13A)	6939	3834	661	80
H(15A)	4711	2764	1122	80
H(15B)	5097	2618	535	80
H(16A)	3311	3315	449	80
H(16B)	3969	4790	322	80
H(18A)	1776	4574	688	80
H(18B)	2217	6214	545	80
H(19A)	1900	5498	1584	80
H(19B)	1072	6451	1204	80
H(21A)	2373	7614	2228	80
H(22A)	810	9058	2245	80
H(22B)	676	7681	1831	80
H(23A)	-107	9945	1473	80
H(23B)	729	9225	1117	80
H(24A)	1087	11916	1798	80
H(24B)	1113	11911	1163	80
H(25A)	2872	11865	1615	80
H(25B)	2667	10385	1252	80
H(26A)	2647	10426	2346	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

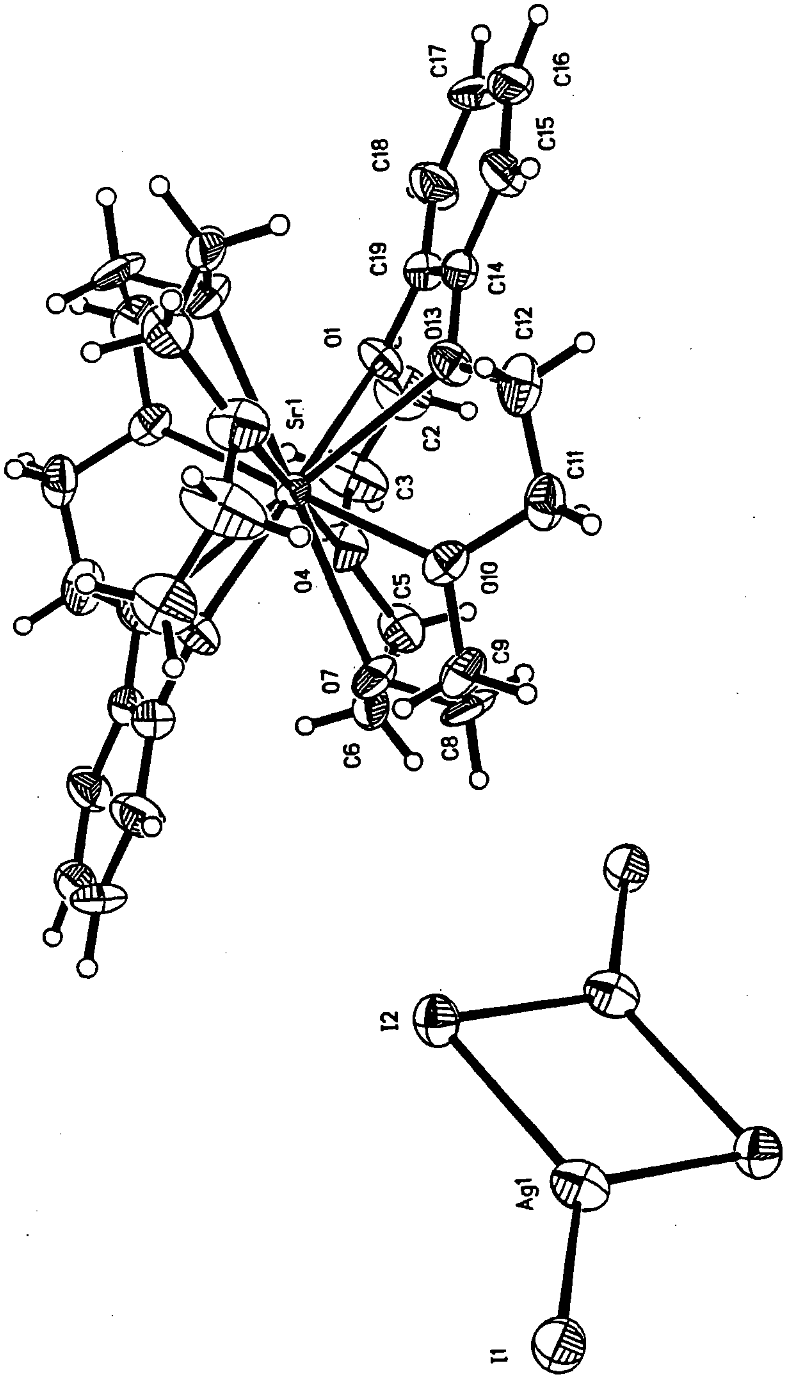


Figure 19. Projection View of [Sr(benzo-15-crown-5)$_2$](Ag$_2$I$_4$) **(III)**

Table 21.
Crystal data and structure refinement for
[Sr(benzo-15-crown-5)$_2$](Ag$_2$I$_4$) **(III)**

Empirical formula	$C_{28}H_{40}Ag_2I_4O_{10}Sr$
Formula weight	1347.56
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	a = 12.016(4) Å α = 90° b = 12.523(4) Å β = 91.47(3)° c = 13.202(4) Å γ = 90°
Volume	1985.9(11) Å^3
Z, Calculated density	2, 2.254 mg/m^3
Absorption coefficient	5.470 mm^{-1}
F(000)	1264
Theta range for data collection	2.24 to 24.11 deg.
Index ranges	$-1\leq h\leq 13$, $-1\leq k\leq 14$, $-15\leq l\leq 15$
Reflections collected / unique	4012 / 3136 [R(int) = 0.0803]
Completeness to 2θ = 24.11	94.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3136 / 0 / 206
Goodness-of-fit on F^2	0.978
Final R indices [I>2σ(I)]	R1 = 0.0548, wR2 = 0.1027
R indices (all data)	R1 = 0.1156, wR2 = 0.1251
Extinction coefficient	0.0024(3)
Largest diff. peak and hole	0.715 and -0.649 Å^{-3}

Table 22.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [Sr(benzo-15-crown-5)$_2$](Ag_2I_4) **(III)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Ag(1)	4711(1)	-6294(1)	381(1)	73(1)
I(1)	4280(1)	-8267(1)	1061(1)	72(1)
Sr(1)	0	0	0	35(1)
I(2)	3220(1)	-4785(1)	-484(1)	66(1)
O(1)	695(7)	2114(6)	-26(5)	53(2)
C(2)	1447(13)	2495(11)	-778(11)	82(5)
C(3)	1460(2)	1806(12)	-1616(11)	103(6)
O(4)	1425(8)	709(7)	-1425(6)	70(3)
C(5)	2477(11)	177(11)	-1514(11)	75(4)
C(6)	2257(11)	-979(12)	-1471(10)	74(4)
O(7)	1724(6)	-1263(7)	-537(7)	63(2)
C(8)	2481(12)	-1645(11)	244(12)	80(5)
C(9)	1820(12)	-1922(11)	1161(10)	71(4)
O(10)	1175(6)	-1046(6)	1479(6)	55(2)
C(11)	1748(11)	-418(10)	2243(10)	64(4)
C(12)	1012(12)	457(11)	2563(8)	69(4)
O(13)	653(7)	1043(6)	1681(5)	53(2)
C(14)	496(9)	2122(9)	1759(9)	49(3)
C(15)	277(12)	2665(11)	2672(10)	67(4)
C(16)	172(11)	3767(13)	2670(13)	76(5)
C(17)	256(13)	3805(11)	859(12)	84(5)
C(19)	555(10)	2712(10)	851(10)	53(3)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 23.
Bond lengths [Å] and angles [°] for
[Sr(benzo-15-crown-5)$_2$](Ag$_2$I$_4$) **(III)**

Ag(1)-I(1)	2.685(2)	C(3)-O(4)	1.40(2)
Ag(1)-I(2)	2.825(2)	O(4)-C(5)	1.436(15)
Ag(1)-I(2)^1	2.829(2)	C(5)-C(6)	1.47(2)
Sr(1)-O(13)	2.676(7)	C(6)-O(7)	1.448(14)
Sr(1)-O(13)^2	2.676(7)	O(7)-C(8)	1.44(2)
Sr(1)-O(7)	2.716(7)	C(8)-C(9)	1.51(2)
Sr(1)-O(7)^2	2.716(7)	C(9)-O(10)	1.412(14)
Sr(1)-O(10)	2.717(8)	O(10)-C(11)	1.440(14)
Sr(1)-O(10)^2	2.717(8)	C(11)-C(12)	1.48(2)
Sr(1)-O(4)^2	2.725(8)	C(12)-O(13)	1.433(13)
Sr(1)-O(4)	2.725(8)	O(13)-C(14)	1.369(13)
Sr(1)-O(1)	2.776(7)	C(14)-C(19)	1.41(2)
Sr(1)-O(1)^2	2.776(7)	C(14)-C(15)	1.415(15)
I(2)-Ag(1)^1	2.829(2)	C(15)-C(16)	1.39(2)
O(1)-C(19)	1.393(13)	C(16)-C(17)	1.39(2)
O(1)-C(2)	1.440(13)	C(17)-C(18)	1.40(2)
C(2)-C(3)	1.40(2)	C(18)-C(19)	1.38(2)
I(1)-Ag(1)-I(2)	128.68(6)	C(3)-O(4)-Sr(1)	117.8(8)
I(1)-Ag(1)-I(2)^1	126.91(6)	C(5)-O(4)-Sr(1)	118.3(8)
I(2)-Ag(1)-I(2)^1	104.33(5)	O(4)-C(5)-C(6)	107.1(10)
O(13)-Sr(1)-O(13)^2	180	O(7)-C(6)-C(5)	111.0(10)
O(13)-Sr(1)-O(7)	107.0(3)	C(6)-O(7)-C(8)	114.1(9)
O(13)^2-Sr(1)-O(7)	73.0(3)	C(6)-O(7)-Sr(1)	115.8(7)
O(13)-Sr(1)-O(7)^2	73.0(3)	C(8)-O(7)-Sr(1)	118.6(7)
O(13)^2-Sr(1)-O(7)^2	107.0(3)	O(7)-C(8)-C(9)	108.5(10)
O(7)-Sr(1)-O(7)^2	180	O(10)-C(9)-C(8)	111.4(10)
O(13)-Sr(1)-O(10)	60.2(2)	C(9)-O(10)-C(11)	112.1(10)
O(13)^2-Sr(1)-O(10)	119.8(2)	C(9)-O(10)-Sr(1)	116.1(7)
O(7)-Sr(1)-O(10)	61.4(2)	C(11)-O(10)-Sr(1)	118.1(7)
O(7)^2-Sr(1)-O(10)	118.6(2)	O(10)-C(11)-C(12)	109.1(10)
O(13)-Sr(1)-O(10)^2	119.8(2)	O(13)-C(12)-C(11)	108.5(10)
O(13)^2-Sr(1)-O(10)^2	60.2(2)	C(14)-O(13)-C(12)	118.9(9)
O(7)-Sr(1)-O(10)^2	118.6(2)	C(14)-O(13)-Sr(1)	120.4(7)
O(7)^2-Sr(1)-O(10)^2	61.4(2)	C(12)-O(13)-Sr(1)	120.0(7)
O(10)-Sr(1)-O(10)^2	180	O(13)-C(14)-C(19)	116.3(10)
O(13)-Sr(1)-O(4)^2	76.2(2)	O(13)-C(14)-C(15)	124.6(12)
O(13)^2-Sr(1)-O(4)^2	103.8(2)	C(19)-C(14)-C(15)	119.1(12)
O(7)-Sr(1)-O(4)^2	119.2(3)	C(16)-C(15)-C(14)	119.8(14)
O(7)^2-Sr(1)-O(4)^2	60.8(3)	C(15)-C(16)-C(17)	120.3(14)
O(10)-Sr(1)-O(4)^2	70.8(3)	C(16)-C(17)-C(18)	120.4(14)
O(10)^2-Sr(1)-O(4)^2	109.2(3)	C(19)-C(18)-C(17)	119.8(15)

Table 23. (cont.)
Bond lengths [Å] and angles [°] for
[Sr(benzo-15-crown-5)$_2$](Ag$_2$I$_4$) **(III)**

O(13)-Sr(1)-O(4)	103.8(2)	C(18)-C(19)-O(1)	123.7(13)
O(13)^2-Sr(1)-O(4)	76.2(2)	C(18)-C(19)-C(14)	120.5(12)
O(7)-Sr(1)-O(4)	60.8(3)	O(1)-C(19)-C(14)	115.7(10)
O(7)^2-Sr(1)-O(4)	119.2(3)	O(4)-C(3)-C(2)	117.5(12)
O(10)-Sr(1)-O(4)	109.2(3)	C(3)-O(4)-C(5)	114.2(11)
O(10)^2-Sr(1)-O(4)	70.8(3)	O(7)-Sr(1)-O(1)^2	71.3(2)
O(4)^2-Sr(1)-O(4)	180	O(7)^2-Sr(1)-O(1)^2	108.7(2)
O(13)-Sr(1)-O(1)	57.5(2)	O(10)-Sr(1)-O(1)^2	71.5(2)
O(13)^2-Sr(1)-O(1)	122.5(2)	O(10)^2-Sr(1)-O(1)^2	108.5(2)
O(7)-Sr(1)-O(1)	108.7(2)	O(4)^2-Sr(1)-O(1)^2	59.1(2)
O(7)^2-Sr(1)-O(1)	71.3(2)	O(4)-Sr(1)-O(1)^2	120.9(2)
O(10)-Sr(1)-O(1)	108.5(2)	O(1)-Sr(1)-O(1)^2	180
O(10)^2-Sr(1)-O(1)	71.5(2)	Ag(1)-I(2)-Ag(1)^2	75.67(5)
O(4)^2-Sr(1)-O(1)	120.9(2)	C(19)-O(1)-C(2)	119.0(9)
O(4)-Sr(1)-O(1)	59.1(2)	C(19)-O(1)-Sr(1)	117.4(6)
O(13)-Sr(1)-O(1)^2	122.5(2)	C(2)-O(1)-Sr(1)	121.3(7)
O(13)^2-Sr(1)-O(1)^2	57.5(2)	C(3)-C(2)-O(1)	111.1(11)

Symmetry transformations used to generate equivalent atoms:
1=-x+1,-y-1,-z 2= -x,-y,-z

Table 24.
Anisotropic displacement parameters ($Å^2 \times 10^3$) for $[Sr(benzo\text{-}15\text{-}crown\text{-}5)_2](Ag_2I_4)$ **(III)**

atom	U11	U22	U33	U23	U13	U12
Ag(1)	89(1)	66(1)	65(1)	-3(1)	16(1)	-7(1)
I(1)	68(1)	64(1)	85(1)	13(1)	-6(1)	-8(1)
Sr(1)	31(1)	40(1)	34(1)	-1(1)	5(1)	-2(1)
I(2)	63(1)	70(1)	64(1)	7(1)	-2(1)	-10(10)
O(1)	68(6)	47(4)	44(5)	-6(4)	12(4)	-18(4)
C(2)	96(13)	64(9)	87(11)	20(9)	18(10)	-24(9)
C(3)	170(2)	76(11)	65(10)	1(9)	49(11)	-29(12)
O(4)	71(7)	80(6)	61(6)	3(5)	34(5)	-6(5)
C(5)	52(9)	105(12)	70(9)	-27(9)	31(7)	-19(9)
C(6)	36(8)	123(13)	62(9)	-41(9)	2(7)	13(8)
O(7)	34(5)	81(6)	74(6)	2(5)	6(5)	21(5)
C(8)	54(9)	66(9)	120(13)	-10(9)	9(9)	39(8)
C(9)	72(10)	68(9)	74(10)	19(8)	-18(8)	21(8)
O(10)	44(5)	57(5)	65(6)	2(4)	6(4)	6(4)
C(11)	48(8)	67(9)	76(10)	13(8)	-15(8)	-12(7)
C(12)	70(10)	98(11)	37(7)	22(7)	-9(7)	-4(9)
O(13)	73(6)	52(5)	34(4)	-3(4)	-4(4)	-4(4)
C(14)	32(7)	55(7)	60(8)	-11(7)	1(6)	-4(6)
C(15)	65(10)	75(10)	62(9)	-28(8)	-2(7)	-4(8)
C(16)	34(8)	94(13)	101(13)	-50(10)	4(8)	-4(8)
C(17)	84(12)	54(9)	150(2)	-48(11)	-7(12)	31(9)
C(18)	109(13)	46(8)	95(12)	-19(8)	-24(10)	4(8)
C(19)	46(8)	50(8)	64(9)	-14(7)	0(7)	3(6)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 25.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [Sr(benzo-15-crown-5)$_2$](Ag$_2$I$_4$) **(III)**

atom	x	y	z	U(eq)
H(2A)	2196	2485	-508	80
H(2B)	1255	3219	-947	80
H(3A)	2055	1979	-2059	80
H(3B)	769	1955	-1969	80
H(5A)	2992	397	-986	80
H(5B)	2782	355	-2157	80
H(6A)	2950	-1356	-1506	80
H(6B)	1797	-1194	-2041	80
H(8A)	2977	-1075	438	80
H(8B)	2913	-2239	17	80
H(9A)	2289	-2194	1701	80
H(9B)	1322	-2482	948	80
H(11A)	2394	-99	1953	80
H(11B)	1990	-852	2806	80
H(12A)	1393	920	3037	80
H(12B)	382	149	2887	80
H(15A)	227	2277	3296	80
H(16A)	13	4149	3280	80
H(17A)	189	5101	1784	80
H(18A)	540	4212	250	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

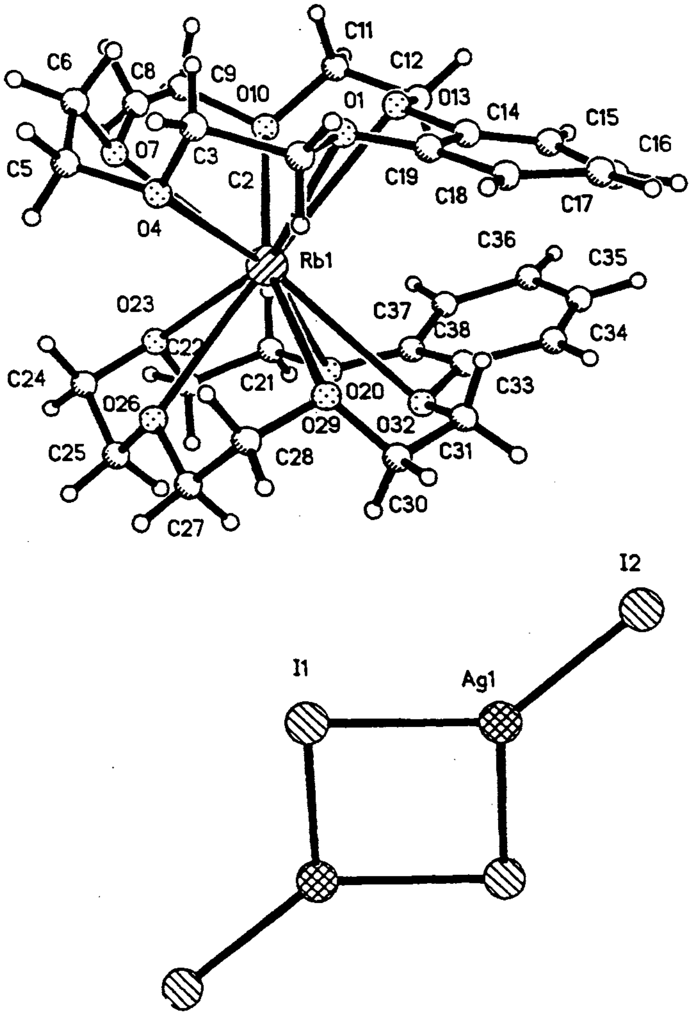


Figure 20. Projection View of [Rb(benzo-15-crown-5)$_2$]$_2$(Ag$_2$I$_4$) **(IV)**

Table 26.
Crystal data and structure refinement for $[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2I_4)$ **(IV)**

Empirical formula	$C_{56} H_{80} Ag_2 I_4 O_{20} Rb_2$
Formula weight	1967.48
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	a = 12.3140(10) Å α = 102.96(2)° b = 12.436(2) Å β = 94.730(10) ° c = 12.6000(10) Å γ = 110.150(10) °
Volume	1738.2(3) A^3
Z, Calculated density	1, 1.880 mg/m^3
Absorption coefficient	3.796 mm^{-1}
F(000)	956
Theta range for data collection	1.79 to 30.00 deg.
Index ranges	$-17 \leq h \leq 1$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$
Reflections collected / unique	11254 / 9982 [R(int) = 0.2464]
Completeness to 2θ = 30.00°	98.5%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9982 / 0 / 380
Goodness-of-fit on F^2	0.965
Final R indices [$I>2\sigma(I)$]	R1 = 0.1379, wR2 = 0.2244
R indices (all data)	R1 = 0.4228, wR2 = 0.3455
Extinction coefficient	0.0000(4)
Largest diff. peak and hole	0.910 and -1.039 eA^{-3}

Table 27.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Rb(benzo-15-crown-5)$_2$]$_2$(Ag$_2$I$_4$) **(IV)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
I(1)	992(2)	6828(2)	269(2)	87(1)
I(2)	1183(2)	5162(2)	3512(2)	109(1)
Ag(1)	506(2)	5138(2)	1458(2)	98(1)
Rb(1)	7169(2)	8601(2)	2130(2)	58(1)
O(1)	758(2)	10120(2)	453(2)	88(6)
C(2)	7000(3)	10910(3)	4520(2)	102(11)
C(3)	7660(4)	11810(3)	3960(4)	190(2)
O(4)	745(2)	11158(17)	2840(2)	113(7)
C(5)	8280(4)	11760(3)	2160(3)	123(13)
C(6)	9390(2)	11550(4)	2190(3)	124(15)
O(7)	912(2)	10370(2)	1660(2)	116(8)
C(8)	10020(3)	10070(5)	1820(5)	350(5)
C(9)	10340(3)	9440(4)	1980(4)	230(3)
O(10)	9534(15)	855(2)	240(2)	104(7)
C(11)	10040(3)	8370(3)	3360(3)	117(13)
C(12)	9140(3)	7860(2)	4020(3)	117(13)
O(13)	861(2)	8698(15)	428(2)	84(6)
C(14)	7740(3)	8430(3)	4910(2)	88(10)
C(15)	7510(3)	7540(3)	5340(3)	122(12)
C(16)	6510(4)	7470(3)	5980(3)	160(2)
C(17)	6170(6)	8300(7)	6310(5)	270(5)
C(18)	6330(4)	9090(5)	5690(3)	190(3)
C(19)	7220(3)	9300(3)	4980(2)	77(9)
O(20)	6536(15)	604(2)	800(2)	92(6)
C(21)	7370(3)	6050(3)	30(3)	130(14)
C(22)	7110(3)	6690(4)	-750(3)	130(15)
O(23)	7377(15)	787(2)	-188(14)	85(6)
C(24)	6890(3)	8470(3)	-810(2)	109(11)
C(25)	5640(3)	8170(3)	-710(2)	104(10)
O(26)	5565(12)	8737(14)	371(14)	70(5)
C(27)	4400(2)	8520(2)	551(16)	71(7)
C(28)	4370(2)	8970(2)	1780(2)	78(8)
O(29)	4773(13)	8428(14)	2477(13)	68(5)
C(30)	3930(2)	7360(2)	244(2)	64(7)
C(31)	4440(2)	6640(2)	2880(2)	72(7)
O(32)	5157(13)	6290(14)	2141(13)	69(5)

Table 27. (continued)
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2I_4)$ **(IV)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
C(33)	5810(2)	5640(2)	2360(3)	85(9)
C(34)	5750(2)	5150(3)	3280(2)	89(9)
C(35)	6510(4)	4610(3)	3420(4)	150(2)
C(36)	7330(4)	4530(3)	2770(4)	150(2)
C(37)	7330(3)	4960(3)	1820(4)	150(2)
C(38)	6550(2)	5480(2)	1590(3)	80(9)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 28.
Bond lengths [Å] and angles [°] for
[Rb(benzo-15-crown-5)$_2$]$_2$(Ag$_2$I$_4$) **(IV)**

I(1)-Ag(1)	2.776(3)	C(14)-C(15)	1.30(4)
I(1)-Ag(1)^{1}	2.821(3)	C(14)-C(19)	1.43(4)
I(2)-Ag(1)	2.644(3)	C(15)-C(16)	1.51(5)
Ag(1)-I(1)^{1}	2.821(3)	C(16)-C(17)	1.24(7)
Rb(1)-O(7)	2.85(2)	C(17)-C(18)	1.36(8)
Rb(1)-O(26)	2.919(15)	C(18)-C(19)	1.46(6)
Rb(1)-O(23)	2.92(2)	O(20)-C(38)	1.34(3)
Rb(1)-O(10)	2.93(2)	O(20)-C(21)	1.47(3)
Rb(1)-O(29)	2.959(15)	C(21)-C(22)	1.48(4)
Rb(1)-O(4)	2.99(2)	C(22)-O(23)	1.38(4)
Rb(1)-O(20)	3.04(2)	O(23)-C(24)	1.42(3)
Rb(1)-O(13)	3.07(2)	C(24)-C(25)	1.48(3)
Rb(1)-O(1)	3.08(2)	C(25)-O(26)	1.42(3)
Rb(1)-O(32)	3.08(2)	O(26)-C(27)	1.41(2)
Rb(1)-C(8)	3.46(4)	C(27)-C(28)	1.54(3)
Rb(1)-C(19)	3.49(3)	C(28)-O(29)	1.37(2)
O(1)-C(19)	1.24(3)	O(29)-C(30)	1.36(3)
O(1)-C(2)	1.39(3)	C(30)-C(31)	1.44(3)
C(2)-C(3)	1.50(5)	C(31)-O(32)	1.43(2)
C(3)-O(4)	1.42(4)	O(32)-C(33)	1.37(2)
O(4)-C(5)	1.51(3)	C(33)-C(38)	1.41(4)
C(5)-C(6)	1.47(4)	C(33)-C(34)	1.43(4)
C(6)-O(7)	1.37(4)	C(34)-C(35)	1.34(4)
O(7)-C(8)	1.30(3)	C(35)-C(36)	1.37(5)
C(8)-C(9)	1.04(5)	C(36)-C(37)	1.41(5)
C(9)-O(10)	1.44(5)	C(37)-C(38)	1.37(3)
O(10)-C(11)	1.42(3)	C(14)-O(13)-C(12)	116(2)
C(11)-C(12)	1.49(4)	C(14)-O(13)-Rb(1)	100.5(15)
C(12)-O(13)	1.41(3)	C(12)-O(13)-Rb(1)	107(2)
O(13)-C(14)	1.38(3)	C(15)-C(14)-O(13)	123(4)
C(8)-C(9)-O(10)	114(3)	C(15)-C(14)-C(19)	130(4)
C(8)-C(9)-Rb(1)	68(3)	O(13)-C(14)-C(19)	107(2)
O(10)-C(9)-Rb(1)	47.1(11)	C(15)-C(14)-Rb(1)	132(2)
C(11)-O(10)-C(9)	114(3)	O(13)-C(14)-Rb(1)	57.4(12)
C(11)-O(10)-Rb(1)	122(2)	C(19)-C(14)-Rb(1)	74.8(15)
C(9)-O(10)-Rb(1)	112(2)	C(14)-C(15)-C(16)	110(4)
O(10)-C(11)-C(12)	112(3)	C(17)-C(16)-C(15)	125(4)
O(13)-C(12)-C(11)	104(2)	C(16)-C(17)-C(18)	116(4)
O(13)-C(12)-Rb(1)	51.7(12)	C(17)-C(18)-C(19)	124(5)
C(11)-C(12)-Rb(1)	83.8(16)	O(1)-C(19)-C(14)	121(3)
Ag(1)-I(1)-Ag(1)^{1}	82.22(9)	O(1)-C(19)-C(18)	130(3)
I(2)-Ag(1)-I(1)	134.69(12)	C(14)-C(19)-C(18)	109(4)
I(2)-Ag(1)-I(1)^{1}	127.51(12)	O(1)-C(19)-Rb(1)	60.8(14)
I(1)-Ag(1)-I(1)^{1}	97.78(9)	C(14)-C(19)-Rb(1)	81.9(14)
O(7)-Rb(1)-O(26)	91.7(5)	C(18)-C(19)-Rb(1)	135(2)

Table 28. (cont.)
Bond lengths [Å] and angles [°] for
[Rb(benzo-15-crown-5)$_2$]$_2$(Ag$_2$I$_4$) **(IV)**

O(7)-Rb(1)-O(23)	70.4(6)	C(38)-O(20)-C(21)	119(2)
O(26)-Rb(1)-O(23)	58.9(5)	C(38)-O(20)-Rb(1)	103(2)
O(7)-Rb(1)-O(10)	58.1(6)	C(21)-O(20)-Rb(1)	106.9(15)
O(26)-Rb(1)-O(10)	136.2(6)	O(20)-C(21)-C(22)	106(2)
O(23)-Rb(1)-O(10)	80.1(6)	O(20)-C(21)-Rb(1)	51.0(11)
O(7)-Rb(1)-O(29)	134.1(6)	C(22)-C(21)-Rb(1)	83(2)
O(26)-Rb(1)-O(29)	60.5(5)	O(23)-C(22)-C(21)	109(3)
O(23)-Rb(1)-O(29)	114.0(5)	C(22)-O(23)-C(24)	112(2)
O(10)-Rb(1)-O(29)	162.9(6)	C(22)-O(23)-Rb(1)	123(2)
O(7)-Rb(1)-O(4)	60.3(7)	C(24)-O(23)-Rb(1)	109.6(14)
O(26)-Rb(1)-O(4)	78.2(5)	O(23)-C(24)-C(25)	109(2)
O(23)-Rb(1)-O(4)	112.0(7)	O(23)-C(24)-Rb(1)	48.9(11)
O(10)-Rb(1)-O(4)	106.8(6)	C(25)-C(24)-Rb(1)	82.0(13)
O(29)-Rb(1)-O(4)	77.7(5)	O(26)-C(25)-C(24)	109(2)
O(7)-Rb(1)-O(20)	117.3(6)	O(26)-C(25)-Rb(1)	45.1(11)
O(26)-Rb(1)-O(20)	85.7(5)	C(24)-C(25)-Rb(1)	74.9(14)
O(23)-Rb(1)-O(20)	55.2(6)	C(27)-O(26)-C(25)	114(2)
O(10)-Rb(1)-O(20)	82.4(5)	C(27)-O(26)-Rb(1)	116.0(12)
O(29)-Rb(1)-O(20)	97.6(4)	C(25)-O(26)-Rb(1)	114.8(14)
O(4)-Rb(1)-O(20)	163.6(6)	O(26)-C(27)-C(28)	111(2)
O(7)-Rb(1)-O(13)	91.9(6)	O(29)-C(28)-C(27)	116(2)
O(26)-Rb(1)-O(13)	168.8(5)	O(29)-C(28)-Rb(1)	50.7(10)
O(23)-Rb(1)-O(13)	132.3(6)	C(27)-C(28)-Rb(1)	82.7(12)
O(10)-Rb(1)-O(13)	53.9(6)	C(30)-O(29)-C(28)	111(2)
O(29)-Rb(1)-O(13)	109.9(5)	C(30)-O(29)-Rb(1)	120.7(12)
O(4)-Rb(1)-O(13)	94.4(5)	C(28)-O(29)-Rb(1)	108.3(14)
O(20)-Rb(1)-O(13)	102.0(5)	O(29)-C(30)-C(31)	111(2)
O(7)-Rb(1)-O(1)	91.1(6)	O(32)-C(31)-C(30)	109(2)
O(26)-Rb(1)-O(1)	121.5(5)	C(33)-O(32)-C(31)	123(2)
O(23)-Rb(1)-O(1)	161.4(6)	C(33)-O(32)-Rb(1)	98.9(13)
O(10)-Rb(1)-O(1)	92.4(6)	C(31)-O(32)-Rb(1)	106.5(12)
O(29)-Rb(1)-O(1)	76.9(5)	O(32)-C(33)-C(38)	115(3)
O(4)-Rb(1)-O(1)	53.7(6)	O(32)-C(33)-C(34)	123(3)
O(20)-Rb(1)-O(1)	141.1(6)	C(38)-C(33)-C(34)	122(3)
O(13)-Rb(1)-O(1)	47.8(5)	O(32)-C(33)-Rb(1)	58.7(11)
O(7)-Rb(1)-O(32)	166.1(6)	C(38)-C(33)-Rb(1)	79.0(15)
O(26)-Rb(1)-O(32)	85.6(4)	C(34)-C(33)-Rb(1)	133(2)
O(23)-Rb(1)-O(32)	96.7(5)	C(35)-C(34)-C(33)	116(3)
O(10)-Rb(1)-O(32)	115.8(5)	C(34)-C(35)-C(36)	126(4)
O(29)-Rb(1)-O(32)	55.2(4)	C(35)-C(36)-C(37)	117(4)
O(4)-Rb(1)-O(32)	132.0(5)	C(38)-C(37)-C(36)	121(3)
O(20)-Rb(1)-O(32)	48.9(5)	O(20)-C(38)-C(37)	127(3)
O(13)-Rb(1)-O(32)	93.3(5)	O(20)-C(38)-C(33)	114(2)
O(1)-Rb(1)-O(32)	101.9(5)	C(37)-C(38)-C(33)	118(3)
O(7)-Rb(1)-C(8)	21.1(8)	O(20)-C(38)-Rb(1)	56.1(12)

Table 28. (cont.)
Bond lengths [Å] and angles [°] for
[Rb(benzo-15-crown-5)$_2$]$_2$(Ag$_2$I$_4$) **(IV)**

O(26)-Rb(1)-C(8)	108.5(9)	C(37)-C(38)-Rb(1)	127(2)
O(23)-Rb(1)-C(8)	70.9(11)	C(33)-C(38)-Rb(1)	78.2(14)
O(10)-Rb(1)-C(8)	37.1(8)	C(19)-O(1)-C(2)	121(3)
O(29)-Rb(1)-C(8)	154.3(9)	C(19)-O(1)-Rb(1)	98.6(15)
O(4)-Rb(1)-C(8)	77.3(10)	C(2)-O(1)-Rb(1)	107.3(14)
O(20)-Rb(1)-C(8)	104.8(11)	O(1)-C(2)-C(3)	108(3)
O(13)-Rb(1)-C(8)	77.7(10)	O(1)-C(2)-Rb(1)	51.9(12)
O(1)-Rb(1)-C(8)	92.8(12)	C(3)-C(2)-Rb(1)	87(2)
O(32)-Rb(1)-C(8)	150.4(9)	O(4)-C(3)-C(2)	104(3)
O(7)-Rb(1)-C(19)	108.6(8)	C(3)-O(4)-C(5)	114(3)
O(26)-Rb(1)-C(19)	129.3(6)	C(3)-O(4)-Rb(1)	123(2)
O(23)-Rb(1)-C(19)	171.7(7)	C(5)-O(4)-Rb(1)	105(2)
O(10)-Rb(1)-C(19)	92.4(7)	C(6)-C(5)-O(4)	115(3)
O(29)-Rb(1)-C(19)	72.8(6)	C(6)-C(5)-Rb(1)	80(2)
O(4)-Rb(1)-C(19)	73.3(8)	O(4)-C(5)-Rb(1)	51.6(12)
O(20)-Rb(1)-C(19)	120.7(7)	O(7)-C(6)-C(5)	108(3)
O(13)-Rb(1)-C(19)	39.6(6)	O(7)-C(6)-Rb(1)	42.1(13)
O(1)-Rb(1)-C(19)	20.6(5)	C(5)-C(6)-Rb(1)	77(2)
O(32)-Rb(1)-C(19)	83.4(6)	C(8)-O(7)-C(6)	111(4)
C(8)-Rb(1)-C(19)	105.1(12)	C(8)-O(7)-Rb(1)	107(2)
C(6)-O(7)-Rb(1)	119(2)	C(9)-C(8)-Rb(1)	96(3)
C(9)-C(8)-O(7)	148(5)	O(7)-C(8)-Rb(1)	52(2)

Symmetry transformations used to generate equivalent atoms:
1 = -x,-y+1,-z

Table 29.
Anisotropic displacement parameters ($Å^2$ x 10^3) for
$[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2I_4)$ **(IV)**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	67(1)	96(2)	89(2)	29(1)	15(1)	16(1)
I(2)	101(2)	115(2)	80(2)	35(1)	15(1)	-1(1)
Ag(1)	75(2)	134(2)	85(2)	36(2)	22(1)	32(2)
Rb(1)	46(1)	58(2)	59(2)	14(1)	5(1)	9(1)
O(1)	80(14)	85(15)	100(2)	35(13)	11(11)	29(13)
C(2)	110(2)	130(3)	40(2)	2(18)	-36(15)	30(2)
C(3)	210(4)	60(2)	310(6)	-50(3)	40(4)	130(3)
O(4)	130(2)	69(14)	150(2)	19(14)	3(15)	68(14)
C(5)	190(4)	80(2)	70(2)	20(2)	40(3)	0(3)
C(6)	40(2)	160(4)	110(3)	70(3)	-10(2)	-50(2)
O(7)	96(16)	76(15)	160(2)	72(15)	17(15)	-8(14)
C(8)	100(3)	560(12)	630(12)	420(11)	220(6)	230(6)
C(9)	70(2)	290(5)	370(7)	20(5)	120(3)	140(3)
O(10)	51(11)	110(2)	160(2)	37(14)	56(13)	36(12)
C(11)	130(3)	70(2)	140(3)	20(2)	-60(2)	50(2)
C(12)	120(3)	35(17)	160(3)	70(2)	-40(2)	-20(2)
O(13)	85(13)	55(12)	110(2)	41(11)	-9(11)	26(11)
C(14)	100(2)	55(19)	70(2)	30(16)	-5(16)	-30(2)
C(15)	140(3)	70(2)	100(3)	30(2)	-30(2)	-30(2)
C(16)	190(4)	130(3)	30(2)	1(2)	10(2)	-90(3)
C(17)	260(7)	390(11)	120(5)	30(6)	170(5)	60(7)
C(18)	220(5)	270(7)	60(3)	-70(3)	-30(3)	150(5)
C(19)	100(2)	70(2)	21(14)	-49(13)	-8(14)	30(2)
O(20)	81(13)	68(13)	140(2)	23(12)	50(12)	37(11)
C(21)	90(2)	140(3)	150(3)	-50(3)	30(2)	80(2)
C(22)	130(3)	230(5)	70(2)	20(3)	40(2)	120(3)
O(23)	74(12)	100(2)	48(12)	-12(11)	8(9)	21(12)
C(24)	110(2)	190(3)	60(2)	90(2)	60(2)	50(3)
C(25)	120(3)	140(3)	50(2)	40(2)	20(2)	30(2)
O(26)	39(9)	80(12)	81(13)	30(10)	2(8)	5(9)
C(27)	80(2)	110(2)	25(13)	18(13)	-9(12)	40(2)
C(28)	51(15)	100(2)	80(2)	30(17)	-10(13)	40(2)
O(29)	56(10)	42(10)	80(12)	-7(8)	-14(8)	6(9)
C(30)	60(2)	60(2)	70(2)	0(13)	-4(13)	30(2)
C(31)	50(15)	90(2)	80(2)	30(2)	32(14)	17(15)

Table 29. (cont.)

Anisotropic displacement parameters (Å^2 x 10^3) for
[Rb(benzo-15-crown-5)$_2$]$_2$(Ag$_2$I$_4$) **(IV)**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(32)	46(9)	84(13)	87(13)	34(10)	19(9)	29(9)
C(33)	38(15)	50(2)	140(3)	4(2)	-40(2)	1(13)
C(34)	80(2)	100(2)	80(2)	20(2)	-1(15)	10(2)
C(35)	140(4)	60(2)	270(6)	60(3)	-20(3)	70(3)
C(36)	150(4)	60(3)	260(6)	40(3)	-20(4)	70(3)
C(37)	70(2)	100(3)	310(6)	70(3)	80(3)	70(2)
C(38)	40(14)	37(15)	180(3)	60(2)	60(2)	3(12)

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{2*} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 30. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **(IV)**

atom	x	y	z	U(eq)
H(2A)	6972	11290	5266	80
H(2B)	6215	10538	4105	80
H(3A)	8477	12002	4215	80
H(3B)	7503	12532	4061	80
H(5A)	8453	12603	2416	80
H(5B)	7906	11507	1399	80
H(6A)	9746	11694	2943	80
H(6B)	9923	12051	1837	80
H(8A)	10660	10823	2121	80
H(8B)	10071	9833	1048	80
H(9A)	10914	9908	2632	80
H(9B)	10725	9069	1472	80
H(11A)	10532	9149	3813	80
H(11B)	10519	7915	3182	80
H(12A)	9497	7745	4665	80
H(12B)	8596	7101	3561	80
H(15A)	7879	6967	5245	80
H(16A)	6275	6831	6322	80
H(17A)	5590	8203	6782	80
H(18A)	5936	9641	5799	80
H(21A)	7272	5261	-365	80
H(21B)	8158	6447	443	80
H(22A)	6311	6297	-1136	80
H(22B)	7614	6697	-1293	80
H(24A)	6947	8210	-1571	80
H(24B)	7322	9309	-547	80
H(25A)	5252	8435	-1233	80
H(27A)	3987	7671	357	80
H(27B)	4006	8838	93	80
H(28A)	3592	8924	1871	80
H(28B)	4886	9791	2011	80
H(30A)	3532	6941	1698	80
H(30B)	3367	7511	2876	80
H(31A)	3850	5940	2979	80
H(31B)	4925	7095	3583	80
H(34A)	5165	5208	3720	80
H(35A)	6499	4323	4063	80
H(36A)	7795	4070	2905	80
H(37A)	7962	4945	1432	80

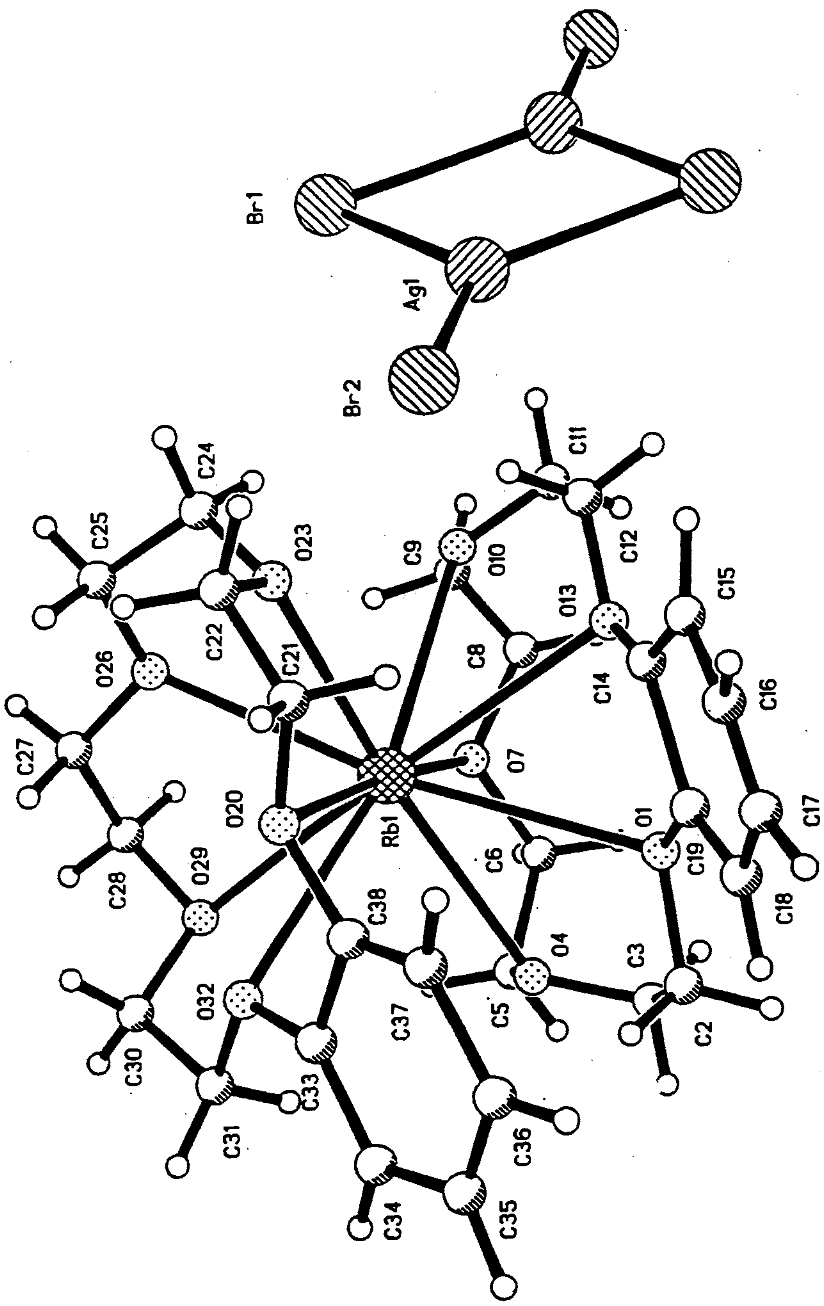


Figure 21. Projection View of $[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2Br_4)$ (V)

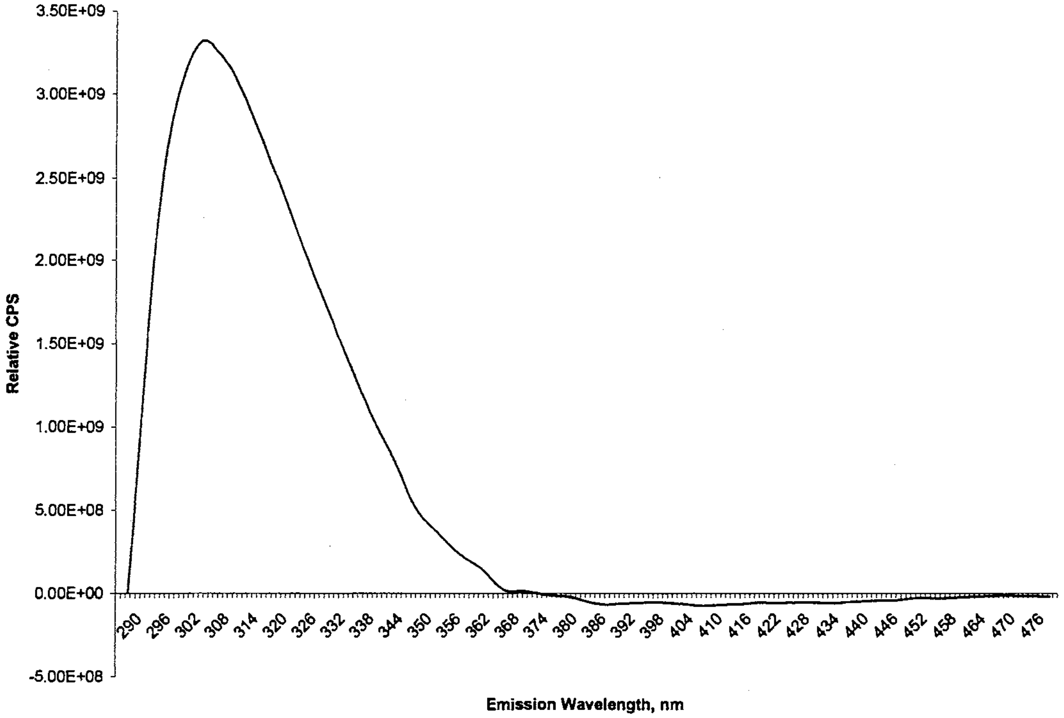


Figure 22. Emission Spectrum of $[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2Br_4)$ **(V)**

Table 31.
Crystal data and structure refinement for
$[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2Br_4)$ **(V)**

Empirical formula	$C_{56}H_{80}Ag_2Br_4O_{20}Rb_2$
Formula weight	1783.55
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 12.023(5) Å α = 106.13(3)°
	b = 12.476(4) Å β = 91.07(3)°
	c = 12.986(6) Å γ = 111.42(3)°
Volume	1726.2(12) $Å^3$
Z, Calculated density	1, 1.716 Mg/m^3
Absorption coefficient	4.349 mm^{-1}
F(000)	888
Theta range for data collection	2.04° to 23.26°.
Index ranges	$-13 \leq h \leq 1, -13 \leq k \leq 13, -14 \leq l \leq 14$
Reflections collected / unique	5734 / 4905 [R(int) = 0.1295]
Completeness to 2θ = 23.26°	98.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4905 / 0 / 380
Goodness-of-fit on F^2	0.982
Final R indices [$I>2\sigma(I)$]	R1 = 0.1479, wR2 = 0.2674
R indices (all data)	R1 = 0.4044, wR2 = 0.3851
Extinction coefficient	0.0000(10)
Largest diff. peak and hole	1.058 and -0.658 $e.Å^{-3}$

Table 32

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2Br_4)$ **(V)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Rb(1)	7192(3)	8742(3)	2055(2)	63(1)
Ag(1)	10423(3)	5235(3)	1394(2)	107(2)
Br(1)	11084(4)	6672(3)	163(3)	90(2)
Br(2)	11009(5)	5468(5)	3322(3)	165(3)
O(1)	5110(2)	6500(2)	2210(2)	85(10)
C(2)	4270(4)	6800(3)	2930(3)	100(2)
C(3)	3850(3)	7470(3)	2470(3)	70(14)
O(4)	4740(2)	8510(2)	2450(17)	70(8)
C(5)	4290(3)	9070(3)	1740(3)	94(17)
C(6)	4340(4)	8570(3)	500(2)	88(14)
O(7)	5600(3)	8690(2)	326(19)	102(10)
C(8)	5660(5)	7850(6)	-660(4)	420(9)
C(9)	6650(4)	8180(4)	-960(2)	110(2)
O(10)	731(2)	7660(2)	-261(15)	84(9)
C(11)	7070(3)	6510(3)	-710(3)	94(17)
C(12)	7350(4)	5940(3)	180(3)	90(15)
O(13)	6620(3)	6110(2)	950(2)	114(13)
C(14)	6670(5)	5720(4)	1850(6)	180(4)
C(15)	6960(6)	5020(5)	1960(6)	260(6)
C(16)	6920(6)	4730(4)	3150(7)	240(4)
C(17)	6120(3)	4810(5)	3510(4)	130(2)
C(18)	5470(3)	5410(3)	3370(4)	96(15)
C(19)	5630(5)	5820(3)	2500(3)	100(2)
O(20)	8800(2)	8900(2)	4050(2)	87(9)
C(21)	9530(4)	8210(3)	3690(3)	100(2)
C(22)	10340(4)	8550(3)	2970(3)	81(13)
O(23)	9530(2)	8520(2)	2040(2)	78(9)
C(24)	10150(3)	9130(3)	1350(3)	100(2)
C(25)	10410(4)	10410(5)	1720(4)	140(2)
O(26)	9270(3)	1060(2)	1680(2)	98(11)
C(27)	9280(4)	11760(4)	2080(3)	110(2)
C(28)	8150(4)	11900(3)	2050(3)	90(15)
O(29)	7420(2)	11310(2)	2740(2)	89(9)
C(30)	7700(4)	11980(3)	3840(3)	90(14)
C(31)	7120(4)	11190(3)	4540(3)	130(2)
O(32)	7670(2)	10330(2)	4389(14)	70(7)
C(33)	7400(4)	9500(3)	4990(2)	62(12)

Table 32 (cont.)

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
C(34)	6530(3)	9340(4)	5650(3)	110(2)
C(35)	6310(5)	8380(4)	6130(3)	160(3)
C(36)	6810(4)	7660(4)	5870(3)	110(2)
C(37)	7740(4)	7830(3)	5230(3)	110(2)
C(38)	7930(3)	8650(4)	4690(3)	66(12)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 33.
Bond lengths [Å] and angles [°] for
[Rb(benzo-15-crown-5)$_2$]$_2$(Ag$_2$Br$_4$) (**V**)

Rb(1)-O(26)	2.88(2)	C(24)-C(25)	1.44(5)
Rb(1)-O(7)	2.90(3)	C(25)-O(26)	1.46(5)
Rb(1)-O(23)	2.92(3)	O(26)-C(27)	1.41(5)
Rb(1)-O(4)	2.93(2)	C(27)-C(28)	1.43(5)
Rb(1)-O(10)	2.97(2)	C(28)-O(29)	1.42(4)
Rb(1)-O(29)	2.98(2)	O(29)-C(30)	1.41(3)
Rb(1)-O(13)	3.00(3)	C(30)-C(31)	1.52(4)
Rb(1)-O(32)	3.04(2)	C(31)-O(32)	1.42(5)
Rb(1)-O(1)	3.06(2)	O(32)-C(33)	1.42(4)
Rb(1)-O(20)	3.13(3)	C(33)-C(34)	1.36(4)
Rb(1)-C(38)	3.55(4)	C(33)-C(38)	1.39(5)
Rb(1)-C(24)	3.58(3)	C(34)-C(35)	1.45(6)
Ag(1)-Br(2)	2.496(6)	C(35)-C(36)	1.23(7)
Ag(1)-Br(1)	2.646(5)	C(36)-C(37)	1.40(5)
Ag(1)-Br(1)^1	2.659(5)	C(37)-C(38)	1.36(4)
Br(1)-Ag(1)^1	2.659(5)	O(26)-Rb(1)-O(7)	94.7(8)
O(1)-C(19)	1.34(5)	O(26)-Rb(1)-O(23)	59.3(8)
O(1)-C(2)	1.47(4)	O(7)-Rb(1)-O(23)	130.6(7)
C(2)-C(3)	1.38(5)	O(26)-Rb(1)-O(4)	135.2(8)
C(3)-O(4)	1.35(3)	O(7)-Rb(1)-O(4)	62.0(7)
O(4)-C(5)	1.50(4)	O(23)-Rb(1)-O(4)	163.7(7)
C(5)-C(6)	1.58(4)	O(26)-Rb(1)-O(10)	78.6(6)
C(6)-O(7)	1.49(4)	O(7)-Rb(1)-O(10)	57.4(7)
O(7)-C(8)	1.43(5)	O(23)-Rb(1)-O(10)	75.7(7)
C(8)-C(9)	1.22(5)	O(4)-Rb(1)-O(10)	111.8(6)
C(9)-O(10)	1.60(4)	O(26)-Rb(1)-O(29)	59.8(7)
O(10)-C(11)	1.30(3)	O(7)-Rb(1)-O(29)	79.5(6)
C(11)-C(12)	1.61(5)	O(23)-Rb(1)-O(29)	112.7(6)
C(12)-O(13)	1.37(4)	O(4)-Rb(1)-O(29)	77.7(7)
O(13)-C(14)	1.39(8)	O(10)-Rb(1)-O(29)	116.6(7)
C(14)-C(15)	1.10(12)	O(26)-Rb(1)-O(13)	121.2(8)
C(14)-C(19)	1.54(7)	O(7)-Rb(1)-O(13)	88.2(8)
C(15)-C(16)	1.68(9)	O(23)-Rb(1)-O(13)	75.0(7)
C(16)-C(17)	1.10(8)	O(4)-Rb(1)-O(13)	97.2(7)
C(17)-C(18)	1.30(5)	O(10)-Rb(1)-O(13)	54.5(8)
C(18)-C(19)	1.35(5)	O(29)-Rb(1)-O(13)	167.6(8)
O(20)-C(38)	1.35(4)	O(26)-Rb(1)-O(32)	87.1(6)
O(20)-C(21)	1.44(5)	O(7)-Rb(1)-O(32)	126.2(7)
C(21)-C(22)	1.41(4)		
C(22)-O(23)	1.53(4)		
O(23)-C(24)	1.39(4)		

Table 33. (continued)
Bond lengths [Å] and angles [°] for
[Rb(benzo-15-crown-5)$_2$]$_2$(Ag$_2$Br$_4$) **(V)**

O(23)-Rb(1)-O(32)	95.9(6)	O(13)-Rb(1)-C(24)	84.0(8)
O(4)-Rb(1)-O(32)	79.5(6)	O(32)-Rb(1)-C(24)	103.6(7)
O(10)-Rb(1)-O(32)	165.6(6)	O(1)-Rb(1)-C(24)	130.7(9)
O(29)-Rb(1)-O(32)	55.5(7)	O(20)-Rb(1)-C(24)	71.3(8)
O(13)-Rb(1)-O(32)	135.2(8)	C(38)-Rb(1)-C(24)	93.2(9)
O(26)-Rb(1)-O(1)	171.1(7)	Br(2)-Ag(1)-Br(1)	134.2(2)
O(7)-Rb(1)-O(1)	85.6(8)	Br(2)-Ag(1)-Br(1)^1	130.3(2)
O(23)-Rb(1)-O(1)	114.0(7)	Br(1)-Ag(1)-Br(1)^1	95.45(14)
O(4)-Rb(1)-O(1)	52.4(8)	Ag(1)-Br(1)-Ag(1)^1	84.55(14)
O(10)-Rb(1)-O(1)	94.2(6)	C(19)-O(1)-C(2)	115(3)
O(29)-Rb(1)-O(1)	128.8(7)	C(19)-O(1)-Rb(1)	106(2)
O(13)-Rb(1)-O(1)	49.8(7)	C(2)-O(1)-Rb(1)	112(2)
O(32)-Rb(1)-O(1)	99.9(6)	C(3)-C(2)-O(1)	104(3)
O(26)-Rb(1)-O(20)	86.8(7)	O(4)-C(3)-C(2)	112(3)
O(7)-Rb(1)-O(20)	175.4(7)	C(3)-O(4)-C(5)	110(3)
O(23)-Rb(1)-O(20)	53.8(7)	C(3)-O(4)-Rb(1)	124(2)
O(4)-Rb(1)-O(20)	114.0(7)	C(5)-O(4)-Rb(1)	109(2)
O(10)-Rb(1)-O(20)	127.3(8)	O(4)-C(5)-C(6)	115(3)
O(29)-Rb(1)-O(20)	97.6(6)	O(4)-C(5)-Rb(1)	48.7(15)
O(13)-Rb(1)-O(20)	94.8(8)	C(6)-C(5)-Rb(1)	84(2)
O(32)-Rb(1)-O(20)	49.4(7)	O(7)-C(6)-C(5)	110(3)
O(1)-Rb(1)-O(20)	93.6(7)	C(8)-O(7)-C(6)	113(3)
O(26)-Rb(1)-C(38)	105.2(8)	C(8)-O(7)-Rb(1)	109(4)
O(7)-Rb(1)-C(38)	154.2(8)	C(6)-O(7)-Rb(1)	120(2)
O(23)-Rb(1)-C(38)	74.7(8)	C(9)-C(8)-O(7)	113(4)
O(4)-Rb(1)-C(38)	92.2(8)	C(9)-C(8)-Rb(1)	88(4)
O(10)-Rb(1)-C(38)	142.2(10)	O(7)-C(8)-Rb(1)	49(3)
O(29)-Rb(1)-C(38)	96.3(9)	C(8)-C(9)-O(10)	99(5)
O(13)-Rb(1)-C(38)	95.2(10)	C(11)-O(10)-C(9)	112(3)
O(32)-Rb(1)-C(38)	41.1(8)	C(11)-O(10)-Rb(1)	124(2)
O(1)-Rb(1)-C(38)	77.3(8)	C(9)-O(10)-Rb(1)	108(2)
O(20)-Rb(1)-C(38)	22.0(7)	O(10)-C(11)-C(12)	109(3)
O(26)-Rb(1)-C(24)	41.2(9)	O(13)-C(12)-C(11)	106(3)
O(7)-Rb(1)-C(24)	112.6(8)	O(13)-C(12)-Rb(1)	48.1(13)
O(23)-Rb(1)-C(24)	21.8(8)	C(11)-C(12)-Rb(1)	81.8(15)
O(4)-Rb(1)-C(24)	174.3(9)	C(14)-O(13)-C(12)	120(4)
O(10)-Rb(1)-C(24)	64.4(7)	C(14)-O(13)-Rb(1)	100(3)
O(29)-Rb(1)-C(24)	100.0(8)	C(12)-O(13)-Rb(1)	112(2)
O(13)-C(14)-C(19)	110(7)	C(15)-C(14)-O(13)	130(7)
C(15)-C(14)-C(19)	113(7)	O(13)-C(14)-C(19)	110(7)

Table 33. (continued)
Bond lengths [Å] and angles [°] for
[Rb(benzo-15-crown-5)$_2$](Ag$_2$Br$_4$) **(V)**

C(14)-C(15)-C(16)	120(5)
C(17)-C(16)-C(15)	111(6)
C(16)-C(17)-C(18)	131(7)
C(17)-C(18)-C(19)	117(5)
O(1)-C(19)-C(18)	128(5)
O(1)-C(19)-C(14)	112(5)
C(18)-C(19)-C(14)	119(7)
O(1)-C(19)-Rb(1)	54(2)
C(18)-C(19)-Rb(1)	136(2)
C(14)-C(19)-Rb(1)	72(3)
C(38)-O(20)-C(21)	126(3)
C(38)-O(20)-Rb(1)	97(2)
C(21)-O(20)-Rb(1)	109(2)
C(22)-C(21)-O(20)	118(3)
C(21)-C(22)-O(23)	102(3)
C(24)-O(23)-C(22)	113(3)
C(24)-O(23)-Rb(1)	107(2)
C(22)-O(23)-Rb(1)	129(2)
O(23)-C(24)-C(25)	113(3)
O(23)-C(24)-Rb(1)	51(2)
C(25)-C(24)-Rb(1)	86(2)
C(24)-C(25)-O(26)	109(3)
C(27)-O(26)-C(25)	120(4)
C(27)-O(26)-Rb(1)	114(2)
C(25)-O(26)-Rb(1)	116(2)
O(26)-C(27)-C(28)	118(3)
O(26)-C(27)-Rb(1)	46(2)
C(28)-C(27)-Rb(1)	79(2)
C(27)-C(28)-O(29)	110(4)
C(27)-C(28)-Rb(1)	79(2)
O(29)-C(28)-Rb(1)	50.4(13)
C(30)-O(29)-C(28)	114(3)
C(30)-O(29)-Rb(1)	120(2)
C(15)-C(14)-Rb(1)	152(5)
O(13)-C(14)-Rb(1)	57(3)
C(19)-C(14)-Rb(1)	83(3)
C(28)-O(29)-Rb(1)	108(2)
O(29)-C(30)-C(31)	111(3)
O(32)-C(31)-C(30)	106(3)
C(31)-O(32)-C(33)	121(3)
C(31)-O(32)-Rb(1)	112(2)
C(33)-O(32)-Rb(1)	103.6(15)
C(34)-C(33)-C(38)	120(4)
C(34)-C(33)-O(32)	124(5)
C(38)-C(33)-O(32)	114(3)
C(34)-C(33)-Rb(1)	131(3)
C(38)-C(33)-Rb(1)	75(2)
O(32)-C(33)-Rb(1)	54.1(12)
C(33)-C(34)-C(35)	117(5)
C(36)-C(35)-C(34)	121(4)
C(35)-C(36)-C(37)	122(5)
C(38)-C(37)-C(36)	119(4)
O(20)-C(38)-C(37)	124(5)
O(20)-C(38)-C(33)	116(4)
C(37)-C(38)-C(33)	118(4)
O(20)-C(38)-Rb(1)	61(2)
C(37)-C(38)-Rb(1)	139(2)
C(33)-C(38)-Rb(1)	82(2)

Symmetry transformations used to generate equivalent atoms:
1= -x+2,-y+1,-z

Table 34.
Anisotropic displacement parameters (Å^2 x 10^3) for [Rb(benzo-15-crown-5)$_2$]$_2$(Ag$_2$Br$_4$) **(V)**

atom	U11	U22	U33	U23	U13	U12
Rb(1)	54(2)	60(2)	69(2)	13(1)	17(2)	18(2)
Ag(1)	97(3)	125(3)	93(2)	26(2)	34(2)	40(2)
Br(1)	84(3)	72(2)	103(3)	21(2)	21(2)	20(2)
Br(2)	141(5)	184(5)	90(3)	37(3)	17(3)	-24(4)
O(1)	130(3)	40(13)	100(2)	45(13)	80(2)	36(14)
C(2)	160(5)	70(3)	50(2)	40(2)	10(3)	0(3)
C(3)	30(2)	50(2)	120(3)	30(2)	60(2)	-3(2)
O(4)	40(2)	98(18)	84(16)	16(13)	-2(12)	48(15)
C(5)	0(2)	90(3)	140(3)	-20(2)	30(2)	1(2)
C(6)	190(5)	90(2)	80(3)	70(2)	30(3)	130(3)
O(7)	110(3)	90(2)	110(2)	12(13)	50(2)	60(2)
C(8)	130(6)	500(12)	200(6)	-150(7)	120(5)	-160(7)
C(9)	110(4)	250(5)	50(2)	80(3)	-20(2)	140(4)
O(10)	50(2)	120(2)	58(13)	-1(13)	40(12)	34(14)
C(11)	60(3)	90(3)	80(3)	-20(2)	60(2)	10(2)
C(12)	90(3)	60(2)	140(3)	10(2)	70(3)	70(2)
O(13)	140(3)	90(2)	140(2)	60(2)	90(2)	50(2)
C(14)	150(5)	50(3)	240(7)	-50(4)	140(5)	0(3)
C(15)	160(6)	90(4)	300(8)	-170(5)	160(6)	-40(4)
C(16)	110(6)	120(4)	580(13)	180(6)	-60(8)	100(4)
C(17)	0(2)	240(6)	240(5)	100(4)	-10(3)	120(3)
C(18)	30(3)	70(3)	190(5)	30(3)	20(3)	40(2)
C(19)	170(5)	20(2)	110(3)	40(2)	40(3)	0(2)
O(20)	80(2)	71(15)	90(2)	0(13)	15(15)	19(14)
C(21)	160(5)	60(2)	80(3)	30(2)	-10(3)	60(3)
C(22)	90(3)	70(2)	80(3)	20(2)	0(3)	40(2)
O(23)	51(18)	75(14)	100(2)	19(12)	42(16)	23(13)
C(24)	1(19)	120(3)	130(3)	-30(3)	30(2)	0(2)
C(25)	110(5)	190(6)	130(4)	40(3)	90(4)	60(4)
O(26)	170(3)	44(14)	100(2)	36(12)	60(2)	60(2)
C(27)	80(4)	100(4)	130(3)	60(3)	20(3)	0(3)
C(28)	100(4)	50(2)	120(3)	10(2)	30(3)	40(2)
O(29)	140(2)	71(14)	56(14)	18(12)	32(15)	44(15)
C(30)	120(4)	60(2)	100(3)	20(2)	-30(2)	50(2)
C(31)	180(5)	60(2)	100(3)	-30(2)	20(3)	50(3)
O(32)	100(2)	110(2)	33(11)	21(13)	17(12)	70(15)

Table 34 (continued)
Anisotropic displacement parameters ($Å^2 \times 10^3$).

atom	U11	U22	U33	U23	U13	U12
C(33)	70(3)	80(2)	10(2)	-1(2)	-20(2)	0(2)
C(34)	50(3)	120(3)	130(3)	20(3)	50(3)	0(2)
C(35)	240(6)	80(3)	90(3)	0(3)	110(4)	-10(4)
C(36)	130(4)	90(3)	70(3)	-10(2)	40(3)	10(3)
C(37)	220(6)	70(2)	50(2)	30(2)	50(3)	80(3)
C(38)	40(3)	120(3)	50(2)	30(2)	8(18)	40(2)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{2*} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 35.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for [Rb(benzo-15-crown-5)$_2$]$_2$(Ag$_2$Br$_4$) **(V)**

atom	x	y	z	U(eq)
H(2A)	4699	7287	3638	80
H(2B)	3635	6091	2985	80
H(3A)	3251	7661	2875	80
H(3B)	3458	6980	1748	80
H(5A)	4771	9923	1958	80
H(5B)	3469	8970	1843	80
H(6A)	4080	8959	57	80
H(6B)	3827	7726	266	80
H(8A)	5200	8015	-1163	80
H(8B)	5319	7008	-725	80
H(9A)	7051	9045	-695	80
H(9B)	6726	7912	-1714	80
H(11A)	7530	6406	-1303	80
H(11B)	6229	6097	-991	80
H(12A)	8189	6378	481	80
H(12B)	7212	5105	-125	80
H(14A)	6183	5977	2373	80
H(15A)	7442	4675	1503	80
H(16A)	7432	4402	3412	80
H(17A)	5960	4514	4121	80
H(18A)	4893	5590	3806	80
H(19A)	6175	5585	2053	80
H(21A)	8979	7392	3335	80
H(21B)	9950	8198	4324	80
H(22A)	10718	7982	2719	80
H(22B)	10953	9339	3312	80
H(24A)	9665	8780	658	80
H(24B)	10895	9016	1274	80
H(25A)	10918	10819	1276	80
H(25B)	10822	10733	2444	80
H(27A)	9809	12272	1710	80
H(27B)	9606	12083	2829	80
H(28A)	7763	11519	1320	80
H(28B)	8258	12735	2258	80
H(30A)	7528	12697	3981	80
H(30B)	8544	12210	4045	80

Table 35. (continued)
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2Br_4)$ **(V)**

atom	x	y	z	U(eq)
H(31A)	6289	10786	4236	80
H(31B)	7182	11636	5291	80
H(34A)	6102	9871	5771	80
H(35A)	5744	8305	6646	80
H(36A)	6564	6996	6164	80
H(37A)	8225	7355	5161	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

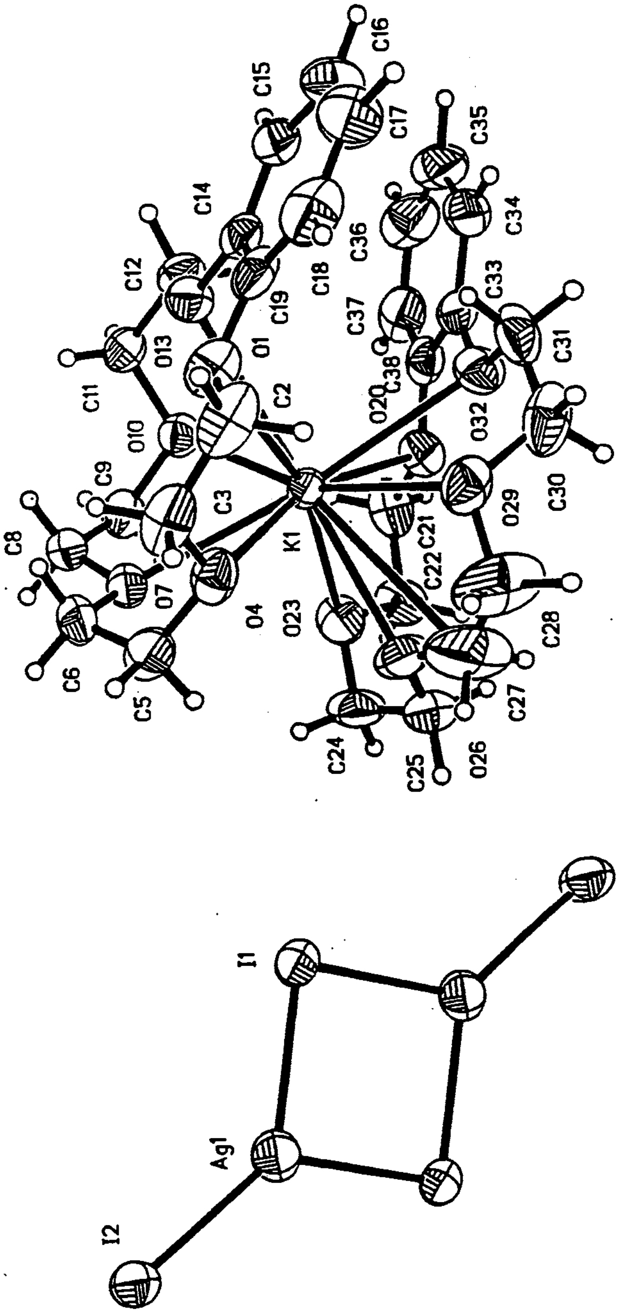


Figure 23. Projection View of $[K(\text{benzo-15-crown-5})_2]_2(Ag_2I_4)$ **(VI)**

Table 36.
Crystal data and structure refinement for
$[K(\text{benzo-15-crown-5})_2]_2(Ag_2I_4)$ **(VI)**

Empirical formula	$C_{56}\ H_{80}\ Ag_2\ I_4\ K_2\ O_{20}$	
Formula weight	1874.25	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, $P\overline{1}$	
Unit cell dimensions	a = 12.3310(10) Å	α = 103.320(10)°
	b = 12.4520(10) Å	β = 95.330(10)°
	c = 12.6870(10) Å	γ = 111.110(10)°
Volume	1734.9(2) $Å^3$	
Z, Calculated density	1, 1.794 Mg/m^3	
Absorption coefficient	4.860 mm^{-1}	
F(000)	920	
Theta range for data collection	1.80 to 30.00 deg.	
Index ranges	$-17 \le h \le 1$, $-15 \le k \le 16$, $-17 \le l \le 17$	
Reflections collected / unique	11189 / 9925 [R(int) = 0.0385]	
Completeness to 2θ = 30.00°	98.0%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9925 / 0 / 379	
Goodness-of-fit on F^2	0.997	
Final R indices $[I>2\sigma(I)]$	R1 = 0.0617, wR2 = 0.1371	
R indices (all data)	R1 = 0.1385, wR2 = 0.1741	
Largest diff. peak and hole	0.801 and -0.644 $e.Å^{-3}$	

Table37.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for
[K(benzo-15-crown-5)$_2$]$_2$(Ag$_2$I$_4$) **(VI)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
I(1)	3943(1)	3161(1)	4713(1)	82(1)
I(2)	3777(1)	4822(1)	1498(1)	107(1)
Ag(1)	4477(1)	4857(1)	3544(1)	93(1)
K(1)	2204(1)	-1360(1)	7111(1)	54(1)
O(1)	1599(4)	-3920(4)	5866(4)	82(1)
C(2)	2381(7)	-3964(8)	5114(8)	102(3)
C(3)	2139(7)	-3358(8)	4307(7)	100(3)
O(4)	2418(4)	-2152(4)	4858(4)	78(1)
C(5)	1929(7)	-1556(8)	4245(6)	100(3)
C(6)	684(6)	-1764(7)	4319(5)	85(2)
O(7)	638(4)	-1235(4)	5425(3)	71(1)
C(8)	-531(6)	-1455(6)	5586(6)	74(2)
C(9)	-500(6)	-938(6)	6775(6)	75(2)
O(10)	-103(3)	-1525(4)	7484(3)	63(1)
C(11)	-1025(5)	-2634(6)	7493(6)	67(2)
C(12)	-454(6)	-3327(6)	7956(5)	66(2)
O(13)	249(4)	-3633(4)	7205(3)	67(1)
C(14)	852(6)	-4309(5)	7423(6)	67(2)
C(15)	762(7)	-4824(6)	8278(7)	91(2)
C(16)	1495(12)	-5448(8)	8423(11)	133(4)
C(17)	2225(11)	-5574(9)	7719(13)	134(4)
C(18)	2283(8)	-5101(7)	6863(11)	118(4)
C(19)	1595(6)	-4456(5)	6695(7)	79(2)
O(20)	2561(4)	87(4)	9455(4)	76(1)
C(21)	2082(7)	1013(8)	9520(6)	90(2)
C(22)	2740(8)	1811(7)	8890(6)	91(2)
O(23)	2445(5)	1125(4)	7780(4)	90(1)
C(24)	3184(9)	1727(7)	7110(7)	101(3)
C(25)	4315(9)	1588(9)	7152(9)	127(4)
O(26)	4093(5)	395(5)	6707(5)	101(2)
C(27)	5092(11)	100(18)	6649(17)	249(12)
C(28)	5272(11)	-608(12)	6945(16)	197(8)
O(29)	4477(4)	-1491(5)	7342(5)	94(2)
C(30)	5027(8)	-1607(8)	8309(9)	112(3)
C(31)	4160(9)	-2122(8)	8940(8)	104(3)
O(32)	3509(5)	-1401(4)	9177(4)	87(1)
C(33)	2708(7)	-1558(6)	9867(5)	77(2)

Table37. (continued)

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
C(34)	2446(9)	-2451(8)	10395(7)	111(3)
C(35)	1571(12)	-2508(10)	11079(7)	134(5)
C(36)	1074(11)	-1674(11)	11195(8)	133(4)
C(37)	1362(7)	-793(9)	10681(6)	102(3)
C(38)	2180(6)	-737(7)	10007(5)	74(2)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 38.
Bond lengths [Å] and angles [°] for
[K(benzo-15-crown-5)$_2$]$_2$(Ag$_2$I$_4$) **(VI)**

I(1)-Ag(1)	2.7773(9)	Ag(1)-I(1)-Ag(1)^1	82.31(2)
I(1)-Ag(1)^1	2.8285(9)	I(2)-Ag(1)-I(1)	134.46(3)
I(2)-Ag(1)	2.6436(8)	I(2)-Ag(1)-I(1)^1	127.82(3)
Ag(1)-I(1)^1	2.8285(9)	I(1)-Ag(1)-I(1)^1	97.69(2)
K(1)-O(26)	2.745(5)	O(29)-C(30)	1.408(11)
K(1)-O(7)	2.816(4)	C(30)-C(31)	1.448(13)
K(1)-O(29)	2.858(5)	C(31)-O(32)	1.407(9)
K(1)-O(10)	2.869(4)	O(32)-C(33)	1.372(9)
K(1)-O(4)	2.871(4)	C(33)-C(38)	1.385(10)
K(1)-O(23)	2.909(5)	C(33)-C(34)	1.383(10)
K(1)-O(32)	2.967(5)	C(34)-C(35)	1.44(2)
K(1)-O(1)	2.993(5)	C(35)-C(36)	1.372(15)
K(1)-O(20)	3.000(5)	C(36)-C(37)	1.359(14)
K(1)-O(13)	3.021(4)	C(37)-C(38)	1.374(10)
O(1)-C(19)	1.369(9)	C(25)-O(26)	1.376(11)
O(1)-C(2)	1.424(9)	O(26)-C(27)	1.409(12)
C(2)-C(3)	1.472(12)	C(27)-C(28)	1.116(13)
C(3)-O(4)	1.401(9)	C(28)-O(29)	1.412(11)
O(4)-C(5)	1.422(10)	O(26)-K(1)-O(7)	91.53(15)
C(5)-C(6)	1.478(10)	O(26)-K(1)-O(29)	60.5(2)
C(6)-O(7)	1.422(8)	O(7)-K(1)-O(29)	136.3(2)
O(7)-C(8)	1.410(8)	O(26)-K(1)-O(10)	133.36(15)
C(8)-C(9)	1.488(10)	O(7)-K(1)-O(10)	61.41(12)
C(9)-O(10)	1.435(8)	O(29)-K(1)-O(10)	161.5(2)
O(10)-C(11)	1.442(7)	O(26)-K(1)-O(4)	71.5(2)
C(11)-C(12)	1.476(9)	O(7)-K(1)-O(4)	61.12(14)
C(12)-O(13)	1.425(7)	O(29)-K(1)-O(4)	77.5(2)
O(13)-C(14)	1.363(7)	O(10)-K(1)-O(4)	116.60(13)
C(14)-C(15)	1.376(10)	O(26)-K(1)-O(23)	60.3(2)
O(13)-C(14)	1.363(7)	O(7)-K(1)-O(23)	76.35(14)
C(14)-C(19)	1.388(10)	O(29)-K(1)-O(23)	110.7(2)
C(15)-C(16)	1.412(13)	O(10)-K(1)-O(23)	75.96(14)
C(16)-C(17)	1.349(16)	O(4)-K(1)-O(23)	113.3(2)
C(17)-C(18)	1.346(16)	O(26)-K(1)-O(32)	95.2(2)
C(18)-C(19)	1.394(11)	O(7)-K(1)-O(32)	168.19(14)
O(20)-C(38)	1.345(8)	O(29)-K(1)-O(32)	55.40(2)
O(20)-C(21)	1.463(8)	O(10)-K(1)-O(32)	107.15(14)
C(21)-C(22)	1.479(11)	O(4)-K(1)-O(32)	130.35(15)
C(22)-O(23)	1.404(8)	O(23)-K(1)-O(32)	98.65(14)
O(23)-C(24)	1.435(9)	O(26)-K(1)-O(1)	118.4(2)
C(24)-C(25)	1.462(13)		

Table 38.(continued)
Bond lengths [Å] and angles [°] for
[K(benzo-15-crown-5)$_2$](Ag$_2$I$_4$) **(VI)**

O(7)-K(1)-O(1)	88.65(14)	C(14)-O(13)-C(12)	119.3(5)
O(29)-K(1)-O(1)	78.34(14)	C(14)-O(13)-K(1)	102.7(3)
O(10)-K(1)-O(1)	99.42(12)	C(12)-O(13)-K(1)	109.1(3)
O(4)-K(1)-O(1)	55.39(15)	O(13)-C(14)-C(15)	125.0(7)
O(23)-K(1)-O(1)	164.76(15)	O(13)-C(14)-C(19)	114.4(6)
O(32)-K(1)-O(1)	96.59(14)	C(15)-C(14)-C(19)	120.6(7)
O(26)-K(1)-O(20)	92.3(2)	C(14)-C(15)-C(16)	117.9(10)
O(7)-K(1)-O(20)	120.59(13)	C(17)-C(16)-C(15)	121.0(11)
O(29)-K(1)-O(20)	95.19(15)	C(16)-C(17)-C(18)	120.9(10)
O(10)-K(1)-O(20)	74.00(12)	C(17)-C(18)-C(19)	120.4(11)
O(4)-K(1)-O(20)	163.75(14)	O(1)-C(19)-C(14)	115.6(6)
O(23)-K(1)-O(20)	55.38(14)	O(1)-C(19)-C(18)	125.3(9)
O(32)-K(1)-O(20)	49.58(13)	C(14)-C(19)-C(18)	119.1(9)
O(1)-K(1)-O(20)	137.96(15)	C(38)-O(20)-C(21)	120.4(6)
O(26)-K(1)-O(13)	168.4(2)	C(38)-O(20)-K(1)	104.5(4)
O(7)-K(1)-O(13)	88.20(12)	C(21)-O(20)-K(1)	111.3(3)
O(29)-K(1)-O(13)	112.59(14)	O(20)-C(21)-C(22)	106.6(6)
O(10)-K(1)-O(13)	55.83(11)	O(23)-C(22)-C(21)	106.9(6)
O(4)-K(1)-O(13)	98.32(13)	C(22)-O(23)-C(24)	112.5(6)
O(23)-K(1)-O(13)	130.67(14)	C(22)-O(23)-K(1)	122.8(4)
O(32)-K(1)-O(13)	87.11(13)	C(24)-O(23)-K(1)	106.5(4)
O(1)-K(1)-O(13)	49.99(12)	O(23)-C(24)-C(25)	113.6(7)
O(20)-K(1)-O(13)	97.89(13)	O(26)-C(25)-C(24)	108.7(8)
C(19)-O(1)-C(2)	119.8(6)	C(25)-O(26)-C(27)	116.5(11)
C(19)-O(1)-K(1)	102.5(4)	C(25)-O(26)-K(1)	120.4(5)
C(2)-O(1)-K(1)	109.3(4)	C(27)-O(26)-K(1)	113.0(6)
O(1)-C(2)-C(3)	106.6(6)	C(28)-C(27)-O(26)	127.9(11)
O(4)-C(3)-C(2)	108.9(7)	C(27)-C(28)-O(29)	126.5(11)
C(3)-O(4)-C(5)	114.1(6)	C(28)-O(29)-C(30)	111.7(9)
C(3)-O(4)-K(1)	122.9(5)	C(28)-O(29)-K(1)	110.0(6)
C(5)-O(4)-K(1)	107.4(4)	C(30)-O(29)-K(1)	122.9(5)
O(4)-C(5)-C(6)	113.7(6)	O(29)-C(30)-C(31)	111.0(7)
O(7)-C(6)-C(5)	108.9(5)	O(32)-C(31)-C(30)	108.7(7)
C(8)-O(7)-C(6)	112.6(5)	C(33)-O(32)-C(31)	123.6(7)
C(8)-O(7)-K(1)	117.0(4)	C(33)-O(32)-K(1)	104.9(4)
C(6)-O(7)-K(1)	116.9(4)	C(31)-O(32)-K(1)	110.6(5)
O(7)-C(8)-C(9)	108.9(5)	O(32)-C(33)-C(38)	114.4(6)
O(10)-C(9)-C(8)	113.5(5)	O(32)-C(33)-C(34)	123.5(9)
C(9)-O(10)-C(11)	112.4(5)	C(38)-C(33)-C(34)	122.1(8)
C(9)-O(10)-K(1)	106.8(4)	C(33)-C(34)-C(35)	116.7(10)
C(11)-O(10)-K(1)	122.6(3)	C(36)-C(35)-C(34)	119.2(9)
O(10)-C(11)-C(12)	107.6(5)	C(37)-C(36)-C(35)	122.9(11)

Table 38.(continued)
Bond lengths [Å] and angles [°] for
$[K(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2I_4)$ **(VI)**

C(36)-C(37)-C(38)	118.8(10)
O(20)-C(38)-C(37)	125.6(8)
O(20)-C(38)-C(33)	114.1(6)
C(37)-C(38)-C(33)	120.3(8)
O(13)-C(12)-C(11)	107.2(5)

Symmetry transformations used to generate equivalent atoms:
1= -x+1,-y+1,-z+1

Table 39.
Anisotropic displacement parameters ($Å^2$ x 10^3) for $[K(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2I_4)$ **(VI)**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	66(1)	84(1)	82(1)	22(1)	9(1)	16(1)
I(2)	106(1)	102(1)	72(1)	25(1)	10(1)	-4(1)
Ag(1)	78(1)	122(1)	78(1)	28(1)	21(1)	36(1)
K(1)	47(1)	52(1)	56(1)	12(1)	6(1)	13(1)
O(1)	63(3)	71(3)	107(4)	8(3)	25(3)	30(2)
C(2)	69(5)	85(5)	125(7)	-22(5)	33(5)	29(4)
C(3)	69(5)	108(6)	87(5)	-14(5)	21(4)	19(4)
O(4)	67(3)	89(3)	57(2)	1(2)	8(2)	19(2)
C(5)	91(6)	115(6)	54(4)	16(4)	16(4)	-1(5)
C(6)	72(4)	106(5)	60(4)	27(4)	-2(3)	17(4)
O(7)	58(2)	85(3)	62(2)	25(2)	6(2)	19(2)
C(8)	63(4)	76(4)	82(4)	33(4)	4(3)	20(3)
C(9)	66(4)	75(4)	86(5)	17(4)	10(3)	34(3)
O(10)	54(2)	64(2)	69(2)	17(2)	7(2)	22(2)
C(11)	49(3)	72(4)	78(4)	21(3)	21(3)	20(3)
C(12)	63(4)	65(4)	63(3)	18(3)	22(3)	14(3)
O(13)	64(2)	72(3)	72(3)	25(2)	18(2)	32(2)
C(14)	58(4)	41(3)	88(4)	12(3)	-4(3)	10(3)
C(15)	86(5)	54(4)	114(6)	24(4)	-12(4)	13(4)
C(16)	58(10)	67(6)	164(11)	51(6)	-9(8)	34(6)
C(17)	133(9)	84(7)	199(13)	45(8)	3(9)	63(7)
C(18)	96(6)	60(5)	192(11)	6(6)	11(6)	44(5)
C(19)	53(4)	44(3)	119(6)	7(4)	1(4)	10(3)
O(20)	79(3)	88(3)	70(3)	25(2)	19(2)	40(3)
C(21)	97(5)	112(6)	61(4)	-5(4)	9(4)	62(5)
C(22)	125(7)	73(4)	79(5)	15(4)	15(5)	48(5)
O(23)	108(4)	72(3)	83(3)	13(3)	5(3)	38(3)
C(24)	137(8)	58(4)	101(6)	39(4)	24(6)	21(5)
C(25)	117(8)	117(8)	117(7)	67(6)	6(6)	-4(6)
O(26)	76(3)	82(4)	148(5)	59(3)	27(3)	19(3)
C(27)	108(9)	370(3)	440(3)	330(3)	155(14)	136(14)
C(28)	120(9)	200(13)	390(2)	175(15)	164(13)	111(10)
O(29)	63(3)	97(4)	125(4)	30(3)	22(3)	36(3)
C(30)	69(5)	89(6)	154(9)	-11(6)	-9(6)	40(5)
C(31)	104(7)	90(6)	116(7)	17(5)	-26(5)	53(5)

Table 39. (cont.)
Anisotropic displacement parameters ($Å^2 \times 10^3$) for
$[K(\text{benzo-15-crown-5})_2]_2(Ag_2I_4)$ **(VI)**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(32)	92(3)	80(3)	106(4)	37(3)	19(3)	46(3)
C(33)	79(4)	72(4)	51(3)	18(3)	-8(3)	1(4)
C(34)	136(8)	83(5)	72(5)	26(4)	-28(5)	6(5)
C(35)	178(11)	102(7)	58(5)	35(5)	-9(6)	-19(7)
C(36)	143(9)	135(9)	72(6)	33(6)	31(6)	-5(8)
C(37)	88(5)	127(7)	68(4)	18(5)	17(4)	22(5)
C(38)	62(4)	86(5)	52(3)	8(3)	2(3)	14(4)

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 40.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[K(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2I_4)$ **(VI)**

atom	x	y	z	U(eq)
H(2A)	2231	-4784	4749	80
H(2B)	3182	-3572	5519	80
H(3A)	2621	-3415	3762	80
H(3B)	1324	-3744	3937	80
H(5A)	1980	-1797	3482	80
H(5B)	2392	-708	4525	80
H(6A)	366	-1429	3821	80
H(6B)	221	-2612	4117	80
H(8A)	-1002	-2303	5368	80
H(8B)	-894	-1089	5156	80
H(9A)	28	-107	6992	80
H(9B)	-1273	-977	6880	80
H(11A)	-1458	-3082	6756	80
H(11B)	-1569	-2468	7934	80
H(12A)	38	-2858	8666	80
H(12B)	-1050	-4037	8039	80
H(15A)	224	-4753	8764	80
H(16A)	1447	-5817	9013	80
H(17A)	2732	-5972	7875	80
H(18A)	2782	-5239	6355	80
H(21A)	2175	1449	10275	80
H(21B)	1254	659	9192	80
H(22A)	3576	2105	9166	80
H(22B)	2515	2484	8967	80
H(24A)	3352	2568	7374	80
H(24B)	2771	1448	6357	80
H(25A)	4794	2056	6734	80
H(25B)	4740	1863	7900	80
H(27A)	5577	724	7300	80
H(27B)	5435	289	6033	80
H(28A)	5305	-1012	6214	80
H(28B)	6042	-370	7383	80
H(30A)	5582	-839	8770	80
H(30B)	5450	-2116	8122	80
H(31A)	3628	-2911	8499	80
H(31B)	4522	-2191	9610	80

Table 40.(cont)
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[K(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_2I_4)$ **(VI)**

atom	x	y	z	U(eq)
H(34A)	2810	-3021	10296	80
H(35A)	1356	-3108	11467	80
H(36A)	491	-1714	11652	80
H(37A)	981	-237	0764	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

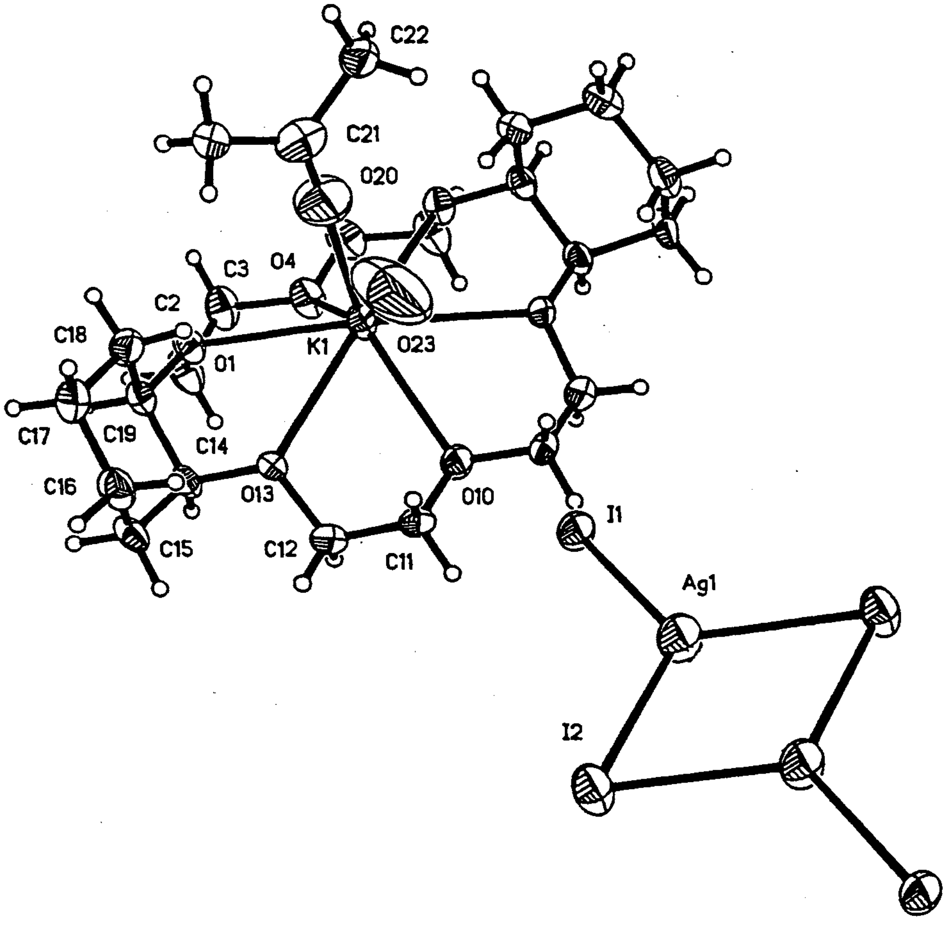


Figure 24. Projection View of $[K(dicyclohexano\text{-}18\text{-}crown\text{-}6)(C_3H_6O)(H_2O)]_2(Ag_2I_4)$
(VII)

Table 41.
Crystal data and structure refinement for [K(dicyclohexano-18-crown-6)(C_3H_6O)(H_2O)]$_2$(Ag_2I_4) **(VII)**

Empirical formula	$C_{46}\ H_{84}\ Ag_2\ I_4\ K_2\ O_{16}$
Formula weight	1698.70
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/m
Unit cell dimensions	a = 14.216(2) Å α = 90° b = 17.910(3) Å β = 91.98(1)° c = 12.111(2) Å γ = 90°
Volume	3081.7(8) $Å^3$
Z, Calculated density	2, .915 Mg/m^3
Absorption coefficient	1.42 mm^{-1}
F(000)	836
Theta range for data collection	1.83 to 30.01 deg.
Index ranges	$-1\leq h\leq 19$, $-25\leq k\leq 1$, $-17\leq l\leq 17$
Reflections collected / unique	5372 / 4584 [R(int) = 0.1145]
Completeness to $2\theta = 30.01°$	49.5%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4584 / 0 / 172
Goodness-of-fit on F^2	1.039
Final R indices [$I>2\sigma(I)$]	R1 = 0.0703, wR2 = 0.1645
R indices (all data)	R1 = 0.1201, wR2 = 0.1932
Extinction coefficient	0.00016(13)
Largest diff. peak and hole	2.050 and -1.432 e.$Å^{-3}$

Table 42.
Atomic coordinates (x 10^4) and equivalent isotropic
displacement parameters ($Å^2$ x 10^3) for
[K(dicyclohexano-18-crown-6)(C_3H_6O)(H_2O)]$_2$(Ag_2I_4) **(VII)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
I(1)	1375(1)	0	7028(1)	58(1)
I(2)	0	1334(1)	10000	68(1)
Ag(1)	478(1)	0	8936(1)	74(1)
K(1)	3287(2)	0	2101(2)	47(1)
O(1)	3776(3)	1305(3)	1010(4)	48(1)
C(2)	3312(7)	1317(4)	-83(6)	67(2)
C(3)	3633(7)	663(5)	-706(6)	64(2)
O(4)	3350(6)	0	-144(6)	59(2)
O(10)	1602(5)	0	3118(6)	56(2)
C(11)	1401(5)	654(4)	3717(6)	53(2)
C(12)	1539(5)	1310(4)	3029(7)	55(2)
O(13)	2504(3)	1384(2)	2733(4)	45(1)
C(14)	2677(5)	2041(3)	2101(6)	46(1)
C(15)	2639(6)	2749(4)	2800(7)	64(2)
C(16)	3365(6)	2745(4)	3734(7)	61(2)
C(17)	4342(5)	2648(5)	3302(6)	59(2)
C(18)	4415(5)	1962(4)	2560(6)	54(2)
C(19)	3666(5)	1972(3)	1653(5)	46(1)
O(20)	4937(8)	0	3462(11)	111(4)
C(21)	5693(11)	0	3948(14)	89(4)
C(22)	6201(5)	-706(5)	4263(8)	68(2)
O(23)	3928(14)	0	4470(5)	420(3)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 43.
Bond lengths [A] and angles [deg] for
[K(dicyclohexano-18-crown-6)(C_3H_6O)(H_2O)]$_2$ (Ag_2I_4) **(VII)**

I(1)-Ag(1)	2.6778(11)	O(10)-K(1)-O(1)^2	116.81(12)
I(2)-Ag(1)	2.8085(8)	O(4)-K(1)-O(1)	60.60(11)
I(2)-Ag(1)^1	2.8085(8)	O(10)-K(1)-O(1)	116.81(12)
Ag(1)-I(2)^1	2.8085(8)	O(1)^2-K(1)-O(1)	114.2(2)
Ag(1)-Ag(1)^1	2.9555(16)	O(4)-K(1)-O(20)	121.9(3)
K(1)-O(4)	2.723(7)	O(10)-K(1)-O(20)	117.4(3)
K(1)-O(10)	2.731(7)	O(1)^2-K(1)-O(20)	93.5(2)
K(1)-O(1)^2	2.783(4)	O(1)-K(1)-O(20)	93.5(2)
K(1)-O(1)	2.783(4)	O(4)-K(1)-O(13)	107.25(13)
K(1)-O(20)	2.820(11)	O(10)-K(1)-O(13)	61.25(9)
K(1)-O(13)	2.834(4)	O(1)^2-K(1)-O(13)	165.8(2)
K(1)-O(13)^2	2.834(4)	O(1)-K(1)-O(13)	60.05(13)
K(1)-O(23)	2.98(5)	O(20)-K(1)-O(13)	99.7(2)
O(1)-C(19)	1.437(8)	O(4)-K(1)-O(13)^2	107.25(13)
O(1)-C(2)	1.459(9)	O(10)-K(1)-O(13)^2	61.25(9)
C(2)-C(3)	1.475(11)	O(1)^2-K(1)-O(13)^2	60.05(13)
C(3)-O(4)	1.433(8)	O(1)-K(1)-O(13)^2	165.8(2)
O(4)-C(3)^1	1.433(8)	O(20)-K(1)-O(13)^2	99.7(2)
O(10)-C(11)	1.412(8)	O(13)-K(1)-O(13)^2	122.0(2)
O(10)-C(11)^1	1.412(8)	O(4)-K(1)-O(23)	160.3(6)
C(11)-C(12)	1.459(11)	O(10)-K(1)-O(23)	79.0(6)
C(12)-O(13)	1.435(8)	O(1)^2-K(1)-O(23)	112.6(3)
O(13)-C(14)	1.430(8)	O(1)-K(1)-O(23)	112.6(3)
C(14)-C(15)	1.527(9)	O(20)-K(1)-O(23)	38.4(6)
C(14)-C(19)	1.530(9)	O(13)-K(1)-O(23)	81.4(3)
C(15)-C(16)	1.505(11)	O(13)^2-K(1)-O(23)	81.4(3)
C(16)-C(17)	1.511(11)	C(19)-O(1)-C(2)	115.1(5)
C(17)-C(18)	1.53(1)	C(19)-O(1)-K(1)	114.1(3)
C(18)-C(19)	1.50(1)	C(2)-O(1)-K(1)	109.3(4)
O(20)-C(21)	1.21(2)	O(1)-C(2)-C(3)	108.3(6)
C(21)-C(22)^1	1.499(12)	O(4)-C(3)-C(2)	108.5(6)
C(21)-C(22)	1.499(12)	C(3)-O(4)-C(3)^2	111.8(8)
Ag(1)-I(2)-Ag(1)^1	63.49(3)	C(3)-O(4)-K(1)	119.6(4)
I(1)-Ag(1)-I(2)^1	121.74(2)	C(3)^2-O(4)-K(1)	119.6(4)
I(1)-Ag(1)-I(2)	121.74(2)	C(11)-O(10)-C(11)^2	112.1(8)
I(2)^1-Ag(1)-I(2)	116.51(3)	C(11)-O(10)-K(1)	115.3(4)
I(1)-Ag(1)-Ag(1)^1	178.95(7)	C(11)^2-O(10)-K(1)	115.3(4)
I(2)^1-Ag(1)-Ag(1)^1	58.25(2)	O(10)-C(11)-C(12)	110.0(6)
I(2)-Ag(1)-Ag(1)^1	58.25(2)	O(13)-C(12)-C(11)	111.4(6)
O(4)-K(1)-O(10)	120.7(3)	C(14)-O(13)-C(12)	113.2(5)
O(4)-K(1)-O(1)^2	60.60(11)	C(14)-O(13)-K(1)	119.9(4)

Table 43. (cont.) Bond lengths [Å] and angles [°] for [K(dicyclohexano-18-crown-6)(C_3H_6O)(H_2O)]$_2$ (Ag_2I_4) (**VII**)

C(12)-O(13)-K(1)	112.0(4)
O(13)-C(14)-C(15)	112.1(6)
O(13)-C(14)-C(19)	107.5(5)
C(15)-C(14)-C(19)	108.3(6)
C(16)-C(15)-C(14)	112.1(6)
C(15)-C(16)-C(17)	110.8(7)
C(16)-C(17)-C(18)	112.2(6)
C(19)-C(18)-C(17)	111.1(6)
O(1)-C(19)-C(18)	107.4(5)
O(1)-C(19)-C(14)	112.2(5)
C(18)-C(19)-C(14)	112.2(6)
C(21)-O(20)-K(1)	173.4(12)
O(20)-C(21)-C(22)^2	122.4(6)
O(20)-C(21)-C(22)	122.4(6)
C(22)^2-C(21)-C(22)	115.1(12)

Symmetry transformations used to generate equivalent atoms:
1= -x,-y,-z+2 2= x,-y,z

Table 44.
Anisotropic displacement parameters ($Å^2$ x 10^3) for ?.
[K(dicyclohexano-18-crown-6)(C_3H_6O)(H_2O)]$_2$ (Ag_2I_4) **(VII)**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	68(1)	56(1)	53(1)	0	27(1)	0
I(2)	108(1)	48(1)	51(1)	0	22(1)	0
Ag(1)	99(1)	72(1)	54(1)	0	35(1)	0
K(1)	66(1)	34(1)	42(1)	0	18(1)	0
O(1)	69(3)	40(2)	37(2)	6(2)	7(2)	4(2)
C(2)	112(7)	46(4)	43(4)	4(3)	-5(4)	-1(4)
C(3)	98(6)	57(4)	38(3)	10(3)	8(3)	-9(4)
O(4)	89(5)	48(4)	39(3)	0	11(3)	0
O(10)	63(4)	46(4)	61(4)	0	29(3)	0
C(11)	49(3)	50(4)	64(4)	-8(3)	22(3)	6(3)
C(12)	46(4)	49(4)	72(5)	-2(3)	8(3)	7(3)
O(13)	42(2)	31(2)	63(3)	3(2)	9(2)	4(2)
C(14)	53(4)	29(3)	56(4)	4(3)	0(3)	2(3)
C(15)	81(5)	27(3)	84(6)	-10(3)	14(4)	6(3)
C(16)	82(5)	42(4)	61(4)	-12(3)	8(4)	-4(4)
C(17)	70(5)	54(4)	55(4)	-1(3)	3(3)	-17(4)
C(18)	52(4)	49(4)	61(4)	-4(3)	7(3)	-8(3)
C(19)	61(4)	32(3)	46(3)	6(3)	4(3)	-1(3)
O(20)	91(8)	128(10)	112(9)	0	-22(7)	0
C(21)	62(8)	110(13)	96(11)	0	9(7)	0
C(22)	54(4)	54(5)	97(6)	-10(4)	12(4)	-3(4)
O(23)	136(16)	112(15)	1010(9)	0	-170(3)	0

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 45.
Hydrogen coordinates (x 10^4) and isotropic
displacement parameters ($Å^2$ x 10^3) for
[K(dicyclohexano-18-crown-6)(C_3H_6O)(H_2O)$]_2$ (Ag_2I_4) **(VII)**

atom	x	y	z	U(eq)
H(2A)	3489	1762	-464	80
H(2B)	2640	1314	-31	80
H(3A)	3361	671	-1443	80
H(3B)	4306	668	-756	80
H(11A)	1815	678	4359	80
H(11B)	766	635	3959	80
H(12A)	1141	1280	2374	80
H(12B)	1363	1747	3433	80
H(14A)	2222	2071	1498	80
H(15A)	2020	2800	3084	80
H(15B)	2751	3172	2336	80
H(16A)	3232	2343	4228	80
H(16B)	3329	3205	4137	80
H(17A)	4505	3087	2897	80
H(17B)	4784	2599	3915	80
H(18A)	5023	1956	2239	80
H(18B)	4353	1516	2991	80
H(19A)	3777	2392	1183	80
H(22A)	6791	-599	4638	80
H(22B)	5814	-995	4737	80
H(22C)	6312	-984	3602	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

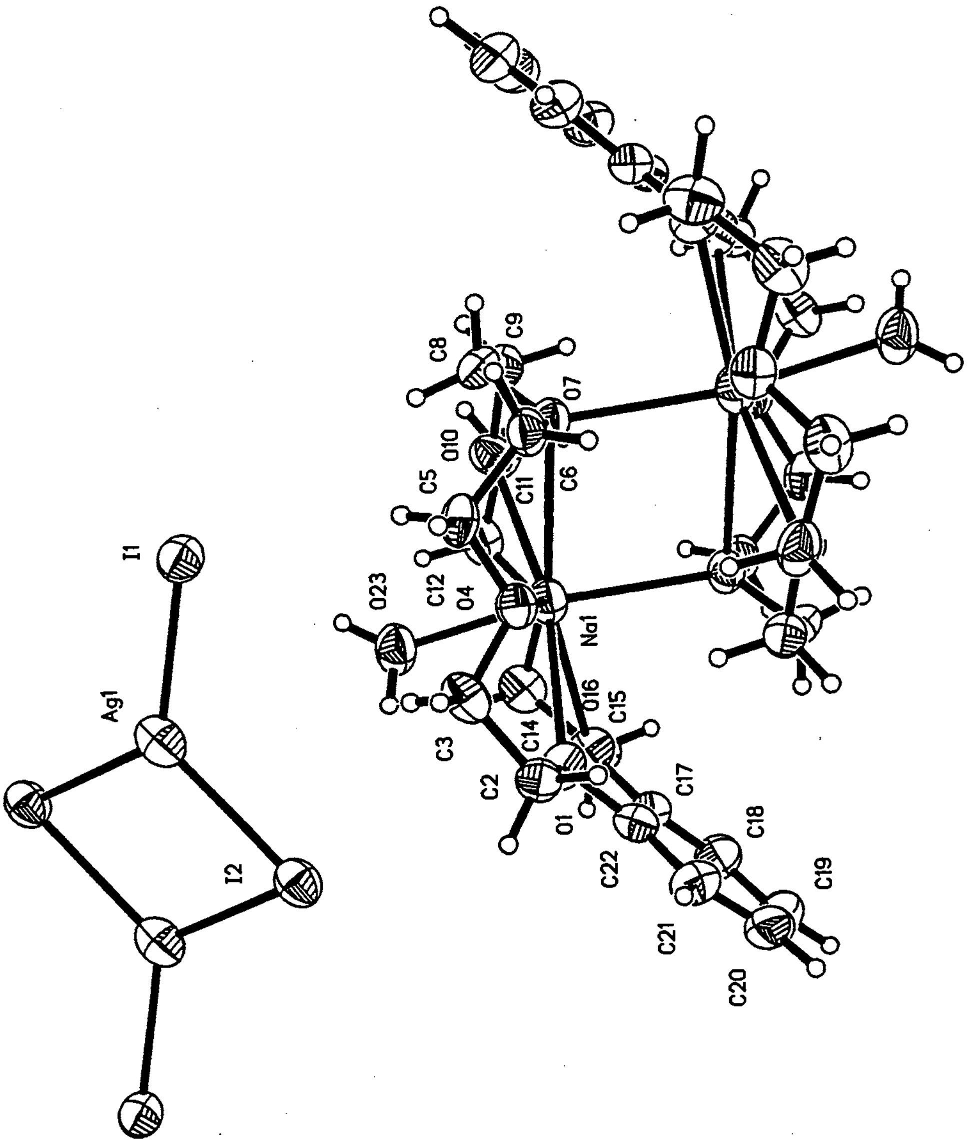


Figure 25. Projection View of [Na(benzo-18-crown-6)(H_2O)]$_2$(Ag_2I_4) **(VIII)**

Table 46.
Crystal data and structure refinement for

$[Na(benzo\text{-}18\text{-}crown\text{-}6)(H_2O)]_2(Ag_2I_4)$ **(VIII)**

Empirical formula	$C_{32}H_{52}Ag_2I_4Na_2O_{14}$
Formula weight	715.03
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 9.316(1) Å a = 91.94(1)° b = 9.691(1) Å ß = 95.17(1) ° c = 12.880(1) Å γ = 100.61(1) °
Volume	1136.78(19) $Å^3$
Z, Calculated density	2, 2.089 Mg/m^3
Absorption coefficient	3.653 mm^{-1}
F(000)	684
Theta range for data collection	2.23° to 30.00°
Index ranges	$-13 \le h \le 1$, $-13 \le k \le 13$, $-18 \le l \le 18$
Reflections collected / unique	7689 / 6579 [R(int) = 0.0534]
Completeness to 2θ = 30.00°	99.3%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6579 / 0 / 245
Goodness-of-fit on F^2	0.993
Final R indices $[I>2\sigma(I)]$	R1 = 0.0674, wR2 = 0.1260
R indices (all data)	R1 = 0.1628, wR2 = 0.1630
Extinction coefficient	0.0000(4)
Largest diff. peak and hole	0.825 and -0.513 $e.A^{-3}$

Table 47.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [Na(benzo-18-crown-6)(H_2O)]$_2$(Ag_2I_4) **(VIII)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
I(1)	4685(1)	5533(1)	6736(1)	75(1)
I(2)	4655(1)	2596(1)	9681(1)	79(1)
Ag(1)	5026(1)	5237(1)	8806(1)	88(1)
Na(1)	491(4)	990(4)	6502(3)	67(1)
O(1)	2083(6)	-383(6)	7739(5)	62(2)
C(2)	3527(9)	-557(10)	7518(7)	62(2)
C(3)	4063(9)	629(10)	6856(7)	66(2)
O(4)	3108(6)	491(6)	5914(5)	65(2)
C(5)	3611(9)	1445(9)	5154(7)	63(2)
C(6)	2594(10)	1067(9)	4188(7)	63(2)
O(7)	1150(6)	1295(6)	4330(5)	60(2)
C(8)	1003(11)	2706(9)	4158(8)	66(2)
C(9)	-477(11)	2906(10)	4390(8)	70(3)
O(10)	-581(7)	2858(6)	5476(5)	65(2)
C(11)	-1921(11)	3206(10)	5760(9)	75(3)
C(12)	-1886(11)	3259(10)	6906(8)	71(3)
O(13)	-1799(6)	1928(6)	7270(5)	63(2)
C(14)	-1624(11)	1919(11)	8377(8)	75(3)
C(15)	-1636(11)	425(12)	8667(8)	78(3)
O(16)	-365(7)	70(7)	8268(5)	71(2)
C(17)	-87(10)	-1238(10)	8479(7)	62(2)
C(18)	-976(13)	-2259(12)	8919(8)	83(3)
C(19)	-603(15)	-3560(13)	9072(9)	93(3)
C(20)	722(15)	-3784(12)	8798(8)	85(3)
C(21)	1678(13)	-2744(11)	8392(8)	78(3)
C(22)	1300(10)	-1481(10)	8212(7)	59(2)
O(23)	1753(7)	2895(7)	7517(6)	81(2)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 48.
Bond lengths [Å] and angles [°] for [Na(benzo-18-crown-6)(H_2O)]$_2$(Ag_2I_4) **(VIII)**

I(1)-Ag(1)	2.6872(11)	O(23)-Na(1)-O(10)	83.7(2)
I(2)-Ag(1)^{1}	2.7728(11)	O(23)-Na(1)-O(7)^{2}	169.3(3)
I(2)-Ag(1)	2.8079(13)	O(10)-Na(1)-O(7)^{2}	101.1(2)
Ag(1)-I(2)	2.7728(11)	O(23)-Na(1)-O(16)	84.2(3)
Ag(1)-Ag(1)^{1}	3.130(2)	O(10)-Na(1)-O(16)	124.4(2)
Na(1)-O(23)	2.293(7)	O(7)^{1}-Na(1)-O(16)	85.2(2)
Na(1)-O(10)	2.571(7)	O(23)-Na(1)-O(1)	82.7(2)
Na(1)-O(7)^{2}	2.586(6)	O(10)-Na(1)-O(1)	165.8(2)
Na(1)-O(16)	2.610(7)	O(7)^{2}-Na(1)-O(1)	93.0(2)
Na(1)-O(1)	2.638(7)	O(16)-Na(1)-O(1)	58.1(2)
Na(1)-O(13)	2.719(7)	O(23)-Na(1)-O(13)	80.5(2)
Na(1)-O(4)	2.737(7)	O(10)-Na(1)-O(13)	63.1(2)
Na(1)-O(7)	2.931(7)	O(7)^{2}-Na(1)-O(13)	93.1(2)
Na(1)-Na(1)^{2}	4.207(7)	O(16)-Na(1)-O(13)	61.4(2)
O(1)-C(22)	1.369(10)	O(1)-Na(1)-O(13)	118.3(2)
O(1)-C(2)	1.438(10)	O(23)-Na(1)-O(4)	88.9(2)
C(2)-C(3)	1.493(13)	O(10)-Na(1)-O(4)	114.9(2)
C(3)-O(4)	1.426(10)	O(7)^{2}-Na(1)-O(4)	97.6(2)
O(4)-C(5)	1.420(10)	O(16)-Na(1)-O(4)	118.9(2)
C(5)-C(6)	1.486(12)	O(1)-Na(1)-O(4)	60.8(2)
C(6)-O(7)	1.429(10)	O(13)-Na(1)-O(4)	169.3(2)
O(7)-C(8)	1.422(10)	O(23)-Na(1)-O(7)	109.8(3)
O(7)-Na(1)^{2}	2.586(6)	O(10)-Na(1)-O(7)	62.6(2)
C(8)-C(9)	1.482(13)	O(7)^{2}-Na(1)-O(7)	80.8(2)
C(9)-O(10)	1.412(11)	O(16)-Na(1)-O(7)	165.6(2)
O(10)-C(11)	1.426(11)	O(1)-Na(1)-O(7)	118.8(2)
C(11)-C(12)	1.473(13)	O(13)-Na(1)-O(7)	122.8(2)
C(12)-O(13)	1.401(11)	O(4)-Na(1)-O(7)	60.0(2)
O(13)-C(14)	1.422(11)	O(23)-Na(1)-Na(1)^{2}	147.2(3)
C(14)-C(15)	1.505(14)	O(10)-Na(1)-Na(1)^{2}	78.3(2)
C(15)-O(16)	1.425(10)	O(7)^{2}-Na(1)-Na(1)^{2}	43.45(15)
O(16)-C(17)	1.371(11)	O(16)-Na(1)-Na(1)^{2}	128.6(2)
C(17)-C(18)	1.344(13)	O(1)-Na(1)-Na(1)^{2}	111.6(2)
C(17)-C(22)	1.424(12)	O(13)-Na(1)-Na(1)^{2}	114.2(2)
C(18)-C(19)	1.384(15)	O(4)-Na(1)-Na(1)^{2}	74.5(2)
C(19)-C(20)	1.367(16)	O(7)-Na(1)-Na(1)^{2}	37.36(12)
C(20)-C(21)	1.368(15)	C(22)-O(1)-C(2)	115.1(6)
C(21)-C(22)	1.356(13)	C(22)-O(1)-Na(1)	115.0(5)
Ag(1)^{1}-I(2)-Ag(1)	68.22(3)	C(2)-O(1)-Na(1)	121.5(5)
I(1)-Ag(1)-I(2)^{1}	125.10(4)	O(1)-C(2)-C(3)	105.5(7)
I(1)-Ag(1)-I(2)	122.49(4)	O(4)-C(3)-C(2)	108.2(7)
I(2)^{1}-Ag(1)-I(2)	111.78(3)	C(5)-O(4)-C(3)	113.8(7)
I(1)-Ag(1)-Ag(1)^{1}	172.43(5)	C(5)-O(4)-Na(1)	109.8(5)
I(2)^{1}-Ag(1)-Ag(1)^{1}	56.42(3)	C(3)-O(4)-Na(1)	105.2(5)
I(2)-Ag(1)-Ag(1)^{1}	55.36(3)	O(4)-C(5)-C(6)	107.2(7)

Table 48. (continued)
Bond lengths [Å] and angles [°] for
[Na(benzo-18-crown-6)(H$_2$O)]$_2$(Ag$_2$I$_4$) **(VIII)**

O(16)-C(15)-C(14)	104.8(8)	O(7)-C(6)-C(5)	111.8(7)
C(17)-O(16)-C(15)	116.1(8)	C(8)-O(7)-C(6)	111.9(7)
C(17)-O(16)-Na(1)	114.3(5)	C(8)-O(7)-Na(1)^{2}	128.0(5)
C(15)-O(16)-Na(1)	121.3(5)	C(6)-O(7)-Na(1)^{2}	102.6(4)
C(18)-C(17)-O(16)	126.1(9)	C(8)-O(7)-Na(1)	102.5(5)
C(18)-C(17)-C(22)	119.1(9)	C(6)-O(7)-Na(1)	111.8(5)
O(16)-C(17)-C(22)	114.7(8)	Na(1)^{2}-O(7)-Na(1)	99.2(2)
C(17)-C(18)-C(19)	121.4(11)	O(7)-C(8)-C(9)	109.5(8)
C(20)-C(19)-C(18)	118.7(11)	O(10)-C(9)-C(8)	109.6(8)
C(19)-C(20)-C(21)	121.1(11)	C(9)-O(10)-C(11)	112.1(7)
C(22)-C(21)-C(20)	120.4(11)	C(9)-O(10)-Na(1)	119.4(5)
C(21)-C(22)-O(1)	127.1(9)	C(11)-O(10)-Na(1)	118.1(6)
C(21)-C(22)-C(17)	119.2(10)	O(10)-C(11)-C(12)	108.7(8)
O(1)-C(22)-C(17)	113.6(8)	O(13)-C(12)-C(11)	109.4(7)
C(14)-O(13)-Na(1)	108.7(5)	C(12)-O(13)-C(14)	112.9(7)
O(13)-C(14)-C(15)	107.8(8)	C(12)-O(13)-Na(1)	109.8(5)

Symmetry transformations used to generate equivalent atoms:
1=-x+1,-y+1,-z+2 2=-x,-y,-z+1

Table 49.

Anisotropic displacement parameters (Å2 x 103)

$[Na(benzo\text{-}18\text{-}crown\text{-}6)(H_2O)]_2(Ag_2I_4)$ **(VIII)**

atom	U11	U22	U33	U23	U13	U12
I(1)	82(1)	68(1)	75(1)	4(1)	13(1)	12(1)
I(2)	79(1)	90(1)	66(1)	-8(1)	7(1)	14(1)
Ag(1)	76(1)	109(1)	75(1)	-10(1)	2(1)	14(1)
Na(1)	60(2)	59(2)	78(2)	-4(2)	-2(2)	4(2)
O(1)	47(3)	63(4)	81(4)	9(3)	14(3)	17(3)
C(2)	55(5)	63(6)	70(6)	8(5)	-3(4)	18(5)
C(3)	41(5)	83(7)	76(6)	-12(5)	-3(4)	21(5)
O(4)	49(3)	68(4)	71(4)	8(3)	-2(3)	-8(3)
C(5)	45(5)	55(5)	83(6)	1(5)	17(5)	-8(4)
C(6)	69(6)	50(5)	64(6)	-7(4)	6(5)	2(4)
O(7)	51(3)	54(3)	71(4)	3(3)	0(3)	3(3)
C(8)	76(7)	52(5)	71(6)	17(4)	9(5)	7(5)
C(9)	73(7)	58(6)	75(7)	5(5)	-7(5)	8(5)
O(10)	57(4)	72(4)	64(4)	3(3)	-6(3)	17(3)
C(19)	100(1)	80(8)	87(8)	22(6)	7(7)	-6(7)
C(20)	110(1)	70(7)	74(7)	7(6)	-7(7)	30(7)
C(21)	88(8)	75(7)	76(7)	16(5)	9(6)	24(6)
C(22)	56(5)	72(6)	49(5)	5(4)	-1(4)	14(5)
O(23)	0(4)	62(4)	114(6)	1(4)	-15(4)	4(3)

The anisotropic displacement factor exponent takes the form:

$-2 \text{ pi}^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 50.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) [Na(benzo-18-crown-6)(H_2O)]$_2$(Ag_2I_4) **(VIII)**

atom	x	y	z	U(eq)
H(2A)	3489	-1439	7143	80
H(2B)	4166	-521	8150	80
H(3A)	5052	7225	6704	80
H(5A)	4589	1358	5021	80
H(5B)	3622	2396	5395	80
H(6A)	2547	96	3985	80
H(6B)	2963	1623	3633	80
H(8A)	1153	2907	3447	80
H(8B)	1732	3341	4603	80
H(9A)	-1208	2184	4022	80
H(9B)	637	3799	4153	80
H(11A)	-2731	2502	5465	80
H(11B)	-2039	4094	5491	80
H(12A)	-2761	3537	7112	80
H(12B)	-1055	3938	7205	80
H(14A)	-2396	2288	8670	80
H(14B)	-700	2490	8640	80
H(15A)	-2510	-174	8344	80
H(15B)	-1592	339	9409	80
H(18A)	-1900	-2092	9118	80
H(19A)	-1252	-4301	9363	80
H(20A)	979	-4691	8883	80
H(21A)	2634	-2888	8247	80
H(23A)	2062	3757	7418	50
H(23B)	2247	2613	8028	50

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

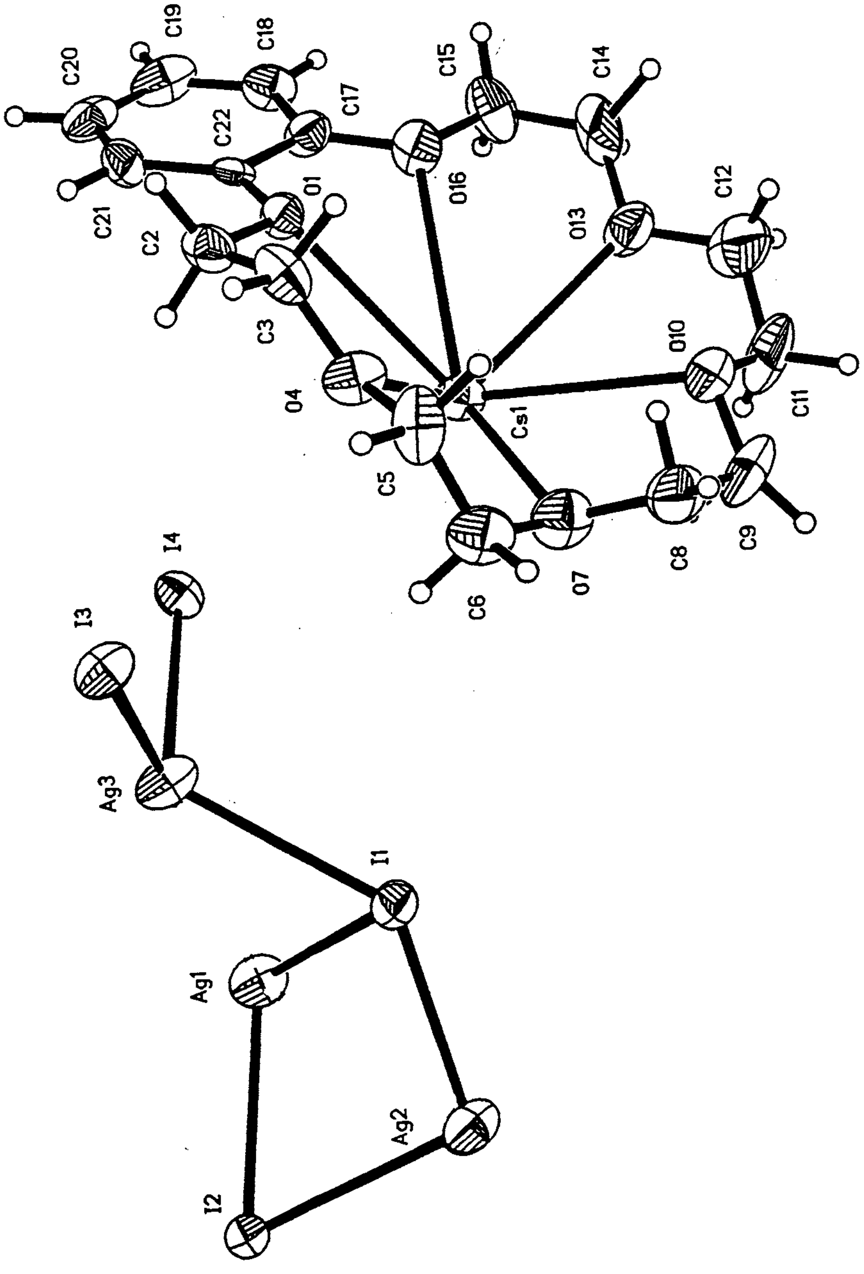


Figure 26. Projection View of [Cs(Benzo-18-crown-6)]$(Ag_3I_4)_n$ **(IX)**

Table 51.
Crystal data and structure refinement for
[Cs(Benzo-18-crown-6)]($(Ag_3I_4)_n$) **(IX)**

Empirical formula	$C_{16}H_{24}Ag_3I_4CsO_6$	
Formula weight	1276.47	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, $P2_1/c$	
Unit cell dimensions	a = 13.835(2) Å	$\alpha = 90^\circ$
	b = 26.260(3) Å	$\beta = 106.11(1)^\circ$
	c = 8.330(1) Å	$\gamma = 90^\circ$
Volume	2907.5(6) $Å^3$	
Z, Calculated density	4, 2.916 Mg/m^3	
Absorption coefficient	7.508 mm^{-1}	
F(000)	2304	
Theta range for data collection	2.18 to 24.71°	
Index ranges	$-16 \leq h \leq 16$, $-1 \leq k \leq 30$, $-1 \leq l \leq 9$	
Reflections collected / unique	6314 / 4935 [R(int) = 0.0507]	
Completeness to 2θ = 24.71°	97.2%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4935 / 0 / 272	
Goodness-of-fit on F^2	1.036	
Final R indices [I>2σ(I)]	R1 = 0.0566, wR2 = 0.1030	
R indices (all data)	R1 = 0.1154, wR2 = 0.1238	
Extinction coefficient	0.00018(7)	
Largest diff. peak and hole	1.081 and -1.087 e.$Å^{-3}$	

Table 52.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [Cs(benzo-18-crown-6)](Ag_3I_4)$_n$ (**IX**)

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Cs(1)	8153(1)	6408(1)	14233(1)	56(1)
I(1)	3979(1)	6202(1)	7745(1)	51(1)
I(2)	2213(1)	7442(1)	4334(1)	53(1)
I(3)	2850(1)	5860(1)	12123(1)	58(1)
I(4)	5295(1)	7066(1)	13208(1)	57(1)
Ag(1)	3680(1)	7264(1)	7553(2)	70(1)
Ag(2)	3684(1)	6617(1)	4451(2)	71(1)
Ag(3)	3554(1)	6677(1)	10620(2)	72(1)
O(1)	7575(7)	6232(4)	17549(12)	51(3)
C(2)	6555(11)	6113(6)	17310(2)	64(5)
C(3)	6328(12)	5653(6)	16280(2)	64(5)
O(4)	6401(8)	5757(4)	14643(14)	62(3)
C(5)	6042(14)	5366(6)	13510(3)	78(6)
C(6)	6068(14)	5526(7)	11840(2)	76(5)
O(7)	7040(10)	5651(4)	11679(15)	79(4)
C(8)	7520(2)	5229(7)	11250(2)	87(6)
C(9)	8560(2)	5370(7)	11220(3)	93(7)
O(10)	9151(11)	5520(5)	12810(2)	83(4)
C(11)	10100(2)	5652(10)	12850(3)	129(10)
C(12)	10730(2)	5705(10)	14590(3)	117(8)
O(13)	10340(9)	6026(5)	15596(17)	79(4)
C(14)	10766(13)	6010(9)	17210(3)	110(8)
C(15)	10505(12)	6378(6)	18320(3)	82(6)
O(16)	9466(8)	6356(4)	18064(15)	66(3)
C(17)	9027(12)	6652(6)	19010(2)	57(4)
C(18)	9549(13)	7000(6)	20220(2)	63(5)
C(19)	9010(2)	7280(6)	21070(2)	79(6)
C(20)	7980(2)	7226(6)	20730(2)	76(6)
C(21)	7485(13)	6885(5)	19590(2)	59(4)
C(22)	7984(10)	6592(5)	18720(2)	42(4)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 53.
Bond lengths [Å] and angles [°] for
[Cs(benzo-18-crown-6)]$(Ag_3I_4)_n$ **(IX)**

Cs(1)-O(7)	3.005(11)	O(13)-C(14)	1.31(2)
Cs(1)-O(4)	3.06(1)	C(14)-C(15)	1.45(3)
Cs(1)-O(13)	3.090(12)	C(15)-O(16)	1.39(2)
Cs(1)-O(10)	3.107(12)	O(16)-C(17)	1.36(2)
Cs(1)-O(1)	3.115(10)	C(17)-C(18)	1.41(2)
Cs(1)-O(16)	3.207(11)	C(17)-C(22)	1.40(2)
Cs(1)-C(20)^{1}	3.58(2)	C(18)-C(19)	1.37(2)
Cs(1)-C(11)	3.78(2)	C(19)-C(20)	1.38(3)
Cs(1)-C(6)	3.80(2)	C(19)-Cs(1)^{4}	3.82(2)
Cs(1)-C(19)^{2}	3.82(2)	C(19)-Cs(1)^{3}	3.92(2)
Cs(1)-C(20)^{2}	3.83(2)	C(20)-C(21)	1.35(2)
Cs(1)-C(22)	3.838(14)	C(20)-Cs(1)^{3}	3.58(2)
I(1)-Ag(1)	2.816(2)	C(20)-Cs(1)^{4}	3.83(2)
I(1)-Ag(2)	2.874(2)	C(21)-C(22)	1.37(2)
I(1)-Ag(3)	2.901(2)	O(7)-Cs(1)-O(4)	56.2(3)
I(2)-Ag(1)	2.917(2)	O(7)-Cs(1)-O(13)	107.6(4)
I(2)-Ag(1)^{2}	2.931(2)	O(4)-Cs(1)-O(13)	120.2(3)
I(2)-Ag(2)	2.956(2)	O(7)-Cs(1)-O(10)	55.1(4)
I(2)-Ag(3)^{2}	2.972(2)	O(4)-Cs(1)-O(10)	94.2(3)
I(3)-Ag(3)	2.794(2)	O(13)-Cs(1)-O(10)	53.3(4)
I(3)-Ag(2)^{3}	2.794(2)	O(7)-Cs(1)-O(1)	108.8(3)
I(4)-Ag(1)^{4}	2.777(2)	O(4)-Cs(1)-O(1)	54.0(3)
I(4)-Ag(3)	2.934(2)	O(13)-Cs(1)-O(1)	95.3(3)
I(4)-Ag(2)^{3}	2.952(2)	O(10)-Cs(1)-O(1)	118.5(3)
Ag(1)-I(4)^{2}	2.777(2)	O(7)-Cs(1)-O(16)	135.6(3)
Ag(1)-I(2)^{4}	2.931(2)	O(4)-Cs(1)-O(16)	96.5(3)
Ag(1)-Ag(3)	3.029(2)	O(13)-Cs(1)-O(16)	52.7(3)
Ag(1)-Ag(2)	3.093(2)	O(10)-Cs(1)-O(16)	99.1(3)
Ag(1)-Ag(3)^{2}	3.194(2)	O(1)-Cs(1)-O(16)	47.6(3)
Ag(1)-Ag(2)^{4}	3.338(2)	O(7)-Cs(1)-C(20)^{1}	85.1(4)
Ag(2)-I(3)^{1}	2.794(2)	O(4)-Cs(1)-C(20)^{1}	123.4(4)
Ag(2)-I(4)^{1}	2.952(2)	O(13)-Cs(1)-C(20)^{1}	109.4(5)
Ag(2)-Ag(3)^{1}	3.150(2)	O(10)-Cs(1)-C(20)^{1}	94.4(4)
Ag(2)-Ag(1)^{2}	3.338(2)	O(1)-Cs(1)-C(20)^{1}	146.7(3)
Ag(3)-I(2)^{4}	2.972(2)	O(16)-Cs(1)-C(20)^{1}	136.7(4)
Ag(3)-Ag(2)^{3}	3.150(2)	O(7)-Cs(1)-C(11)	72.9(5)
Ag(3)-Ag(1)^{4}	3.194(2)	O(4)-Cs(1)-C(11)	113.3(5)
O(1)-C(22)	1.36(2)	O(13)-Cs(1)-C(11)	39.8(5)
O(1)-C(2)	1.40(2)	O(10)-Cs(1)-C(11)	19.8(4)
C(2)-C(3)	1.47(2)	O(1)-Cs(1)-C(11)	125.0(4)
C(3)-O(4)	1.42(2)	O(16)-Cs(1)-C(11)	91.5(5)

Table 53. (cont.)
Bond lengths [Å] and angles [°] for
[Cs(benzo-18-crown-6)](Ag_3I_4)$_n$ **(IX)**

O(4)-C(5)	1.39(2)	C(20)^{1}-Cs(1)-C(11)	87.7(5)
C(5)-C(6)	1.47(2)	O(7)-Cs(1)-C(6)	20.1(4)
C(6)-O(7)	1.43(2)	O(4)-Cs(1)-C(6)	37.8(4)
O(7)-C(8)	1.39(2)	O(13)-Cs(1)-C(6)	121.2(4)
C(8)-C(9)	1.49(3)	O(10)-Cs(1)-C(6)	72.3(4)
C(9)-O(10)	1.40(2)	O(1)-Cs(1)-C(6)	91.8(3)
O(10)-C(11)	1.35(2)	O(16)-Cs(1)-C(6)	129.3(3)
C(11)-C(12)	1.48(3)	C(20)^{1}-Cs(1)-C(6)	93.9(5)
C(12)-O(13)	1.39(2)	C(11)-Cs(1)-C(6)	91.3(5)
O(4)-Cs(1)-C(22)	72.4(3)	O(7)-Cs(1)-C(19)^{2}	157.0(4)
O(13)-Cs(1)-C(22)	90.1(3)	O(4)-Cs(1)-C(19)^{2}	128.8(4)
O(10)-Cs(1)-C(22)	128.3(3)	O(13)-Cs(1)-C(19)^{2}	89.0(4)
O(1)-Cs(1)-C(22)	19.3(3)	O(10)-Cs(1)-C(19)^{2}	135.0(5)
O(16)-Cs(1)-C(22)	37.6(3)	O(1)-Cs(1)-C(19)^{2}	84.7(4)
C(20)^{1}-Cs(1)-C(22)	135.2(3)	O(16)-Cs(1)-C(19)^{2}	67.3(3)
C(11)-Cs(1)-C(22)	127.2(5)	C(20)^{1}-Cs(1)-C(19)^{2}	74.2(4)
C(6)-Cs(1)-C(22)	110.2(4)	C(11)-Cs(1)-C(19)^{2}	115.3(6)
C(19^{2}-Cs(1)-C(22)	66.0(4)	C(6)-Cs(1)-C(19)^{2}	149.8(4)
C(20)^{2}-Cs(1)-C(22)	62.5(3)	O(7)-Cs(1)-C(20)^{2}	141.7(4)
Ag(1)-I(1)-Ag(2)	65.86(4)	O(4)-Cs(1)-C(20)^{2}	111.3(4)
Ag(1)-I(1)-Ag(3)	63.97(4)	O(13)-Cs(1)-C(20)^{2}	109.2(4)
Ag(2)-I(1)-Ag(3)	128.14(5)	O(10)-Cs(1)-C(20)^{2}	154.5(4)
Ag(1)-I(2)-Ag(1)^{2}	96.00(5)	O(1)-Cs(1)-C(20)^{2}	78.2(3)
Ag(1)-I(2)-Ag(2)	63.56(4)	O(16)-Cs(1)-C(20)^{2}	77.6(4)
Ag(1)^{2}-I(2)-Ag(2)	69.08(4)	C(20)^{1}-Cs(1)-C(20)^{2}	72.93(14)
Ag(1)-I(2)-Ag(3)^{2}	65.68(4)	C(11)-Cs(1)-C(20)^{2}	135.0(5)
Ag(1)^{2}-I(2)-Ag(3)^{2}	61.74(4)	C(6)-Cs(1)-C(20)^{2}	129.4(5)
Ag(2)-I(2)-Ag(3)^{2}	101.73(5)	C(19)^{2}-Cs(1)-C(20)^{2}	20.8(4)
Ag(3)-I(3)-Ag(2)^{3}	68.64(5)	O(7)-Cs(1)-C(22)	128.0(3)
Ag(1)^{4}-I(4)-Ag(3)	67.95(5)	Ag(2)^{3}-I(4)-Cs(1)	121.78(4)
Ag(1)^{4}-I(4)-Ag(2)^{3}	71.20(5)	I(4)^{2}-Ag(1)-I(1)	121.27(6)
Ag(3)-I(4)-Ag(2)^{3}	64.73(4)	I(4)^{2}-Ag(1)-I(2)	113.29(5)
Ag(1)^{4}-I(4)-Cs(1)	165.00(5)	I(1)-Ag(1)-I(2)	105.38(5)
Ag(3)-I(4)-Cs(1)	122.91(5)	I(4)^{2}-Ag(1)-I(2)^{4}	111.45(5)
I(2)^{4}-Ag(1)-Ag(2)	136.83(6)	I(1)-Ag(1)-I(2)^{4}	110.09(5)
Ag(3)-Ag(1)-Ag(2)	116.05(6)	I(2)-Ag(1)-I(2)^{4}	91.13(5)
I(4)^{2}-Ag(1)-Ag(3)^{2}	58.35(4)	I(4)^{2}-Ag(1)-Ag(3)	112.83(6)
I(1)-Ag(1)-Ag(3)^{2}	151.31(6)	I(1)-Ag(1)-Ag(3)	59.39(4)
I(2)-Ag(1)-Ag(3)^{2}	57.99(4)	I(2)-Ag(1)-Ag(3)	131.97(6)
I(2)^{4}-Ag(1)-Ag(3)^{2}	94.42(5)	I(2)^{4}-Ag(1)-Ag(3)	59.80(4)
Ag(3)-Ag(1)-Ag(3)^{2}	149.31(6)	I(4)^{2}-Ag(1)-Ag(2)	108.96(6)
Ag(2)-Ag(1)-Ag(3)^{2}	93.99(5)	I(1)-Ag(1)-Ag(2)	57.97(4)

Table 53. (cont.)
Bond lengths [Å] and angles [°] for
[Cs(benzo-18-crown-6)]($(Ag_3L_4)_n$ **(IX)**

I(4)^{2}-Ag(1)-Ag(2)^{4}	56.84(4)	I(2)-Ag(1)-Ag(2)	58.83(4)
I(1)-Ag(1)-Ag(2)^{4}	149.78(6)	Ag(3)^{1}-Ag(2)-Ag(1)"	58.89(4)
I(2)-Ag(1)-Ag(2)^{4}	101.71(5)	I(3)-Ag(3)-I(1)	102.42(5)
I(2)^{4}-Ag(1)-Ag(2)^{4}	55.81(4)	I(3)-Ag(3)-I(4)	104.79(6)
Ag(3)-Ag(1)-Ag(2)^{4}	92.35(5)	I(1)-Ag(3)-I(4)	116.30(6)
Ag(2)-Ag(1)-Ag(2)^{4}	151.56(6)	I(3)-Ag(3)-I(2)^{4}	119.93(6)
Ag(3)^{2}-Ag(1)-Ag(2)^{4}	57.62(4)	I(1)-Ag(3)-I(2)^{4}	106.64(5)
I(3)^{1}-Ag(2)-I(1)	108.38(5)	I(4)-Ag(3)-I(2)^{4}	107.30(5)
I(3)^{1}-Ag(2)-I(4)^{1}	104.32(5)	I(3)-Ag(3)-Ag(1)	151.34(6)
I(1)-Ag(2)-I(4)^{1}	124.40(6)	I(1)-Ag(3)-Ag(1)	56.64(4)
I(3)^{1}-Ag(2)-I(2)	110.56(6)	I(4)-Ag(3)-Ag(1)	102.44(5)
I(1)-Ag(2)-I(2)	102.91(5)	I(2)^{4}-Ag(3)-Ag(1)	58.46(4)
I(4)^{1}-Ag(2)-I(2)	105.99(5)	I(3)-Ag(3)-Ag(2)^{3}	55.68(4)
I(3)^{1}-Ag(2)-Ag(1)	151.02(7)	I(1)-Ag(3)-Ag(2)^{3}	147.87(6)
I(1)-Ag(2)-Ag(1)	56.16(4)	I(4)-Ag(3)-Ag(2)^{3}	57.92(4)
I(4)^{1}-Ag(2)-Ag(1)	104.47(5)	I(2)^{4}-Ag(3)-Ag(2)^{3}	104.99(5)
I(2)-Ag(2)-Ag(1)	57.61(4)	Ag(1)-Ag(3)-Ag(2)^{3}	151.61(6)
I(3)^{1}-Ag(2)-Ag(3)^{1}	55.68(4)	I(3)-Ag(3)-Ag(1)^{4}	114.87(6)
I(1)-Ag(2)-Ag(3)^{1}	159.96(6)	I(1)-Ag(3)-Ag(1)^{4}	142.68(6)
I(4)'-Ag(2)-Ag(3)^{1}	57.36(4)	I(4)-Ag(3)-Ag(1)^{4}	53.70(4)
I(2)-Ag(2)-Ag(3)^{1}	94.85(5)	I(2)^{4}-Ag(3)-Ag(1)^{4}	56.33(4)
Ag(1)-Ag(2)-Ag(3)^{1}	143.66(6)	Ag(1)-Ag(3)-Ag(1)^{4}	88.55(4)
I(3)^{1}-Ag(2)-Ag(1)^{2}	110.61(6)	Ag(2)^{3}-Ag(3)-Ag(1)^{4}	63.48(4)
I(1)-Ag(2)-Ag(1)^{2}	140.09(6)	C(22)-O(1)-C(2)	117.1(12)
I(4)^{1}-Ag(2)-Ag(1)^{2}	51.96(4)	C(22)-O(1)-Cs(1)	111.9(8)
I(2)-Ag(2)-Ag(1)^{2}	55.11(4)	C(2)-O(1)-Cs(1)	113.8(9)
Ag(1)-Ag(2)-Ag(1)^{2}	84.94(3)	O(1)-C(2)-C(3)	107.9(13)
O(1)-C(2)-Cs(1)	46.9(7)	C(18)-C(19)-Cs(1)^{4}	115.6(11)
C(3)-C(2)-Cs(1)	81.1(10)	C(20)-C(19)-Cs(1)^{4}	79.9(11)
O(4)-C(3)-C(2)	110.1(13)	C(18)-C(19)-Cs(1)^{3}	109.8(11)
C(5)-O(4)-C(3)	113.6(12)	C(20)-C(19)-Cs(1)^{3}	65.7(10)
C(5)-O(4)-Cs(1)	118.9(10)	Cs(1)^{4}-C(19)-Cs(1)^{3}	132.7(6)
C(3)-O(4)-Cs(1)	118.9(9)	C(21)-C(20)-C(19)	120(2)
O(4)-C(5)-C(6)	109.5(14)	C(21)-C(20)-Cs(1)^{3}	94.8(10)
O(7)-C(6)-C(5)	115.3(15)	C(19)-C(20)-Cs(1)^{4}	93.7(11)
O(7)-C(6)-Cs(1)	46.5(7)	C(21)-C(20)-Cs(1)^{4}	117.2(11)
C(5)-C(6)-Cs(1)	83.8(10)	C(19)-C(20)-Cs(1)^{4}	79.3(11)
C(8)-O(7)-C(6)	112.0(14)	Cs(1)^{3}-C(20)-Cs(1)^{4}	146.4(6)
C(8)-O(7)-Cs(1)	121.3(11)	C(20)-C(21)-C(22)	121(2)
C(6)-O(7)-Cs(1)	113.4(10)	C(21)-C(22)-O(1)	126.7(14)
O(7)-C(8)-C(9)	110(2)	C(21)-C(22)-C(17)	119.5(15)
O(7)-C(8)-Cs(1)	41.1(8)	O(1)-C(22)-C(17)	113.8(13)

Table 53. (cont.)
Bond lengths [Å] and angles [°] for
[Cs(benzo-18-crown-6)]$(Ag_3I_4)_n$ **(IX)**

C(9)-C(8)-Cs(1)	76.6(10)	C(21)-C(22)-Cs(1)	139.6(9)
O(10)-C(9)-C(8)	111.4(15)	O(1)-C(22)-Cs(1)	48.9(6)
O(10)-C(9)-Cs(1)	48.7(8)	C(17)-C(22)-Cs(1)	81.1(9)
C(8)-C(9)-Cs(1)	81.3(10)	O(13)-C(14)-Cs(1)	43.0(8)
C(11)-O(10)-C(9)	114(2)	C(15)-C(14)-Cs(1)	82.9(11)
C(11)-O(10)-Cs(1)	109.3(13)	O(16)-C(15)-C(14)	107.6(15)
C(9)-O(10)-Cs(1)	111.5(11)	C(17)-O(16)-C(15)	119.5(13)
O(10)-C(11)-C(12)	111(2)	C(17)-O(16)-Cs(1)	109.3(9)
O(10)-C(11)-Cs(1)	50.9(10)	C(15)-O(16)-Cs(1)	115.3(11)
C(12)-C(11)-Cs(1)	85.7(12)	O(16)-C(17)-C(18)	124.3(15)
O(13)-C(12)-C(11)	115(2)	O(16)-C(17)-C(22)	116.0(14)
C(14)-O(13)-C(12)	117(2)	C(18)-C(17)-C(22)	119.7(15)
C(14)-O(13)-Cs(1)	120.1(10)	O(16)-C(17)-Cs(1)	51.3(7)
C(12)-O(13)-Cs(1)	118.6(12)	C(18)-C(17)-Cs(1)	142.9(11)
O(13)-C(14)-C(15)	121(2)	C(22)-C(17)-Cs(1)	77.9(9)
C(18)-C(19)-C(20)	121.(2)	C(19)-C(18)-C(17)	118(2)

Symmetry transformations used to generate equivalent atoms:
1= x,y,z-1 2= x,-y+3/2,z-1/2 3= x,y,z+1
4= x,-y+3/2,z+1/2

Table 54.
Anisotropic displacement parameters ($Å^2 \times 10^3$) for $[Cs(benzo\text{-}18\text{-}crown\text{-}6)](Ag_3I_4)_n$ **(IX)**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs(1)	58(1)	50(1)	54(1)	-2(1)	9(1)	-4(1)
I(1)	56(1)	55(1)	45(1)	3(1)	20(1)	4(1)
I(2)	53(1)	62(1)	43(1)	2(1)	13(1)	10(1)
I(3)	77(1)	52(1)	49(1)	-5(1)	23(1)	-12(1)
I(4)	43(1)	60(1)	62(1)	1(1)	8(1)	2(1)
Ag(1)	82(1)	62(1)	64(1)	2(1)	19(1)	-10(1)
Ag(2)	93(1)	71(1)	52(1)	-9(1)	22(1)	-3(1)
Ag(3)	95(1)	73(1)	49(1)	1(1)	24(1)	-14(1)
O(1)	34(5)	71(7)	45(6)	-6(6)	8(5)	-2(5)
C(2)	41(9)	83(12)	67(12)	22(10)	12(9)	0(8)
C(3)	46(10)	49(9)	93(15)	4(10)	11(10)	-1(8)
O(4)	70(8)	53(6)	56(8)	-11(6)	4(6)	-23(5)
C(5)	64(12)	63(11)	12(2)	-29(12)	42(13)	-19(9)
C(6)	66(13)	77(13)	74(14)	-13(11)	0(11)	-17(10)
O(7)	88(9)	67(8)	75(9)	-16(7)	11(8)	-14(7)
C(8)	130(2)	61(12)	66(14)	-15(10)	16(13)	14(12)
C(9)	150(2)	80(13)	80(2)	-22(11)	75(16)	-20(14)
O(10)	90(10)	106(10)	62(9)	5(8)	34(8)	20(8)
C(11)	140(2)	170(2)	110(2)	-24(2)	100(2)	0(2)
C(12)	69(15)	200(3)	90(2)	20(2)	43(15)	8(16)
O(13)	59(8)	124(10)	59(9)	-11(8)	22(7)	-1(7)
C(14)	28(10)	170(2)	120(2)	-30(2)	15(13)	28(12)
C(15)	46(11)	69(11)	130(2)	-13(12)	21(12)	-4(9)
O(16)	36(6)	91(8)	68(8)	-18(7)	8(6)	-13(6)
C(17)	52(10)	73(11)	45(10)	-5(9)	14(9)	-5(9)
C(18)	64(11)	56(10)	56(11)	-10(9)	-5(9)	-10(9)
C(19)	131(2)	51(11)	51(12)	-12(9)	16(13)	-33(12)
C(20)	140(2)	41(10)	52(12)	10(9)	39(13)	14(11)
C(21)	68(11)	44(9)	69(12)	7(9)	24(10)	20(8)
C(22)	40(9)	49(8)	31(8)	15(7)	-1(7)	11(7)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 55.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for [Cs(benzo-18-crown-6)]$(Ag_3I_4)_n$ **(IX)**

atom	x	y	z	U(eq)
H(2A)	6141	6392	16779	80
H(2B)	6440	6053	18382	80
H(3A)	5663	5532	16211	80
H(3B)	6798	5390	16776	80
H(5A)	5362	5287	13499	80
H(5B)	6444	5065	13844	80
H(6A)	5633	5815	11509	80
H(6B)	5805	5256	11064	80
H(8B)	7799	5157	12423	80
H(8A)	7275	4887	11073	80
H(9B)	8311	5712	11089	80
H(9A)	8761	5401	10213	80
H(11A)	10052	5986	12370	80
H(11B)	10381	5428	12184	80
H(12A)	11383	5826	14583	80
H(12B)	10807	5367	15051	80
H(14B)	11268	6241	17050	80
H(14A)	11278	5762	17669	80
H(15A)	10703	6714	18089	80
H(15B)	10836	6299	19469	80
H(18A)	10267	7032	20484	80
H(19A)	9364	7522	21885	80
H(20A)	7621	7440	21306	80
H(21A)	6772	6847	19392	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

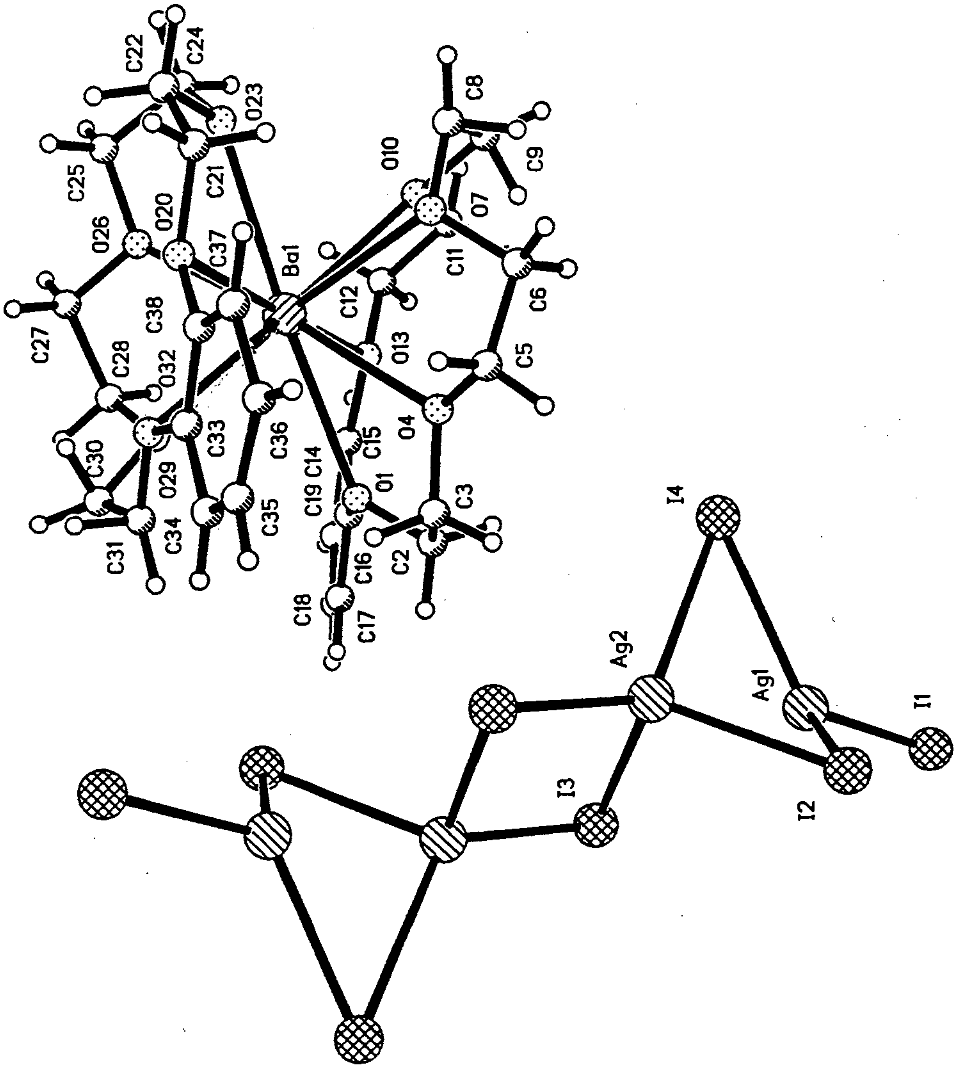


Figure 27. Projection View of [Ba(benzo-15-crown-5)$_2$]$_2$(Ag$_4$I$_8$) (**X**)

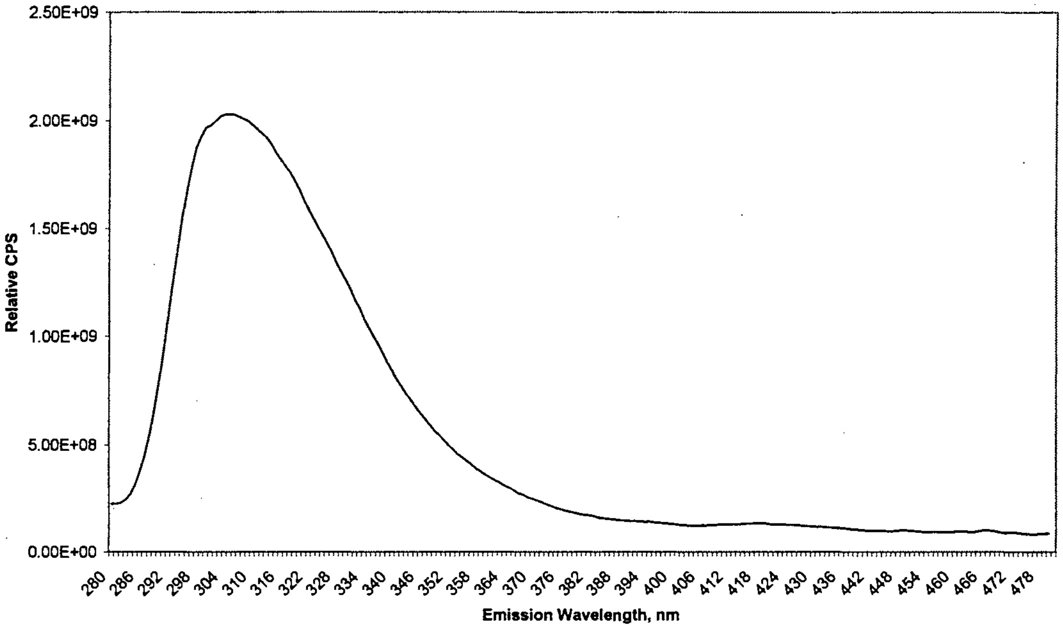


Figure 28. Emission Spectrum of $[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_4I_8)$ **(X)**

Table 56.
Crystal data and structure refinement for
$[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_4I_8)$ **(X)**

Empirical formula	$C_{56}\,H_{80}\,Ag_4\,I_8\,Ba_2\,O_{20}$
Formula weight	2794.56
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 13.372(5) Å $\alpha = 90^\circ$
	b = 11.714(3) Å $\beta = 102.46^\circ$
	c = 25.622(5) Å $\gamma = 90^\circ$
Volume	3918.9(19) $Å^3$
Z, Calculated density	2, 2.368 Mg/m^3
Absorption coefficient	5.181 mm^{-1}
F(000)	2600
Theta range for data collection	2.34 to 20.82°
Index ranges	$-1 \leq h \leq 13$, $-1 \leq k \leq 11$, $-25 \leq l \leq 25$
Reflections collected / unique	5371 / 4100 [R(int) = 0.1042]
Completeness to $2\theta = 20.82^\circ$	93.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4100 / 0 / 407
Goodness-of-fit on F^2	1.006
Final R indices $[I>2\sigma(I)]$	R1 = 0.0759, wR2 = 0.0896
R indices (all data)	R1 = 0.1976, wR2 = 0.1179
Extinction coefficient	0.00010(3)
Largest diff. peak and hole	0.936 and -0.760 $e.Å^{-3}$

Table 57.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_4I_8)$ **(X)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Ba(1)	2272(1)	934(2)	1420(1)	41(1)
Ag(1)	7724(2)	4914(3)	944(1)	108(1)
Ag(2)	6037(2)	4164(4)	171(1)	142(2)
I(1)	9197(2)	6019(2)	1621(1)	67(1)
I(2)	7918(2)	4459(2)	-131(1)	62(1)
I(3)	5546(2)	6428(2)	656(1)	68(1)
I(4)	6827(2)	2888(2)	1245(1)	79(1)
O(1)	3029(14)	330(2)	1452(7)	53(6)
C(2)	3840(2)	3520(3)	1224(10)	71(11)
C(3)	3870(2)	2720(3)	778(10)	53(9)
O(4)	3906(14)	158(18)	968(7)	59(6)
C(5)	4400(2)	750(3)	696(10)	58(9)
C(6)	4710(3)	-210(3)	1057(13)	105(15)
O(7)	383(18)	-630(2)	1244(9)	78(8)
C(8)	4000(3)	-1380(3)	1679(14)	120(2)
C(9)	4370(3)	-900(3)	2200(12)	103(14)
O(10)	365(16)	-60(2)	2282(8)	80(8)
C(11)	3980(3)	620(3)	2758(11)	90(13)
C(12)	3240(3)	1510(3)	2824(11)	93(14)
C(14)	2860(2)	3320(3)	2339(13)	55(10)
C(15)	2800(2)	3820(4)	2809(13)	79(13)
C(16)	2650(3)	5070(4)	2765(15)	110(2)
C(17)	2680(3)	5610(4)	2320(2)	120(2)
C(18)	2780(3)	5050(3)	1876(11)	77(12)
C(19)	2900(2)	3910(3)	1895(12)	44(8)
O(13)	3091(15)	214(2)	2345(7)	55(6)
O(20)	1309(14)	-398(15)	539(7)	54(6)
C(21)	1480(2)	-1610(2)	637(11)	62(10)
C(22)	1090(2)	-1930(2)	1119(11)	71(11)
O(23)	1612(13)	-1279(15)	1560(8)	56(6)
C(24)	1120(2)	-1380(2)	2012(11)	67(10)
C(25)	250(2)	-570(2)	1958(11)	55(9)
O(26)	596(14)	528(2)	1867(7)	58(6)
C(27)	-220(2)	1340(2)	1818(11)	53(9)
C(28)	230(2)	2530(3)	1804(11)	77(11)

Table 57. (continued)
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_4I_8)$ **(X)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
O(29)	818(15)	2621(15)	1395(7)	56(6)
C(30)	270(2)	3090(2)	921(10)	61(10)
C(31)	810(2)	2880(2)	510(10)	53(10)
O(32)	947(15)	1720(2)	463(7)	56(6)
C(33)	1420(2)	1250(3)	85(12)	52(9)
C(34)	1680(2)	1870(3)	-354(10)	45(9)
C(35)	2040(3)	1320(3)	-713(11)	88(14)
C(36)	2270(2)	180(3)	-684(13)	87(12)
C(37)	1980(2)	-510(3)	-271(11)	58(10)
C(38)	1580(3)	80(3)	95(10)	66(12)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 58.
Bond lengths [Å] and angles [°] for [Ba(benzo-15-crown-5)$_2$]$_2$(Ag$_4$I$_8$) **(X)**

Ba(1)-O(29)	2.76(2)	C(33)-C(34)	1.44(3)
Ba(1)-O(26)	2.77(2)	C(34)-C(35)	1.30(3)
Ba(1)-O(13)	2.77(2)	C(35)-C(36)	1.37(4)
Ba(1)-O(23)	2.79(2)	C(36)-C(37)	1.45(4)
Ba(1)-O(4)	2.79(2)	C(37)-C(38)	1.36(4)
Ba(1)-O(10)	2.80(2)	O(29)-Ba(1)-O(26)	60.3(6)
Ba(1)-O(20)	2.82(2)	O(29)-Ba(1)-O(13)	78.6(5)
Ba(1)-O(32)	2.85(2)	O(26)-Ba(1)-O(13)	86.5(6)
Ba(1)-O(7)	2.88(2)	O(29)-Ba(1)-O(23)	115.3(6)
Ba(1)-O(1)	2.89(2)	O(26)-Ba(1)-O(23)	58.6(6)
Ag(1)-I(1)	2.663(3)	O(13)-Ba(1)-O(23)	116.1(6)
Ag(1)-Ag(2)	2.802(4)	O(29)-Ba(1)-O(4)	114.1(6)
Ag(1)-I(4)	2.840(4)	O(26)-Ba(1)-O(4)	174.2(6)
Ag(1)-I(2)	2.872(3)	O(13)-Ba(1)-O(4)	91.0(5)
Ag(2)-I(3)^{1}	2.742(3)	O(23)-Ba(1)-O(4)	127.1(6)
Ag(2)-I(2)	2.809(4)	O(29)-Ba(1)-O(10)	130.8(6)
Ag(2)-I(3)	3.060(5)	O(26)-Ba(1)-O(10)	93.1(6)
Ag(2)-I(4)	3.108(4)	O(13)-Ba(1)-O(10)	57.8(6)
Ag(2)-Ag(2)^{1}	3.353(8)	O(23)-Ba(1)-O(10)	71.5(6)
I(3)-Ag(2)^{1}	2.742(3)	O(4)-Ba(1)-O(10)	90.0(6)
O(1)-C(2)	1.37(3)	O(29)-Ba(1)-O(20)	100.4(5)
O(1)-C(19)	1.41(3)	O(26)-Ba(1)-O(20)	88.0(5)
C(2)-C(3)	1.49(3)	O(13)-Ba(1)-O(20)	174.2(5)
C(3)-O(4)	1.42(3)	O(23)-Ba(1)-O(20)	59.0(5)
O(4)-C(5)	1.44(3)	O(4)-Ba(1)-O(20)	94.6(5)
C(5)-C(6)	1.46(3)	O(10)-Ba(1)-O(20)	120.6(6)
C(6)-O(7)	1.45(4)	O(29)-Ba(1)-O(32)	56.3(5)
O(7)-C(8)	1.40(4)	O(26)-Ba(1)-O(32)	90.2(5)
C(8)-C(9)	1.44(3)	O(13)-Ba(1)-O(32)	129.0(6)
C(9)-O(10)	1.43(4)	O(23)-Ba(1)-O(32)	104.8(5)
O(10)-C(11)	1.45(3)	O(4)-Ba(1)-O(32)	87.3(6)
C(11)-C(12)	1.48(4)	O(10)-Ba(1)-O(32)	172.7(6)
C(12)-O(13)	1.41(3)	O(20)-Ba(1)-O(32)	53.0(5)
C(14)-C(19)	1.34(3)	O(29)-Ba(1)-O(7)	168.5(6)
C(14)-C(15)	1.36(4)	O(26)-Ba(1)-O(7)	129.2(7)
C(14)-O(13)	1.41(3)	O(13)-Ba(1)-O(7)	107.0(6)
C(15)-C(16)	1.49(5)	O(23)-Ba(1)-O(7)	71.8(6)
C(16)-C(17)	1.30(5)	O(4)-Ba(1)-O(7)	56.6(7)
C(17)-C(18)	1.35(4)	O(10)-Ba(1)-O(7)	59.0(6)
C(33)-C(38)	1.39(4)	O(20)-Ba(1)-O(7)	75.1(6)
C(18)-C(19)	1.35(3)		

Table 58. (cont.)

Bond lengths [Å] and angles [°] for

[Ba(benzo-15-crown-5)$_2$]$_2$(Ag$_4$I$_8$) **(X)**

O(20)-C(38)	1.38(3)	O(32)-Ba(1)-O(7)	114.0(6)
O(20)-C(21)	1.45(3)	O(29)-Ba(1)-O(1)	64.5(5)
C(21)-C(22)	1.49(3)	O(26)-Ba(1)-O(1)	117.3(6)
C(22)-O(23)	1.42(3)	O(13)-Ba(1)-O(1)	55.1(5)
O(23)-C(24)	1.46(3)	O(23)-Ba(1)-O(1)	171.2(6)
C(24)-C(25)	1.48(3)	O(4)-Ba(1)-O(1)	57.2(6)
C(25)-O(26)	1.41(3)	O(10)-Ba(1)-O(1)	101.7(6)
O(26)-C(27)	1.43(3)	O(20)-Ba(1)-O(1)	129.7(5)
C(27)-C(28)	1.52(3)	O(32)-Ba(1)-O(1)	82.5(5)
C(28)-O(29)	1.45(3)	O(7)-Ba(1)-O(1)	110.0(6)
O(29)-C(30)	1.39(2)	O(29)-Ba(1)-C(33)	79.4(7)
C(30)-C(31)	1.42(3)	O(26)-Ba(1)-C(33)	108.0(6)
C(31)-O(32)	1.39(3)	O(13)-Ba(1)-C(33)	142.5(7)
O(32)-C(33)	1.38(3)	O(23)-Ba(1)-C(33)	100.6(6)
I(1)-Ag(1)-I(2)	120.49(13)	O(4)-Ba(1)-C(33)	71.1(6)
Ag(2)-Ag(1)-I(2)	59.34(9)	O(10)-Ba(1)-C(33)	149.6(7)
I(4)-Ag(1)-I(2)	103.66(11)	O(20)-Ba(1)-C(33)	41.8(6)
I(3)^{1}-Ag(2)-Ag(1)	174.2(2)	O(32)-Ba(1)-C(33)	23.5(6)
I(3)^{1}-Ag(2)-I(2)	113.92(11)	O(7)-Ba(1)-C(33)	90.6(7)
Ag(1)-Ag(2)-I(2)	61.57(9)	O(1)-Ba(1)-C(33)	88.0(6)
I(3)^{1}-Ag(2)-I(3)	109.63(13)	I(1)-Ag(1)-Ag(2)	169.2(2)
Ag(1)-Ag(2)-I(3)	69.64(11)	I(1)-Ag(1)-I(4)	121.75(12)
I(2)-Ag(2)-I(3)	106.78(14)	Ag(2)-Ag(1)-I(4)	66.85(11)
I(3)^{1}-Ag(2)-I(4)	128.38(15)	Ag(1)-I(4)-Ag(2)	56.00(9)
Ag(1)-Ag(2)-I(4)	57.15(9)	C(2)-O(1)-C(19)	118(2)
I(2)-Ag(2)-I(4)	98.60(11)	C(2)-O(1)-Ba(1)	121(2)
I(3)-Ag(2)-I(4)	96.86(9)	C(19)-O(1)-Ba(1)	115(2)
I(3)^{1}-Ag(2)-Ag(2)^{1}	59.25(9)	O(1)-C(2)-C(3)	110(3)
Ag(1)-Ag(2)-Ag(2)^{1}	119.7(2)	O(4)-C(3)-C(2)	110(2)
I(2)-Ag(2)-Ag(2)^{1}	126.5(2)	C(3)-O(4)-C(5)	117(2)
I(3)-Ag(2)-Ag(2)^{1}	50.37(12)	C(3)-O(4)-Ba(1)	115.1(2)
I(4)-Ag(2)-Ag(2)^{1}	128.07(14)	C(5)-O(4)-Ba(1)	120.3(2)
Ag(2)-I(2)-Ag(1)	59.10(9)	O(4)-C(5)-C(6)	108(2)
Ag(2)^{1}-I(3)-Ag(2)	70.37(13)	O(7)-C(6)-C(5)	109(3)
C(25)-O(26)-C(27)	110(2)	C(8)-O(7)-C(6)	118(3)
C(25)-O(26)-Ba(1)	124(2)	C(8)-O(7)-Ba(1)	106(2)
C(27)-O(26)-Ba(1)	121.1(15)	C(6)-O(7)-Ba(1)	120(2)
O(26)-C(27)-C(28)	109(2)	O(7)-C(8)-C(9)	117(3)
O(29)-C(28)-C(27)	111(2)	O(10)-C(9)-C(8)	107(3)
C(30)-O(29)-C(28)	113(2)	C(9)-O(10)-C(11)	114(3)
C(30)-O(29)-Ba(1)	122.8(15)	C(9)-O(10)-Ba(1)	122(2)

Table 58. (cont.)
Bond lengths [Å] and angles [°] for
[Ba(benzo-15-crown-5)$_2$]$_2$(Ag$_4$I$_8$) **(X)**

C(28)-O(29)-Ba(1)	115.0(15)	C(11)-O(10)-Ba(1)	118(2)
O(29)-C(30)-C(31)	109(2)	O(10)-C(11)-C(12)	113(3)
O(32)-C(31)-C(30)	110(2)	O(13)-C(12)-C(11)	104(3)
C(33)-O(32)-C(31)	123(2)	C(19)-C(14)-C(15)	123(3)
C(33)-O(32)-Ba(1)	101(2)	C(19)-C(14)-O(13)	118(3)
C(31)-O(32)-Ba(1)	108(2)	C(15)-C(14)-O(13)	118(3)
O(32)-C(33)-C(38)	118(3)	C(14)-C(15)-C(16)	113(3)
O(32)-C(33)-C(34)	125(3)	C(34)-C(35)-C(36)	124(4)
C(38)-C(33)-C(34)	116(3)	C(35)-C(36)-C(37)	119(3)
O(32)-C(33)-Ba(1)	55.9(13)	C(38)-C(37)-C(36)	116(3)
C(35)-C(34)-C(33)	120(3)	C(37)-C(38)-O(20)	125(3)
O(20)-C(38)-C(33)	110(3)	C(37)-C(38)-C(33)	125(3)

Symmetry transformations used to generate equivalent atoms:
1= -x+1,-y+1,-z

Table 59.
Anisotropic displacement parameters ($Å^2$ x 10^3) for ?.
$[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_4I_8)$ **(X)**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba(1)	38(1)	38(1)	44(1)	0(1)	7(1)	-1(1)
Ag(1)	107(3)	134(3)	83(2)	-39(2)	17(2)	-48(2)
Ag(2)	90(2)	247(5)	86(2)	-23(3)	10(2)	-70(3)
I(1)	69(2)	66(2)	64(1)	-5(1)	9(1)	-16(2)
I(2)	74(2)	53(2)	61(1)	2(1)	18(1)	10(1)
I(3)	79(2)	73(2)	48(1)	-10(1)	5(1)	-2(2)
I(4)	71(2)	63(2)	101(2)	17(2)	11(2)	-4(2)
O(1)	50(15)	60(2)	61(14)	7(13)	28(12)	7(12)
C(2)	110(3)	60(3)	50(2)	-30(2)	40(2)	0(2)
C(3)	40(2)	60(2)	70(2)	10(2)	30(2)	-10(2)
O(4)	60(15)	44(14)	79(15)	-19(13)	27(12)	-12(13)
C(5)	50(2)	60(3)	70(2)	-50(2)	20(2)	-10(2)
C(6)	170(5)	30(3)	120(3)	40(2)	30(3)	20(3)
O(7)	90(2)	70(2)	80(2)	8(14)	20(2)	20(2)
C(8)	120(4)	100(4)	110(3)	-70(3)	-10(3)	20(3)
C(9)	80(3)	140(4)	70(3)	50(3)	-30(2)	10(3)
O(10)	70(2)	100(2)	70(2)	-18(15)	5(14)	20(16)
C(11)	110(4)	110(4)	30(2)	20(2)	-20(2)	-20(3)
C(12)	110(4)	120(4)	20(2)	20(2)	-40(2)	10(3)
C(14)	60(2)	70(3)	30(2)	20(2)	-0(2)	-10(2)
C(15)	70(3)	140(4)	30(2)	0(3)	10(2)	0(3)
C(16)	70(3)	180(6)	60(3)	-90(4)	-10(3)	20(3)
C(17)	140(4)	130(5)	80(3)	-90(4)	20(3)	-30(3)
C(18)	150(3)	30(2)	30(2)	30(2)	-20(2)	-10(2)
C(19)	30(2)	30(2)	80(3)	-10(2)	30(2)	-2(18)
O(13)	80(2)	43(15)	36(13)	3(12)	0(12)	14(14)
O(20)	90(2)	21(13)	64(14)	9(11)	38(12)	0(12)
C(21)	90(3)	10(2)	80(2)	-20(2)	20(2)	-40(2)
C(22)	100(3)	50(2)	90(2)	-20(2)	60(2)	-30(2)
O(23)	37(13)	40(15)	84(15)	2(13)	-1(12)	-17(11)
C(24)	80(3)	50(2)	80(2)	50(2)	40(2)	-10(2)
C(25)	60(3)	30(2)	60(2)	4(19)	0(2)	-10(2)
O(26)	47(14)	80(2)	52(13)	20(13)	16(11)	31(15)
C(27)	50(2)	40(2)	70(2)	0(19)	30(2)	-20(2)
C(28)	90(3)	80(3)	60(2)	0(2)	20(2)	20(3)

Table 59. (cont.)
Anisotropic displacement parameters ($Å^2$ x 10^3) for
$[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_4I_8)$ **(X)**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(29)	80(2)	34(13)	48(13)	9(11)	-10(13)	18(12)
C(30)	30(2)	70(3)	80(2)	40(2)	10(2)	30(2)
C(31)	80(3)	10(2)	80(2)	-30(2)	50(2)	0(2)
O(32)	82(17)	38(15)	51(13)	0(11)	19(12)	3(13)
C(33)	40(2)	50(3)	70(3)	20(2)	20(2)	-10(2)
C(34)	32(19)	60(2)	40(2)	-20(2)	10(2)	0(2)
C(35)	130(3)	90(3)	40(2)	-60(2)	0(2)	40(3)
C(36)	70(3)	90(3)	120(3)	-30(3)	60(2)	30(3)
C(37)	80(3)	40(2)	40(2)	-6(19)	-30(2)	-10(2)
C(38)	150(4)	20(2)	10(2)	-10(2)	-10(2)	-50(2)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 60.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [Ba(benzo-15-crown-5)$_2$]$_2$(Ag$_4$I$_8$) **(X)**

atom	x	y	z	U(eq)
H(2A)	4467	3480	1487	80
H(2B)	3757	4291	1089	80
H(3A)	3269	2818	501	80
H(3B)	4458	2869	630	80
H(5A)	4980	1087	589	80
H(5B)	3931	488	381	80
H(6A)	4978	-812	872	80
H(6B)	5236	27	1354	80
H(8B)	4702	-1367	1651	80
H(8A)	3984	-2194	1632	80
H(9B)	4729	-300	2060	80
H(9A)	4990	-1087	2455	80
H(11A)	4623	969	2749	80
H(11B)	4089	123	3064	80
H(12A)	2605	1194	2876	80
H(12B)	3524	1991	3124	80
H(15A)	2863	3418	3142	80
H(16A)	2518	5502	3062	80
H(17A)	2641	6429	2311	80
H(18A)	2764	5451	1546	80
H(21A)	2199	-1770	690	80
H(21B)	1126	-2038	335	80
H(22A)	368	-1812	1059	80
H(22B)	1229	-2727	1195	80
H(24A)	1601	-1213	2338	80
H(24B)	881	-2147	2031	80
H(25A)	-289	-796	1661	80
H(25B)	-24	-581	2276	80
H(27A)	-525	1291	2122	80
H(27B)	-735	1201	1502	80
H(28A)	-321	3078	1736	80
H(28B)	659	2711	2145	80
H(30B)	-44	2358	847	80
H(30A)	-395	3436	882	80
H(31B)	160	2792	264	80
H(31A)	988	3477	288	80
H(34A)	1579	2678	-382	80

Table 60. (cont.)
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Ag_4I_8)$ **(X)**

atom	x	y	z	U(eq)
H(35A)	2170	1739	-1015	80
H(36A)	2618	-166	-935	80
H(37A)	2086	-1318	-252	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

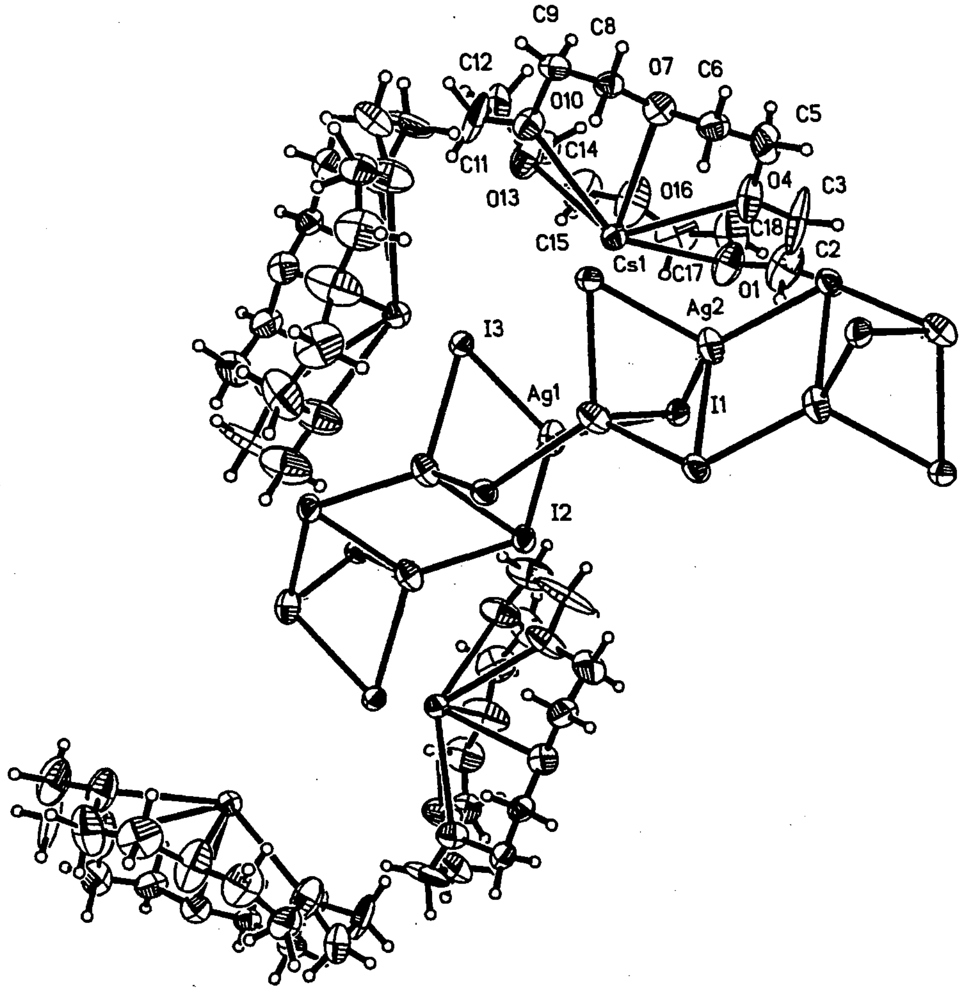


Figure 29. Projection View of [Cs(18-crown-6)]$(Ag_2I_3)_n$ **(XI)**

Table 61.
Crystal data and structure refinement for
[Cs(18-crown-6)]$(Ag_2I_3)_n$ **(XI)**

Empirical formula	$C_{12} H_{24} Ag_2 I_3 Cs O_6$	
Formula weight	3974.65	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, C2/c	
Unit cell dimensions	a = 25.965(2) Å	$\alpha = 90^\circ$
	b = 11.449(1) Å	$\beta = 120.30(1)^\circ$
	c = 18.873(2) Å	$\gamma = 90^\circ$
Volume	4844.0(8) $Å^3$	
Z, Calculated density	8, 2.725 Mg/m^3	
Absorption coefficient	6.943 mm^{-1}	
F(000)	3616	
Theta range for data collection	1.82 to 23.26°	
Index ranges	$-1 \leq h \leq 28$, $-1 \leq k \leq 12$, $-20 \leq l \leq 18$	
Reflections collected / unique	4179 / 3474 [R(int) = 0.0434]	
Completeness to $2\theta = 23.26^\circ$	47.2%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3474 / 0 / 218	
Goodness-of-fit on F^2	1.020	
Final R indices $[I>2\sigma(I)]$	R1 = 0.0617, wR2 = 0.1309	
R indices (all data)	R1 = 0.1056, wR2 = 0.1515	
Extinction coefficient	0.00061(4)	
Largest diff. peak and hole	1.564 and -1.513 $e.Å^{-3}$	

Table 62.
Atomic coordinates (x 10^4) and equivalent isotropic
displacement parameters ($Å^2$ x 10^3) for
[Cs(18-crown-6)]$(Ag_2I_3)_n$ **(XI)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Cs(1)	3693(1)	1493(1)	2097(1)	54(1)
I(1)	4022(1)	4981(1)	2450(1)	55(1)
I(2)	4269(1)	6048(1)	184(1)	65(1)
I(3)	4670(1)	2232(1)	1071(1)	52(1)
Ag(1)	4595(1)	4512(2)	1598(1)	96(1)
Ag(2)	4763(1)	4156(2)	4221(1)	110(1)
O(1)	2482(7)	271(2)	1682(12)	109(6)
C(2)	2533(13)	3210(3)	2420(2)	132(13)
C(3)	2724(14)	2550(4)	3060(2)	170(2)
O(4)	3225(7)	1870(2)	3283(10)	104(6)
C(5)	3376(12)	1120(3)	3945(15)	96(9)
C(6)	3941(12)	530(2)	4189(12)	77(6)
O(7)	3885(6)	-211(13)	3569(8)	70(4)
C(8)	4419(8)	-870(2)	3825(11)	57(5)
C(9)	4303(10)	-1630(2)	3118(12)	67(6)
O(10)	4267(6)	-940(12)	2469(8)	70(4)
C(11)	4175(12)	-1520(3)	1710(2)	126(12)
C(12)	3590(2)	-1710(3)	1220(2)	133(12)
O(13)	3284(9)	-640(2)	853(10)	101(6)
C(14)	2703(15)	-810(2)	300(2)	102(9)
C(15)	2343(12)	190(3)	34(15)	111(10)
O(16)	2399(7)	820(2)	696(11)	125(8)
C(17)	1955(11)	1690(3)	470(2)	113(10)
C(18)	1951(10)	2170(3)	1150(2)	121(11)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 63.
Bond lengths [Å] and angles [°] for
[Cs(18-crown-6)] (Ag$_2$I$_3$)$_n$ **(XI)**

I(1)-Ag(1)	2.738(2)	Cs(1)-O(4)	3.07(2)
I(1)-Ag(2)	3.046(3)	Cs(1)-O(10)	3.070(14)
I(1)-Ag(1)^1	3.147(3)	Cs(1)-O(16)	3.149(15)
I(2)-Ag(2)^2	2.712(2)	Cs(1)-O(1)	3.155(15)
I(2)-Ag(1)	2.941(2)	Cs(1)-O(13)	3.18(2)
I(2)-Ag(2)^1	3.070(3)	Cs(1)-O(7)	3.220(14)
I(3)-Ag(1)	2.835(2)	Cs(1)-C(6)	3.83(2)
I(3)-Ag(2)^1	2.853(2)	Cs(1)-C(11)	3.86(2)
I(3)-Cs(1)^1	3.988 (2)	Cs(1)-C(2)	3.90(3)
Ag(1)-Ag(2)^1	2.817(2)	Cs(1)-C(8)	3.92(2)
Ag(1)-Ag(1)^1	2.967(4)	Cs(1)-I(3)	3.984(2)
Ag(1)-I(1)^1	3.147(3)	Cs(1)-I(3)^1	3.988(2)
Ag(2)-I(2)^3	2.712(2)	O(1)-C(18)	1.38(3)
Ag(2)-Ag(1)^1	2.817(2)	O(1)-C(2)	1.46(3)
Ag(2)-I(3)^1	2.853(2)	C(2)-C(3)	1.29(4)
Ag(2)-I(2)^1	3.070(3)	C(3)-O(4)	1.39(3)
Ag(2)-Ag(2)^4	3.200(4)	O(4)-C(5)	1.40(3)
C(5)-C(6)	1.46(3)	O(13)-C(14)	1.35(3)
C(6)-O(7)	1.39(2)	C(14)-C(15)	1.40(3)
O(7)-C(8)	1.44(2)	C(15)-O(16)	1.39(3)
C(8)-C(9)	1.49(2)	O(16)-C(17)	1.42(3)
C(9)-O(10)	1.48(3)	O(4)-Cs(1)-O(10)	106.5(5)
C(11)-C(12)	1.42(3)	O(10)-Cs(1)-O(16)	99.2(5)
O(4)-Cs(1)-O(1)	53.7(5)	O(10)-Cs(1)-O(1)	140.0(5)
O(4)-Cs(1)-O(13)	122.5(5)	O(16)-Cs(1)-O(1)	52.5(5)
O(10)-Cs(1)-O(13)	54.1(4)	O(16)-Cs(1)-O(13)	51.2(5)
O(1)-Cs(1)-O(13)	103.6(5)	O(13)-Cs(1)-C(8)	85.7(4)
O(4)-Cs(1)-O(7)	53.2(5)	O(7)-Cs(1)-C(8)	20.4(4)
O(10)-Cs(1)-O(7)	53.6(4)	C(6)-Cs(1)-C(8)	35.0(5)
O(16)-Cs(1)-O(7)	100.5(5)	C(2)-Cs(1)-C(8)	107.7(6)
O(13)-Cs(1)-O(7)	91.2(4)	O(4)-Cs(1)-I(3)	155.4(4)
O(4)-Cs(1)-C(6)	72.0(4)	O(16)-Cs(1)-I(3)	108.4(4)
O(16)-Cs(1)-C(6)	110.4(6)	O(1)-Cs(1)-I(3)	125.8(4)
O(1)-Cs(1)-C(6)	90.7(5)	O(10)-Cs(1)-I(3)^1	79.2(2)
O(13)-Cs(1)-C(6)	111.0(5)	O(13)-Cs(1)-I(3)	82.0(4)
O(7)-Cs(1)-C(6)	20.5(4)	O(7)-Cs(1)-I(3)	133.5(3)
O(4)-Cs(1)-C(11)	123.1(7)	C(6)-Cs(1)-I(3)	138.2(4)
O(10)-Cs(1)-C(11)	20.9(5)	C(11)-Cs(1)-I(3)	75.7(5)
O(16)-Cs(1)-C(11)	86.2(5)	C(2)-Cs(1)-I(3)	134.6(6)
O(1)-Cs(1)-C(11)	136.4(6)	C(8)-Cs(1)-I(3)	113.2(3)
O(13)-Cs(1)-C(11)	36.2(5)	O(4)-Cs(1)-I(3)^1	88.8(3)

Table 63. (continued)
Bond lengths [Å] and angles [°] for
[Cs(18-crown-6)]$(Ag_2I_3)_n$ **(XI)**

O(7)-Cs(1)-C(11)	72.3(6)	O(16)-Cs(1)-I(3)^1	177.5(4)
C(6)-Cs(1)-C(11)	91.9(6)	O(1)-Cs(1)-I(3)^1	127.9(4)
O(4)-Cs(1)-C(2)	36.2(6)	O(13)-Cs(1)-I(3)^1	128.1(3)
O(10)-Cs(1)-C(2)	120.5(6)	C(2)-Cs(1)-I(3)^1	109.0(5)
O(7)-Cs(1)-C(2)	88.0(6)	C(8)-Cs(1)-I(3)^1	64.5(3)
C(6)-Cs(1)-C(2)	74.1(7)	I(3)-Cs(1)-I(3)^1	73.44(3)
C(11)-Cs(1)-C(2)	146.1(7)	Ag(1)-I(1)-Ag(2)	110.78(7)
O(4)-Cs(1)-C(8)	71.9(5)	Ag(1)-I(1)-Ag(1)^1	60.07(8)
O(10)-Cs(1)-C(8)	37.5(4)	Ag(2)-I(1)-Ag(1)^1	54.09(5)
O(16)-Cs(1)-C(8)	113.0(5)	Ag(1)-I(1)-Cs(1)	80.98(6)
O(1)-Cs(1)-C(8)	120.9(5)	Ag(2)-I(1)-Cs(1)	80.75(5)
Ag(1)^1-I(1)-Cs(1)	90.64(5)	I(3)-Ag(1)-I(2)	105.76(7)
Ag(2)^2-I(2)-Ag(1)	122.65(8)	I(1)-Ag(1)-Ag(1)^1	66.82(7)
Ag(2^2-I(2)-Ag(2)^1	66.87(8)	Ag(2)^1-Ag(1)-Ag(1)^1	110.87(12)
Ag(1)-I(2)-Ag(2)^1	55.85(5)	I(3)-Ag(1)-Ag(1)^1	105.55(6)
Ag(1)-I(3)-Ag(2)^1	59.37(6)	I(2)-Ag(1)-Ag(1)^1	138.96(7)
Ag(1)-I(3)-Cs(1)	81.43(5)	I(1)-Ag(1)-I(1)^1	115.59(7)
Ag(2)^1-I(3)-Cs(1)	140.81(6)	Ag(2)^1-Ag(1)-I(1)^1	61.13(7)
Ag(1)-I(3)-Cs(1)^1	97.08(6)	I(3)-Ag(1)-I(1)^1	95.53(7)
Ag(2)^1-I(3)-Cs(1)^1	84.44(6)	I(2)-Ag(1)-I(1)^1	98.00(7)
Cs(1)-I(3)-Cs(1)^1	101.24(3)	Ag(1)^1-Ag(1)-I(1)^1	53.11(7)
I(1)-Ag(1)-Ag(2)^1	176.09(10)	I(1)-Ag(1)-Cs(1)	62.41(5)
I(1)-Ag(1)-I(3)	122.73(8)	Ag(2)^1-Ag(1)-Cs(1)	120.98(8)
Ag(2)^1-Ag(1)-I(3)	60.62(6)	I(3)-Ag(1)-Cs(1)	60.36(5)
I(1)-Ag(1)-I(2)	115.02(8)	I(2)-Ag(1)-Cs(1)	134.63(7)
Ag(2)^1-Ag(1)-I(2)	64.40(7)	Ag(1)^1-Ag(1)-Cs(1)	84.42(5)
I(1)^1-Ag(1)-Cs(1)	124.86(7)	C(6)-O(7)-Cs(1)	105.3(12)
I(2)^3-Ag(2)-Ag(1)^1	172.35(11)	C(18)-O(1)-C(2)	117(2)
I(2)^3-Ag(2)-I(3)^1	121.81(9)	C(18)-O(1)-Cs(1)	120(2)
Ag(1)^1-Ag(2)-I(3)^1	60.00(6)	C(2)-O(1)-Cs(1)	109.8(13)
I(2)^3-Ag(2)-I(1)	120.80(9)	C(3)-C(2)-O(1)	118(3)
Ag(1)^1-Ag(2)-I(1)	64.78(7)	C(3)-C(2)-Cs(1)	84(2)
I(3)^1-Ag(2)-I(1)	97.42(6)	O(1)-C(2)-Cs(1)	49.6(11)
I(2)^3-Ag(2)-I(2)^1	113.13(8)	C(2)-C(3)-O(4)	118(3)
Ag(1)^1-Ag(2)-I(2)^1	59.75(7)	C(3)-O(4)-C(5)	114(2)
I(3)^1-Ag(2)-I(2)^1	102.03(8)	C(3)-O(4)-Cs(1)	121(2)
I(1)-Ag(2)-I(2)^1	97.44(7)	C(5)-O(4)-Cs(1)	122.1(14)
I(2)^3-Ag(2)-Ag(2)^4	61.91(6)	C(5)-C(6)-Cs(1)	85.5(13)
Ag(1)^1-Ag(2)-Ag(2)^4	110.90(11)	C(6)-O(7)-C(8)	111.3(16)
I(3)^1-Ag(2)-Ag(2)^4	130.30(13)	C(9)-C(8)-Cs(1)	82.2(11)
I(1)-Ag(2)-Ag(2)^4	123.93(12)	C(8)-O(7)-Cs(1)	108.3(10)
I(2)^1-Ag(2)-Ag(2)^4	51.21(7)	C(9)-O(10)-C(11)	119.2(19)

Table 63. (continued)
Bond lengths [Å] and angles [°] for
[Cs(18-crown-6)] $(Ag_2I_3)_n$ **(XI)**

O(4)-C(5)-C(6)	110(2)	C(9)-O(10)-Cs(1)	121.2(11)
O(7)-C(6)-C(5)	111(2)	C(12)-C(11)-O(10)	109(2)
O(7)-C(6)-Cs(1)	54.2(9)	C(12)-C(11)-Cs(1)	85(2)
O(7)-C(8)-C(9)	106.4(15)	C(11)-C(12)-O(13)	111(3)
O(7)-C(8)-Cs(1)	51.3(8)	C(14)-O(13)-C(12)	112(2)
O(10)-C(9)-C(8)	110(2)	C(14)-O(13)-Cs(1)	120.7(14)
O(10)-C(11)-Cs(1)	47.8(10)	C(12)-O(13)-Cs(1)	114(2)
O(13)-C(14)-C(15)	116(2)	C(15)-O(16)-C(17)	113(2)
O(16)-C(15)-C(14)	111(2)	C(15)-O(16)-Cs(1)	117.9(15)
C(17)-O(16)-Cs(1)	116.0(14)	C(18)-C(17)-O(16)	112(2)
O(1)-C(18)-C(17)	112(2)		

Symmetry transformations used to generate equivalent atoms:
1= -x+1,y,-z+1/2 2= x,-y+1,z-1/2
3= x,-y+1,z+1/2 4= -x+1,-y+1,-z+1

Table 64.
Anisotropic displacement parameters (Å^2 x 10^3) for [Cs(18-crown-6)] $(Ag_2I_3)_n$ **(XI)**

atom	U11	U22	U33	U23	U13	U12
Cs(1)	54(1)	50(1)	59(1)	-2(1)	30(1)	-1(1)
I(1)	70(1)	51(1)	51(1)	3(1)	37(1)	8(1)
I(2)	92(1)	61(1)	64(1)	16(1)	56(1)	23(1)
I(3)	61(1)	45(1)	54(1)	-2(1)	32(1)	1(1)
Ag(1)	130(2)	91(1)	105(2)	-20(1)	88(1)	0(1)
Ag(2)	168(2)	94(2)	137(2)	-13(1)	129(2)	-8(2)
O(1)	73(11)	120(15)	109(13)	-18(12)	29(10)	32(11)
C(2)	70(2)	150(3)	140(3)	-20(2)	20(2)	50(2)
C(3)	130(3)	260(5)	90(2)	-50(3)	30(2)	120(3)
O(4)	95(12)	150(2)	73(11)	-28(11)	43(9)	35(12)
C(5)	120(2)	110(2)	74(16)	-60(2)	60(2)	-40(2)
C(6)	120(2)	61(14)	53(12)	-2(11)	48(13)	-7(15)
O(7)	62(8)	76(10)	61(8)	-9(8)	22(7)	-9(8)
C(8)	61(12)	48(11)	58(12)	-7(10)	27(10)	-10(10)
C(9)	76(14)	55(13)	73(14)	7(11)	40(12)	-5(11)
O(10)	75(9)	67(9)	58(8)	0(8)	26(7)	11(8)
C(11)	80(2)	110(2)	190(3)	-70(2)	70(2)	20(2)
C(12)	180(4)	110(3)	190(3)	-30(3)	150(3)	0(3)
O(13)	112(14)	107(14)	65(10)	-18(10)	29(10)	28(13)
C(14)	170(3)	80(2)	100(2)	-50(2)	90(2)	-40(2)
C(15)	100(2)	130(3)	61(15)	-40(2)	10(14)	-10(2)
O(16)	62(10)	160(2)	90(12)	-45(13)	-8(9)	33(12)
C(17)	70(2)	130(2)	80(19)	-10(2)	-10(15)	-10(2)
C(18)	43(14)	200(4)	100(2)	-40(2)	21(14)	-10(2)

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 65.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [Cs(18-crown-6)] $(Ag_2I_3)_n$ **(XI)**

atom	x	y	z	U(eq)
H(2A)	2173	3632	2280	80
H(2B)	2855	3765	2630	80
H(3A)	2407	1987	2850	80
H(3B)	2736	2931	3523	80
H(5A)	3078	516	3777	80
H(5B)	3394	1534	4398	80
H(6A)	4093	104	4696	80
H(6B)	4220	1130	4263	80
H(8A)	4522	-1331	4305	80
H(8B)	4743	-353	3947	80
H(9A)	3932	-2035	2928	80
H(9B)	4614	-2207	3286	80
H(11A)	4380	-2256	1864	80
H(11B)	4339	-1053	1452	80
H(12A)	3416	-2064	1510	80
H(12B)	3534	-2232	789	80
H(14B)	2618	-857	739	80
H(14A)	2526	-1566	108	80
H(15B)	2691	585	101	80
H(15A)	2121	453	-525	80
H(17A)	1572	1384	79	80
H(17B)	2047	2329	221	80
H(18A)	1628	2704	994	80
H(18B)	1894	1519	1430	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

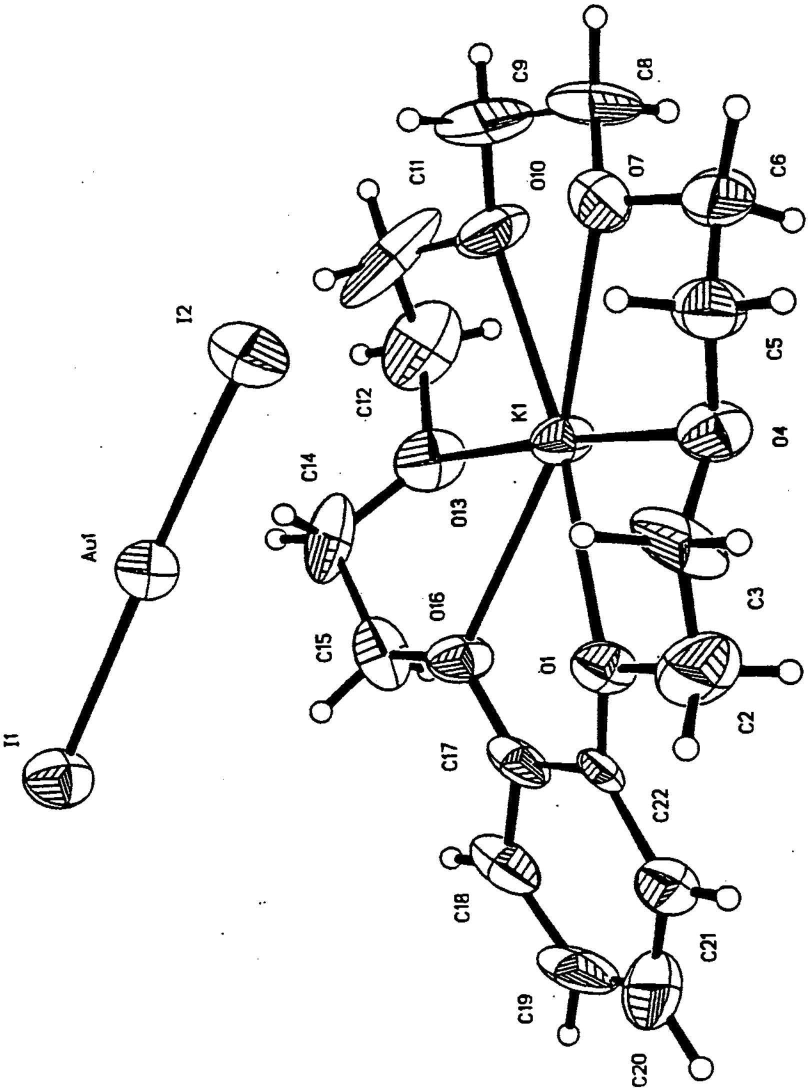


Figure 30. Projection View of [K(benzo-18-crown-6)](AuI_2) **(XII)**

Table 66.
Crystal data and structure refinement for [K(benzo-18-crown-6)](AuI_2) **(XII)**

Empirical formula	$C_{16} H_{24} Au I_2 K O_6$
Formula weight	802.22
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $Pna2_1$
Unit cell dimensions	a = 17.058(5) Å α= 90° b = 15.457(3) Å β = 90° c = 8.831(3) Å γ = 90°
Volume	2328.4(11) $Å^3$
Z, Calculated density	4, 2.288 Mg/m^3
Absorption coefficient	9.174 mm^{-1}
F(000)	1488
Theta range for data collection	1.78 to 30.01°
Index ranges	$-1 \le h \le 23, -1 \le k \le 21, -1 \le l \le 12$
Reflections collected / unique	4498 / 3984 [R(int) = 0.0621]
Completeness to 2θ = 30.01°	99.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3984 / 1 / 236
Goodness-of-fit on F^2	0.981
Final R indices [I>2σ(I)]	R1 = 0.0693, wR2 = 0.0928
R indices (all data)	R1 = 0.2032, wR2 = 0.1246
Absolute structure parameter	0.001(13)
Extinction coefficient	0.00115(11)
Largest diff. peak and hole	0.763 and -0.689 e.$Å^{-3}$

Table 67.

Atomic coordinates (x 10^4) and equivalent isotropic
displacement parameters (Å^2 x 10^3) for
[K(benzo-18-crown-6)](AuI$_2$) **(XII)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Au(1)	810(1)	2090(1)	1770(1)	63(1)
I(1)	1872(1)	1362(1)	232(2)	78(1)
I(2)	-245(1)	2791(1)	3367(2)	86(1)
K(1)	807(2)	2266(2)	7071(10)	68(2)
O(1)	877(8)	501(8)	636(2)	62(5)
C(2)	281(14)	-22(14)	6950(5)	120(1)
C(3)	-458(13)	470(2)	6870(5)	111(10)
O(4)	-420(8)	122(1)	7870(2)	73(5)
C(5)	-1121(12)	165(2)	7890(3)	82(8)
C(6)	-1059(13)	249(2)	8660(4)	93(9)
O(7)	-600(9)	3044(10)	775(2)	72(4)
C(8)	-507(15)	391(2)	8310(4)	99(10)
C(9)	9(17)	4401(13)	7330(5)	124(15)
O(10)	737(11)	4064(10)	737(2)	99(8)
C(11)	1260(2)	4450(2)	6360(5)	180(3)
C(12)	1970(2)	417(2)	6710(6)	137(12)
O(13)	2079(9)	3226(11)	6230(3)	92(7)
C(14)	2275(15)	2920(2)	4680(3)	100(11)
C(15)	2578(12)	204(2)	4850(3)	75(7)
O(16)	1983(7)	1487(9)	542(2)	69(5)
C(17)	2164(12)	670(2)	5660(3)	73(8)
C(18)	2910(13)	290(2)	5370(3)	91(8)
C(19)	3010(3)	-590(3)	5780(4)	170(2)
C(20)	2480(3)	-1120(3)	6210(4)	130(2)
C(21)	1710(2)	-756(16)	6440(3)	91(9)
C(22)	1575(14)	129(14)	622(2)	54(6)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 68.
Bond lengths [Å] and angles [^{o}] for
[K(benzo-18-crown-6)](AuI$_2$) **(XII)**

Au(1)-I(1)	2.529(2)	O(13)-C(14)	1.48(3)
Au(1)-I(2)	2.530(2)	C(14)-C(15)	1.46(3)
Au(1)-K(1)^1	4.159(9)	C(15)-O(16)	1.42(2)
I(1)-K(1)^1	3.611(8)	O(16)-C(17)	1.31(3)
I(2)-K(1)	3.819(9)	C(17)-C(22)	1.40(3)
K(1)-O(13)	2.732(15)	C(17)-C(18)	1.42(3)
K(1)-O(4)	2.737(14)	C(18)-C(19)	1.42(4)
K(1)-O(7)	2.753(15)	C(19)-C(20)	1.29(5)
K(1)-O(16)	2.756(15)	C(20)-C(21)	1.44(4)
K(1)-O(10)	2.794(15)	C(21)-C(22)	1.40(3)
K(1)-O(1)	2.802(13)	I(1)-Au(1)-I(2)	178.45(8)
K(1)-C(14)	3.43(3)	I(1)-Au(1)-K(1)^1	59.59(8)
K(1)-C(6)	3.50(2)	I(2)-Au(1)-K(1)^1	121.83(8)
K(1)-C(5)	3.50(2)	Au(1)-I(1)-K(1)^1	83.26(11)
K(1)-C(11)	3.52(3)	Au(1)-I(2)-K(1)	92.98(10)
K(1)-C(3)	3.53(2)	O(13)-K(1)-O(4)	176.7(5)
K(1)-I(1)^2	3.611(8)	O(13)-K(1)-O(7)	121.0(5)
O(1)-C(22)	1.33(2)	O(4)-K(1)-O(7)	62.2(5)
O(1)-C(2)	1.40(3)	O(13)-K(1)-O(16)	61.0(5)
C(2)-C(3)	1.47(3)	O(4)-K(1)-O(16)	115.8(5)
C(3)-O(4)	1.47(3)	O(7)-K(1)-O(16)	160.3(6)
O(4)-C(5)	1.37(2)	O(13)-K(1)-O(10)	61.3(5)
C(5)-C(6)	1.48(3)	O(4)-K(1)-O(10)	122.0(6)
C(6)-O(7)	1.41(3)	O(7)-K(1)-O(10)	60.5(5)
O(7)-C(8)	1.43(3)	O(16)-K(1)-O(10)	121.1(5)
C(8)-C(9)	1.45(4)	O(13)-K(1)-O(1)	115.7(5)
C(9)-O(10)	1.35(3)	O(4)-K(1)-O(1)	61.0(4)
O(10)-C(11)	1.40(4)	O(7)-K(1)-O(1)	120.8(5)
C(11)-C(12)	1.33(3)	O(16)-K(1)-O(1)	54.9(4)
C(12)-O(13)	1.52(3)	O(10)-K(1)-O(1)	172.4(7)
O(10)-K(1)-C(14)	78.3(7)	O(13)-K(1)-C(14)	24.8(6)
O(1)-K(1)-C(14)	96.7(7)	O(4)-K(1)-C(14)	153.0(7)
O(13)-K(1)-C(6)	141.1(6)	O(7)-K(1)-C(14)	130.1(7)
O(4)-K(1)-C(6)	42.2(5)	O(16)-K(1)-C(14)	43.2(7)
O(7)-K(1)-C(6)	22.2(5)	O(16)-K(1)-C(11)	99.5(8)
O(16)-K(1)-C(6)	156.7(6)	O(10)-K(1)-C(11)	21.9(8)
O(10)-K(1)-C(6)	79.8(6)	O(1)-K(1)-C(11)	152.1(9)
O(1)-K(1)-C(6)	103.1(5)	C(14)-K(1)-C(11)	56.5(9)
C(14)-K(1)-C(6)	152.0(7)	C(6)-K(1)-C(11)	100.0(8)
O(13)-K(1)-C(5)	161.9(6)	C(5)-K(1)-C(11)	120.3(7)

Table 68. (cont.)
Bond lengths [Å] and angles [°] for
[K(benzo-18-crown-6)](AuI$_2$) (**XII**)

O(4)-K(1)-C(5)	21.1(4)	O(13)-K(1)-C(3)	154.3(7)
O(7)-K(1)-C(5)	41.8(5)	O(4)-K(1)-C(3)	22.9(6)
O(16)-K(1)-C(5)	132.4(5)	O(7)-K(1)-C(3)	79.7(5)
O(10)-K(1)-C(5)	102.2(6)	O(16)-K(1)-C(3)	94.2(5)
O(1)-K(1)-C(5)	79.7(5)	O(10)-K(1)-C(3)	139.8(6)
C(14)-K(1)-C(5)	153.4(7)	O(1)-K(1)-C(3)	41.1(5)
C(6)-K(1)-C(5)	24.4(5)	C(14)-K(1)-C(3)	130.4(8)
O(13)-K(1)-C(11)	42.0(7)	C(6)-K(1)-C(3)	62.8(6)
O(4)-K(1)-C(11)	141.2(7)	C(5)-K(1)-C(3)	38.8(5)
O(7)-K(1)-C(11)	79.1(7)	C(11)-K(1)-C(3)	151.8(8)
O(13)-K(1)-I(1)^2	91.3(5)	C(6)-O(7)-C(8)	115(2)
O(4)-K(1)-I(1)^2	87.6(4)	C(6)-O(7)-K(1)	110.2(12)
O(7)-K(1)-I(1)^2	116.0(4)	C(8)-O(7)-K(1)	112.7(13)
O(16)-K(1)-I(1)^2	82.8(4)	O(7)-C(8)-C(9)	111(2)
O(10)-K(1)-I(1)^2	109.5(5)	O(10)-C(9)-C(8)	110(2)
O(1)-K(1)-I(1)^2	77.1(3)	O(4)-C(3)-C(2)	110(3)
C(14)-K(1)-I(1)^2	102.9(5)	O(4)-C(3)-K(1)	46.7(9)
C(6)-K(1)-I(1)^2	100.7(5)	C(2)-C(3)-K(1)	82.9(12)
C(5)-K(1)-I(1)^2	101.9(5)	C(5)-O(4)-C(3)	111(2)
C(11)-K(1)-I(1)^2	113.6(6)	C(5)-O(4)-K(1)	112.8(13)
C(3)-K(1)-I(1)^2	92.4(6)	C(3)-O(4)-K(1)	110.4(12)
C(22)-O(1)-C(2)	116(2)	O(4)-C(5)-C(6)	112(2)
C(22)-O(1)-K(1)	118.7(12)	O(4)-C(5)-K(1)	46.1(10)
C(2)-O(1)-K(1)	116.6(14)	C(6)-C(5)-K(1)	77.7(13)
O(1)-C(2)-C(3)	108(2)	O(7)-C(6)-C(5)	108(2)
C(9)-O(10)-C(11)	114(2)	O(7)-C(6)-K(1)	47.6(10)
C(9)-O(10)-K(1)	115.0(13)	C(5)-C(6)-K(1)	77.9(13)
C(11)-O(10)-K(1)	110(2)	O(16)-C(15)-C(14)	110(2)
C(12)-C(11)-O(10)	107(3)	C(17)-O(16)-C(15)	118(2)
C(12)-C(11)-K(1)	81(2)	C(17)-O(16)-K(1)	120.3(15)
O(10)-C(11)-K(1)	48.5(13)	C(15)-O(16)-K(1)	116.5(12)
C(11)-C(12)-O(13)	111(3)	O(16)-C(17)-C(22)	118(2)
C(14)-O(13)-C(12)	126(3)	O(16)-C(17)-C(18)	125(3)
C(14)-O(13)-K(1)	104.8(14)	C(22)-C(17)-C(18)	117(3)
C(12)-O(13)-K(1)	110.1(15)	C(19)-C(18)-C(17)	117(3)
C(15)-C(14)-O(13)	107(2)	C(20)-C(19)-C(18)	127(4)
C(15)-C(14)-K(1)	85.5(13)	C(19)-C(20)-C(21)	116(4)
O(13)-C(14)-K(1)	50.5(10)	C(22)-C(21)-C(20)	121(3)
O(1)-C(22)-C(21)	124(2)	O(1)-C(22)-C(17)	114(2)
C(17)-C(22)-C(21)	121(2)		

Symmetry transformations: 1= x,y,z-1 2= x,y,z+1

Table 69.
Anisotropic displacement parameters (Å^3 x 10^3) for
[K(benzo-18-crown-6)](AuI$_2$) **(XII)**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au(1)	56(1)	60(1)	74(1)	-5(1)	-1(1)	-10(1)
I(1)	66(1)	73(1)	95(1)	-1(1)	16(1)	-1(1)
I(2)	71(1)	97(1)	91(1)	-23(1)	6(1)	3(1)
K(1)	53(2)	47(2)	104(6)	7(4)	15(4)	0(2)
O(1)	63(8)	42(7)	80(15)	-14(8)	9(9)	-14(8)
C(2)	140(3)	56(13)	150(3)	20(3)	20(4)	-10(2)
C(3)	70(2)	100(2)	160(3)	-30(3)	90(2)	-33(15)
O(4)	44(8)	78(10)	97(14)	3(11)	-4(9)	5(8)
C(5)	80(2)	90(2)	80(2)	-10(2)	-0(2)	22(15)
C(6)	58(15)	110(2)	110(3)	20(2)	20(2)	39(14)
O(7)	69(10)	83(11)	66(11)	-9(10)	4(9)	3(9)
C(8)	80(2)	70(2)	140(3)	-70(2)	-20(2)	31(14)
C(9)	150(3)	28(11)	190(5)	-40(2)	-10(3)	33(15)
O(10)	98(14)	54(9)	150(2)	25(12)	6(14)	25(10)
C(11)	150(3)	110(2)	300(7)	120(4)	-120(4)	-20(2)
C(12)	130(3)	100(2)	180(3)	30(4)	-30(4)	-60(2)
O(13)	71(10)	61(10)	140(2)	20(12)	30(13)	-25(8)
C(14)	80(2)	120(3)	100(2)	70(2)	-10(2)	-60(2)
C(15)	59(13)	100(2)	70(2)	-0(2)	11(13)	-50(2)
O(16)	48(8)	52(8)	105(14)	3(11)	19(11)	3(7)
C(17)	47(13)	120(2)	50(2)	-20(2)	-1(13)	39(15)
C(18)	70(2)	140(2)	70(2)	-40(2)	4(18)	20(15)
C(19)	220(5)	190(4)	90(3)	-60(3)	-50(3)	180(4)
C(20)	200(4)	120(3)	70(3)	20(2)	-30(3)	20(3)
C(21)	130(2)	80(2)	60(2)	-10(2)	0(2)	30(2)
C(22)	70(2)	63(14)	29(12)	-13(11)	10(12)	20(14)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 70.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for [K(benzo-18-crown-6)](AuI$_2$) **(XII)**

atom	x	y	z	U(eq)
H(2A)	385	-163	7985	80
H(2B)	249	-549	6373	80
H(3A)	-898	106	7120	80
H(3B)	-523	667	5848	80
H(5A)	-1523	1289	8317	80
H(5B)	-1261	1780	6865	80
H(6A)	-786	2397	9599	80
H(6B)	-1567	2731	8878	80
H(8A)	-288	3887	9308	80
H(8B)	-1014	4174	8374	80
H(9A)	14	4990	7680	80
H(9B)	-188	4393	6316	80
H(11A)	1230	5067	6446	80
H(11B)	1109	4291	5345	80
H(12A)	2088	4253	7759	80
H(12B)	2337	4491	6117	80
H(14A)	2669	3282	4241	80
H(14B)	1823	2915	4032	80
H(15A)	3010	2047	5550	80
H(15B)	2764	1812	3905	80
H(18A)	3313	660	4959	80
H(19A)	3528	-819	5609	80
H(20A)	2615	-1710	6446	80
H(21A)	1303	-1138	6765	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

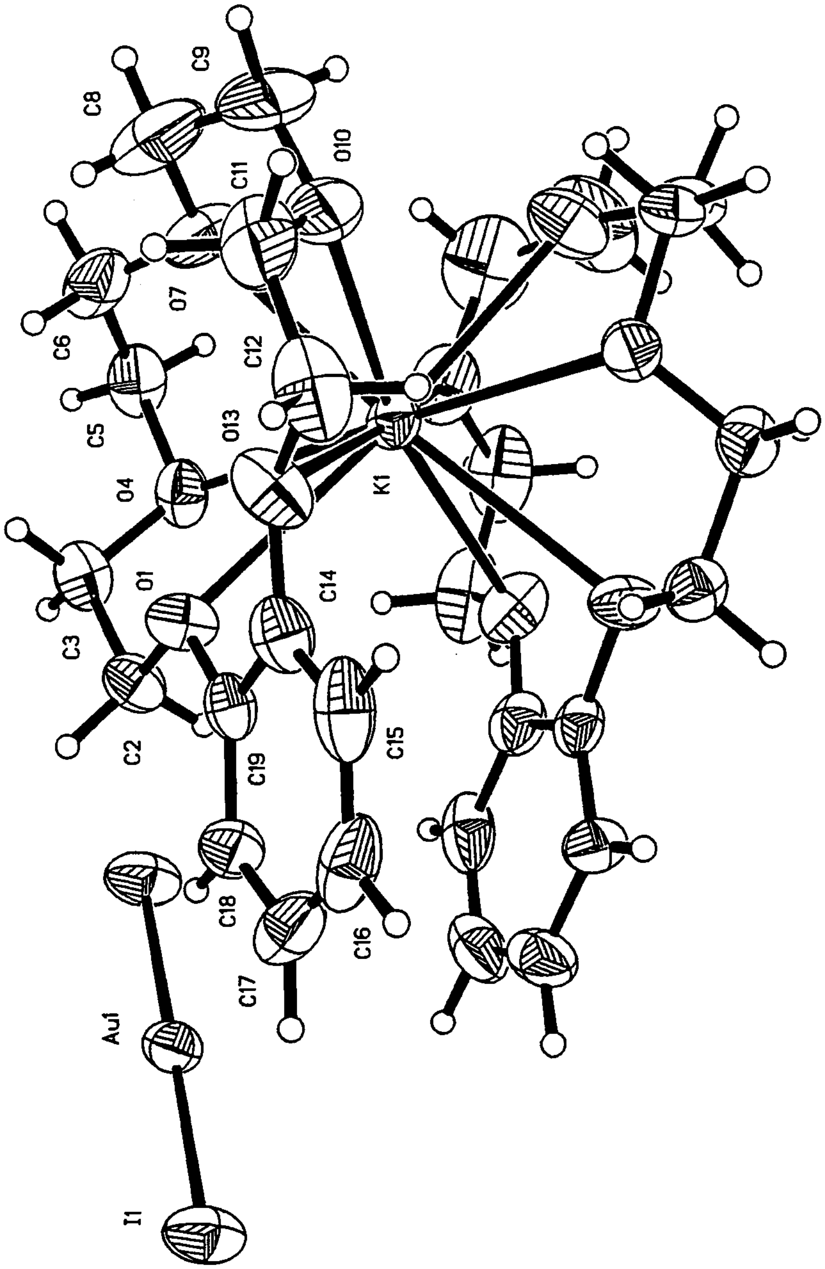


Figure 31. Projection View of [K(benzo-15-crown-5)$_2$](AuI$_2$) **(XIII)**

Table 71.
Crystal data and structure refinement for
$[K(benzo\text{-}15\text{-}crown\text{-}5)_2](AuI_2)$ **(XIII)**

Empirical formula	$C_{28} H_{40} Au I_2 K O_{10}$
Formula weight	1026.47
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, C2/c
Unit cell dimensions	a = 19.483(3) Å $\alpha = 90^\circ$ b = 13.061(2) Å $\beta = 116.63^\circ$ c = 15.421(4) Å $\gamma = 90^\circ$
Volume	3507.9(12) $Å^3$
Z, Calculated density	4, 1.944 Mg/m^3
Absorption coefficient	6.121 mm^{-1}
F(000)	1968
Theta range for data collection	2.11 to 30.00°
Index ranges	$-1 \leq h \leq 27, -1 \leq k \leq 18, -21 \leq l \leq 19$
Reflections collected / unique	5936 / 5079 [R(int) = 0.0461]
Completeness to 2θ =30.00°	47.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5079 / 0 / 193
Goodness-of-fit on F^2	1.004
Final R indices [I>2σ(I)]	R1 = 0.0614, wR2 = 0.1087
R indices (all data)	R1 = 0.1577, wR2 = 0.1385
Extinction coefficient	0.00098(11)
Largest diff. peak and hole	0.906 and -0.621 e.$Å^3$

Table 72.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [K(benzo-15-crown-5)$_2$](AuI$_2$) **(XIII)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Au(1)	2500	2500	0	67(1)
I(1)	3271(1)	4130(1)	450(1)	96(1)
K(1)	5000	-1832(2)	2500	56(1)
O(1)	4695(3)	-296(4)	935(4)	63(1)
C(2)	3903(4)	-95(6)	325(6)	63(2)
C(3)	3568(5)	-1099(7)	-130(6)	70(2)
O(4)	3629(3)	-1797(5)	592(4)	68(2)
C(5)	3490(6)	-2819(7)	254(7)	83(3)
C(6)	4180(7)	-3288(8)	240(8)	91(3)
O(7)	4768(4)	-3406(5)	1174(6)	101(2)
C(8)	5438(11)	-3801(12)	1134(12)	170(7)
C(9)	6082(10)	-3761(11)	2049(13)	151(6)
O(10)	6286(4)	-2797(6)	2452(5)	99(2)
C(11)	6780(6)	-2252(11)	2191(9)	114(4)
C(12)	6808(5)	-1178(11)	2490(8)	106(4)
O(13)	5908(5)	248(8)	1972(6)	70(2)
C(15)	6442(6)	983(10)	2495(6)	88(3)
C(16)	6213(7)	1995(10)	2411(8)	93(3)
C(17)	5455(8)	2262(8)	1802(8)	88(3)
C(18)	4928(5)	1525(6)	1284(6)	67(2)
C(19)	5152(4)	522(6)	1386(5)	55(2)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 73.
Bond lengths [Å] and angles [°] for [K(benzo-15-crown-5)$_2$](AuI$_2$) **(XIII)**

Au(1)-I(1)^1	2.5169(7)	O(4)-C(3)-C(2)	109.5(6)
Au(1)-I(1)	2.5169(7)	C(3)-O(4)-C(5)	112.7(6)
K(1)-O(7)	2.790(7)	C(3)-O(4)-K(1)	121.2(4)
K(1)-O(7)^2	2.790(7)	C(5)-O(4)-K(1)	106.9(5)
K(1)-O(10)^2	2.835(6)	O(4)-C(5)-C(6)	111.7(7)
K(1)-O(10)	2.835(6)	O(7)-C(6)-C(5)	111.2(8)
K(1)-O(13)	2.873(6)	C(6)-O(7)-C(8)	109.8(10)
K(1)-O(13)^2	2.873(6)	C(6)-O(7)-K(1)	117.7(6)
K(1)-O(4)^2	2.957(5)	C(8)-O(7)-K(1)	116.5(7)
K(1)-O(4)	2.957(5)	C(9)-C(8)-O(7)	111.3(12)
K(1)-O(1)^2	2.986(6)	O(10)-C(9)-C(8)	115.6(12)
K(1)-O(1)	2.986(6)	C(9)-O(10)-C(11)	115.6(10)
K(1)-C(14)	3.531(9)	C(9)-O(10)-K(1)	109.7(8)
K(1)-C(14)^2	3.531(9)	C(11)-O(10)-K(1)	120.9(6)
O(1)-C(19)	1.365(9)	O(10)-C(11)-C(12)	109.3(9)
O(1)-C(2)	1.426(8)	O(13)-C(12)-C(11)	107.6(10)
C(2)-C(3)	1.493(11)	C(14)-O(13)-C(12)	122.7(8)
C(3)-O(4)	1.402(9)	C(14)-O(13)-K(1)	107.4(5)
O(4)-C(5)	1.414(10)	C(12)-O(13)-K(1)	111.5(6)
C(5)-C(6)	1.485(13)	O(13)-C(14)-C(15)	124.6(9)
C(6)-O(7)	1.390(11)	O(13)-C(14)-C(19)	115.1(8)
O(7)-C(8)	1.430(15)	C(15)-C(14)-C(19)	120.3(10)
C(8)-C(9)	1.41(2)	O(13)-C(14)-K(1)	50.9(4)
C(9)-O(10)	1.38(2)	C(15)-C(14)-K(1)	136.5(6)
O(10)-C(11)	1.394(13)	C(19)-C(14)-K(1)	81.6(5)
C(11)-C(12)	1.469(15)	C(14)-C(15)-C(16)	118.9(10)
C(12)-O(13)	1.408(10)	C(15)-C(16)-C(17)	120.1(9)
C(16)-C(17)	1.394(15)	C(18)-C(17)-C(16)	120.5(10)
C(17)-C(18)	1.372(12)	O(1)-C(19)-C(18)	126.1(7)
C(18)-C(19)	1.367(11)	O(1)-C(19)-C(14)	113.0(8)
I(1)^1-Au(1)-I(1)	180	C(18)-C(19)-C(14)	120.9(8)
O(7)-K(1)-O(7)^2	85.1(3)	O(13)-C(14)	1.367(11)
O(7)-K(1)-O(10)^2	80.6(2)	C(14)-C(15)	1.379(13)
O(7)^2-K(1)-O(10)^2	60.5(2)	C(14)-C(19)	1.386(11)
O(7)-K(1)-O(10)	60.5(2)	C(15)-C(16)	1.383(14)
O(7)^2-K(1)-O(10)	80.6(2)	O(13)^2 -K(1)-O(1)^2	50.46(15)
O(10)^2-K(1)-O(10)	127.2(4)	O(4)^2-K(1)-O(1)^2	54.67(14)
O(7)-K(1)-O(13)	93.1(2)	O(4)-K(1)-O(1)^2	123.9(2)
O(7)^2-K(1)-O(13)	130.9(2)	O(7)-K(1)-O(1)	89.7(2)
O(10)^2-K(1)-O(13)	166.8(2)	O(7)^2-K(1)-O(1)	174.6(2)
O(10)-K(1)-O(13)	56.9(2)	O(10)^2-K(1)-O(1)	117.5(2)
O(7)-K(1)-O(13)^2	130.9(2)	O(10)-K(1)-O(1)	97.8(2)

Table 73. (cont.)
Bond lengths [Å] and angles [°] for
[K(benzo-15-crown-5)$_2$](AuI$_2$) **(XIII)**

O(7)"-K(1)-O(13)^2	93.1(2)	O(13)-K(1)-O(1)	50.46(15)
O(10)^2-K(1)-O(13)^2	56.9(2)	O(13)^2-K(1)-O(1)	89.5(2)
O(10)-K(1)-O(13)^2	166.8(2)	O(4)^2-K(1)-O(1)	123.9(2)
O(13)-K(1)-O(13)^2	122.6(3)	O(4)-K(1)-O(1)	54.67(14)
O(7)-K(1)-O(4)^2	121.2(2)	O(1-K(1)-O(1)	95.5(2)
O(7)^2-K(1)-O(4)^2	60.3(2)	O(7)-K(1)-C(14)	109.4(2)
O(10)^2-K(1)-O(4)^2	113.3(2)	O(7)^2-K(1)-C(14)	143.4(2)
O(10)-K(1)-O(4)^2	67.6(2)	O(10)^2-K(1)-C(14)	152.6(2)
O(13)-K(1)-O(4)^2	79.91(15)	O(10)-K(1)-C(14)	78.2(2)
O(13)^2-K(1)-O(4)^2	99.22(15)	O(13)-K(1)-C(14)	21.7(2)
O(7)-K(1)-O(4)	60.3(2)	O(13)^2-K(1)-C(14)	100.9(2)
O(7)^2-K(1)-O(4)	121.2(2)	O(4)^2-K(1)-C(14)	84.0(2)
O(10)^2-K(1)-O(4)	67.6(2)	O(4)-K(1)-C(14)	94.6(2)
O(10)-K(1)-O(4)	113.3(2)	O(1)^2-K(1)-C(14)	74.4(2)
O(13)-K(1)-O(4)	99.22(15)	O(1)-K(1)-C(14)	40.1(2)
O(13v-K(1)-O(4)	79.91(15)	O(7)-K(1)-C(14)^2	143.4(2)
O(4)^2-K(1)-O(4)	178.2(2)	O(7)^2-K(1)-C(14)^2	109.4(2)
O(7)-K(1)-O(1)^2	174.6(2)	O(4)^2-K(1)-C(14)^2	94.6(2)
O(7)^2-K(1)-O(1)^2	89.7(2)	O(4)-K(1)-C(14)^2	84.0(2)
O(10)^2-K(1)-O(1)^2	97.8(2)	O(1)^2-K(1)-C(14)^2	40.1(2)
O(10)-K(1)-O(1)	117.5(2)	O(1)-K(1)-C(14)^2	74.4(2)
O(13)-K(1)-O(1)^2	89.5(2)	C(14)-K(1)-C(14)^2	79.4(3)
O(10)^2-K(1)-C(14)^2	78.2(2)	C(19)-O(1)-C(2)	117.3(6)
O(10)-K(1)-C(14)^2	152.6(2)	C(19)-O(1)-K(1)	105.5(4)
O(13)-K(1)-C(14)^2	100.9(2)	C(2)-O(1)-K(1)	114.9(4)
O(13)^2-K(1)-C(14)^2	21.7(2)	O(1)-C(2)-C(3)	105.3(6)

Symmetry transformations used to generate equivalent atoms:
1= -x+1/2,-y+1/2,-z 2= -x+1,y,-z+1/2

Table 74.
Anisotropic displacement parameters ($Å^2 \times 10^3$) for $[K(\text{benzo-15-crown-5})_2](AuI_2)$ **(XIII)**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au(1)	72(1)	56(1)	68(1)	7(1)	26(1)	4(1)
I(1)	91(1)	61(1)	116(1)	5(1)	29(1)	-8(1)
K(1)	61(1)	55(1)	60(1)	0	35(1)	0
O(1)	43(3)	53(3)	81(4)	2(3)	16(3)	-4(2)
C(2)	51(5)	66(5)	62(5)	11(4)	16(4)	2(4)
C(3)	50(5)	89(7)	62(5)	4(5)	17(4)	-8(4)
O(4)	72(3)	77(4)	55(3)	-5(3)	30(3)	-23(3)
C(5)	107(8)	70(6)	69(6)	-15(5)	37(6)	-49(6)
C(6)	134(9)	60(6)	101(8)	-25(6)	71(8)	-34(6)
O(7)	111(5)	75(5)	118(6)	-34(4)	53(5)	6(4)
C(8)	230(2)	122(12)	161(15)	-50(11)	90(15)	48(12)
C(9)	177(15)	126(13)	174(15)	19(12)	101(13)	94(12)
O(10)	111(5)	102(6)	106(5)	15(4)	68(5)	49(4)
C(11)	84(7)	179(14)	98(8)	20(9)	59(7)	55(8)
C(12)	42(5)	192(14)	87(7)	28(8)	31(5)	26(7)
O(13)	39(3)	103(5)	89(4)	29(4)	18(3)	1(3)
C(14)	63(6)	85(7)	65(5)	8(5)	31(5)	-12(5)
C(15)	67(6)	148(11)	56(5)	-5(6)	33(5)	-36(7)
C(16)	106(9)	114(9)	74(7)	-39(7)	54(7)	-57(8)
C(17)	128(10)	71(7)	101(7)	-28(6)	83(8)	-32(6)
C(18)	79(6)	52(5)	74(5)	1(4)	38(5)	-9(5)
C(19)	52(4)	72(6)	47(4)	7(4)	27(4)	-7(4)

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 75.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [K(benzo-15-crown-5)$_2$](AuI$_2$) (XIII)

atom	x	y	z	U(eq)
H(2A)	3846	405	-158	80
H(2B)	3655	152	700	80
H(3A)	3843	-1359	-467	80
H(3B)	3038	-1021	-588	80
H(5A)	3055	-2845	-374	80
H(5B)	3373	-3218	693	80
H(6A)	4343	-2844	-128	80
H(6B)	4051	-3941	-78	80
H(8A)	5329	-4492	897	80
H(9A)	6516	-4103	2043	80
H(9B)	5935	-4137	2474	80
H(11A)	6615	-2265	1503	80
H(11B)	7283	-2551	2504	80
H(12A)	7172	-795	2360	80
H(12B)	6958	-1152	3173	80
H(15A)	6966	798	2906	80
H(16A)	6572	2516	2783	80
H(17A)	5301	2967	1731	80
H(18A)	4403	1697	868	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

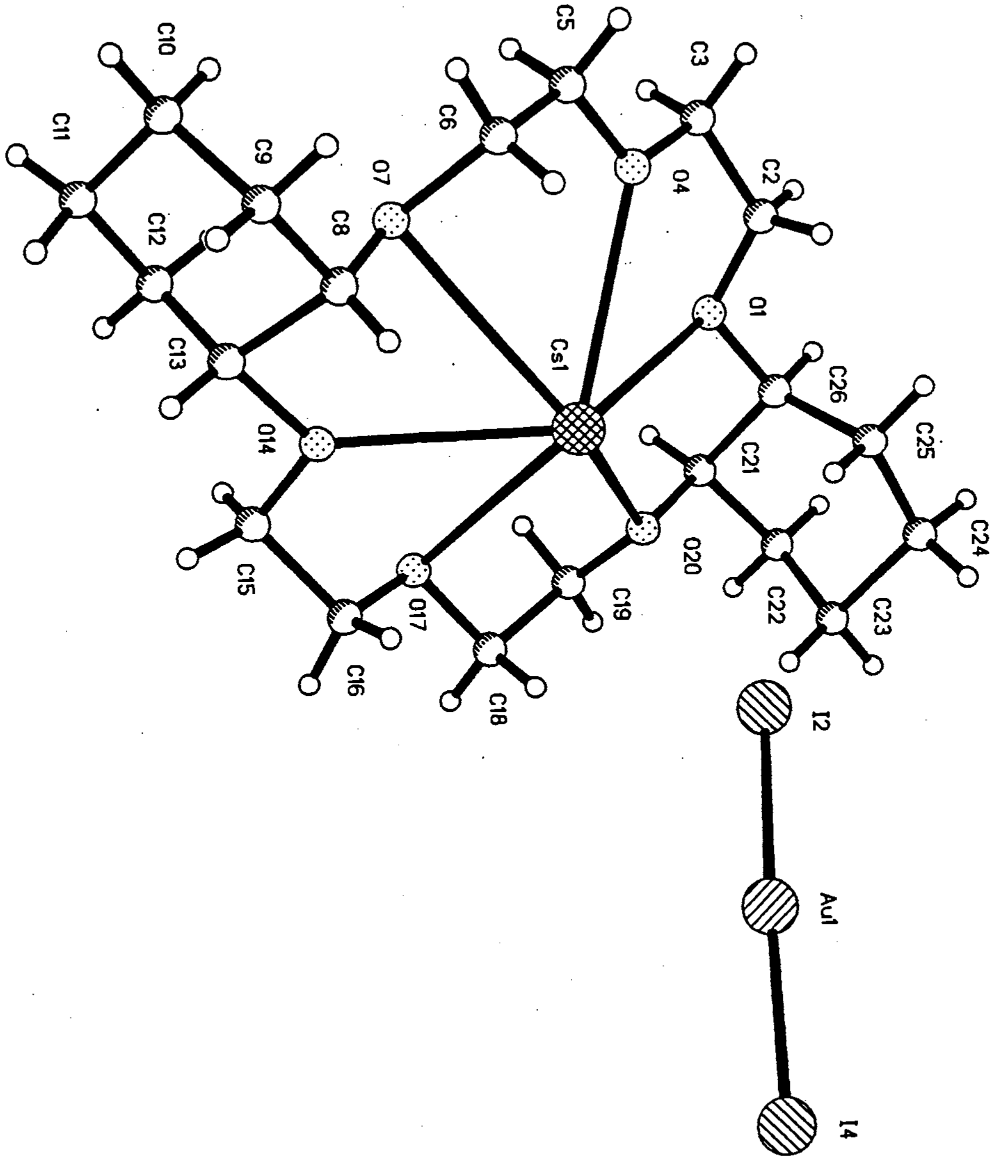


Figure 32. Projection View of [Cs(dicyclohexano-18-crown-6)](AuI_2) **(XIV)**

Table 76.
Crystal data and structure refinement for
[Cs(dicyclohexano-18-crown-6)](AuI_2) (**XIV**)

Empirical formula	$C_{20}\ H_{36}\ Au\ Cs\ I_2\ O_6$	
Formula weight	956.17	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Orthorhombic, $P2_12_12_1$	
Unit cell dimensions	a = 8.486(2) Å	$\alpha = 90^\circ$
	b = 14.258(2) Å	$\beta = 90^\circ$
	c = 22.716(4) Å	$\gamma = 90^\circ$
Volume	2748.5(9) $Å^3$	
Z, Calculated density	4, 2.311 Mg/m^3	
Absorption coefficient	8.934 mm^{-1}	
F(000)	1776	
Theta range for data collection	1.79 to 30.00 °	
Index ranges	$-1 \leq h \leq 11, -20 \leq k \leq 1, -1 \leq l \leq 31$	
Reflections collected / unique	5569 / 5325 [R(int) = 0.1162]	
Completeness to $2\theta = 30.00^\circ$	99.9%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5325 / 0 / 272	
Goodness-of-fit on F^2	0.969	
Final R indices [$I>2\sigma(I)$]	R1 = 0.1258, wR2 = 0.1723	
R indices (all data)	R1 = 0.3795, wR2 = 0.2551	
Absolute structure parameter	0.34(4)	
Extinction coefficient	0.0000(1)	
Largest diff. peak and hole	1.237 and -1.284 e. $Å^{-3}$	

Table 77.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [Cs(dicyclohexano-18-crown-6)](AuI_2) **(XIV)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Au(1)	9830(3)	1754(1)	1801(1)	54(1)
Cs(1)	8270(4)	5630(2)	997(1)	46(1)
I(2)	9950(6)	3153(2)	1126(2)	85(1)
I(4)	9795(7)	305(2)	2437(2)	74(1)
O(1)	9710(4)	637(2)	-184(12)	43(9)
C(2)	10810(7)	7020(3)	-70(2)	70(2)
C(3)	10410(9)	7890(3)	240(2)	90(3)
O(4)	9680(4)	7560(2)	781(13)	71(13)
C(5)	9330(6)	8230(3)	122(2)	90(2)
C(6)	8660(7)	7880(3)	176(2)	100(2)
O(7)	6860(4)	7500(2)	1600(15)	48(10)
C(8)	6340(14)	7060(5)	2000(3)	360(9)
C(9)	6020(5)	7700(4)	2520(2)	80(2)
C(10)	4880(5)	8560(4)	2370(2)	110(3)
C(11)	3280(8)	8170(4)	2170(2)	160(4)
C(12)	3500(8)	7490(4)	1650(2)	100(3)
C(13)	4490(6)	6760(5)	1940(3)	90(3)
O(14)	5050(4)	5970(2)	1480(15)	62(10)
C(15)	3740(5)	5460(4)	1330(3)	90(2)
C(16)	4440(5)	4560(3)	1040(2)	70(2)
O(17)	5110(5)	4790(2)	499(15)	66(11)
C(18)	5670(6)	4000(3)	150(2)	60(2)
C(19)	6620(9)	4370(5)	-400(2)	140(3)
O(20)	8020(5)	4710(2)	-216(15)	70(14)
C(21)	8680(6)	5090(3)	-800(2)	80(2)
C(22)	9340(7)	4280(3)	-122(2)	80(2)
C(23)	10080(7)	3550(3)	-880(2)	100(2)
C(24)	11690(5)	4120(3)	-640(2)	70(2)
C(25)	11530(8)	5000(3)	-300(2)	90(3)
C(26)	10190(6)	5620(4)	-569(15)	80(2)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 78.
Bond lengths [Å] and angles [^{O}] for [Cs(dicyclohexano-18-crown-6)](AuI$_2$) (**XIV**)

Au(1)-I(2)	2.516(4)	C(12)-C(13)-O(14)	112(4)
Au(1)-I(4)	2.523(4)	C(12)-C(13)-C(8)	113(5)
Cs(1)-O(14)	2.98(3)	O(14)-C(13)-C(8)	88(4)
Cs(1)-O(4)	3.04(2)	C(15)-O(14)-C(13)	107(3)
Cs(1)-O(20)	3.06(3)	C(15)-O(14)-Cs(1)	124(3)
Cs(1)-O(1)	3.13(3)	C(13)-O(14)-Cs(1)	129(3)
Cs(1)-O(17)	3.15(4)	O(14)-C(15)-C(16)	104(4)
Cs(1)-O(7)	3.22(3)	O(17)-C(16)-C(15)	109(4)
Cs(1)-C(8)	3.47(4)	O(17)-C(16)-Cs(1)	60(2)
Cs(1)-C(16)	3.59(4)	C(15)-C(16)-Cs(1)	90(2)
Cs(1)-C(6)	3.66(6)	C(16)-O(17)-C(18)	116(3)
Cs(1)-C(18)	3.75(4)	C(16)-O(17)-Cs(1)	97(2)
Cs(1)-C(2)	3.81(6)	C(18)-O(17)-Cs(1)	102(3)
Cs(1)-I(2)	3.820(4)	O(17)-C(18)-C(19)	110(4)
I(4)-Cs(1)^{1}	3.945(5)	O(17)-C(18)-Cs(1)	55(2)
O(1)-C(2)	1.34(5)	C(19)-C(18)-Cs(1)	84(3)
O(1)-C(26)	1.45(4)	O(20)-C(19)-C(18)	109(4)
C(2)-C(3)	1.46(5)	O(20)-C(19)-Cs(1)	43(3)
C(3)-O(4)	1.46(5)	C(18)-C(19)-Cs(1)	73(2)
O(4)-C(5)	1.42(5)	C(19)-O(20)-C(21)	100(3)
C(5)-C(6)	1.42(6)	C(19)-O(20)-Cs(1)	120(4)
C(6)-O(7)	1.66(6)	C(21)-O(20)-Cs(1)	127(2)
O(7)-C(8)	1.19(9)	O(20)-C(21)-C(26)	100(3)
C(8)-C(9)	1.52(7)	O(20)-C(21)-C(22)	112(4)
C(8)-C(13)	1.64(14)	C(26)-C(21)-C(22)	105(4)
C(9)-C(10)	1.60(7)	C(23)-C(22)-C(21)	111(4)
C(10)-C(11)	1.53(9)	C(22)-C(23)-C(24)	100(3)
C(11)-C(12)	1.55(6)	C(25)-C(24)-C(23)	120(5)
C(12)-C(13)	1.49(6)	C(24)-C(25)-C(26)	110(4)
C(13)-O(14)	1.59(7)	O(1)-C(26)-C(25)	113(3)
O(14)-C(15)	1.37(5)	O(1)-C(26)-C(21)	109(4)
C(15)-C(16)	1.56(6)	C(25)-C(26)-C(21)	118(4)
C(16)-O(17)	1.39(6)	O(1)-C(26)-Cs(1)	48(2)
O(17)-C(18)	1.46(5)	C(25)-C(26)-Cs(1)	87(3)
C(18)-C(19)	1.57(7)	C(21)-C(26)-Cs(1)	88(3)
C(19)-O(20)	1.35(7)	O(14)-Cs(1)-O(17)	54.2(10)
O(20)-C(21)	1.55(6)	O(4)-Cs(1)-O(17)	128.5(9)
C(21)-C(26)	1.57(7)	O(20)-Cs(1)-O(17)	56.9(11)
C(21)-C(22)	1.60(6)	O(1)-Cs(1)-O(17)	98.9(8)
C(22)-C(23)	1.44(6)	O(14)-Cs(1)-O(7)	50.9(9)

Table 78. (cont.)
Bond lengths [Å] and angles [°] for [Cs(dicyclohexano-18-crown-6)](AuI_2) (**XIV**)

C(23)-C(24)	1.69(5)	O(4)-Cs(1)-O(7)	57.8(9)
C(24)-C(25)	1.48(6)	O(20)-Cs(1)-O(7)	135.3(9)
C(25)-C(26)	1.56(6)	O(1)-Cs(1)-O(7)	103.3(8)
I(2)-Au(1)-I(4)	177.0(2)	O(17)-Cs(1)-O(7)	98.7(9)
O(14)-Cs(1)-O(4)	105.7(10)	O(14)-Cs(1)-C(8)	40(2)
O(14)-Cs(1)-O(20)	109.7(11)	O(4)-Cs(1)-C(8)	76(2)
O(4)-Cs(1)-O(20)	105.7(9)	O(20)-Cs(1)-C(8)	144(2)
O(14)-Cs(1)-O(1)	128.1(9)	O(1)-Cs(1)-C(8)	123.3(15)
O(4)-Cs(1)-O(1)	53.3(7)	O(17)-Cs(1)-C(8)	93(2)
O(20)-Cs(1)-O(1)	53.2(9)	O(7)-Cs(1)-C(8)	20.1(14)
O(14)-Cs(1)-C(16)	39.8(11)	O(4)-C(3)-C(2)	103(4)
O(4)-Cs(1)-C(16)	138.2(11)	C(5)-O(4)-C(3)	118(3)
O(20)-Cs(1)-C(16)	77.2(12)	C(5)-O(4)-Cs(1)	114(3)
O(1)-Cs(1)-C(16)	121.3(10)	C(3)-O(4)-Cs(1)	127(2)
O(17)-Cs(1)-C(16)	22.6(9)	O(4)-C(5)-C(6)	117(4)
O(7)-Cs(1)-C(16)	90.2(11)	O(4)-C(5)-Cs(1)	46(2)
C(8)-Cs(1)-C(16)	79(2)	C(6)-C(5)-Cs(1)	72(3)
O(14)-Cs(1)-C(6)	76.4(11)	C(5)-C(6)-O(7)	108(4)
O(4)-Cs(1)-C(6)	41.1(7)	C(5)-C(6)-Cs(1)	87(3)
O(20)-Cs(1)-C(6)	143.8(8)	O(7)-C(6)-Cs(1)	62(2)
O(1)-Cs(1)-C(6)	94.1(6)	C(8)-O(7)-C(6)	111(7)
O(17)-Cs(1)-C(6)	125.5(11)	C(8)-O(7)-Cs(1)	92(2)
O(7)-Cs(1)-C(6)	26.9(10)	C(6)-O(7)-Cs(1)	91(2)
C(8)-Cs(1)-C(6)	38(2)	O(7)-C(8)-C(9)	111(7)
C(16)-Cs(1)-C(6)	116.2(12)	O(7)-C(8)-C(13)	115(7)
O(14)-Cs(1)-C(18)	75.7(11)	C(9)-C(8)-C(13)	93(6)
O(4)-Cs(1)-C(18)	135.4(9)	O(7)-C(8)-Cs(1)	68(2)
O(20)-Cs(1)-C(18)	39.4(11)	C(9)-C(8)-Cs(1)	162(7)
O(1)-Cs(1)-C(18)	89.9(9)	C(13)-C(8)-Cs(1)	104(5)
O(17)-Cs(1)-C(18)	22.4(10)	C(8)-C(9)-C(10)	113(4)
O(7)-Cs(1)-C(18)	120.9(10)	C(11)-C(10)-C(9)	109(4)
C(8)-Cs(1)-C(18)	115(2)	C(10)-C(11)-C(12)	110(4)
C(16)-Cs(1)-C(18)	38.4(11)	C(13)-C(12)-C(11)	100(5)
C(6)-Cs(1)-C(18)	147.3(12)	O(4)-Cs(1)-C(2)	37.1(8)
O(14)-Cs(1)-C(2)	131.8(10)	O(20)-Cs(1)-C(2)	71.9(10)
Au(1)-I(2)-Cs(1)	139.9(2)	O(1)-Cs(1)-C(2)	19.2(8)
Au(1)-I(4)-Cs(1)^{1}	114.56(13)	O(17)-Cs(1)-C(2)	116.8(10)
C(2)-O(1)-C(26)	116(4)	O(7)-Cs(1)-C(2)	92.9(9)
C(2)-O(1)-Cs(1)	110(3)	C(8)-Cs(1)-C(2)	112(2)
C(26)-O(1)-Cs(1)	112(3)	C(16)-Cs(1)-C(2)	138.6(11)
O(1)-C(2)-C(3)	121(5)	C(6)-Cs(1)-C(2)	78.0(8)
O(1)-C(2)-Cs(1)	51(2)	C(18)-Cs(1)-C(2)	109.2(10)

Table 78.

Bond lengths [Å] and angles [^{O}] for [Cs(dicyclohexano-18-crown-6)](AuI_2) **(XIV)**

C(3)-C(2)-Cs(1)	90(3)	O(14)-Cs(1)-I(2)	117.7(6)
O(20)-Cs(1)-I(2)	72.5(6)	O(4)-Cs(1)-I(2)	134.6(7)
O(1)-Cs(1)-I(2)	103.4(6)	C(16)-Cs(1)-I(2)	86.8(8)
O(17)-Cs(1)-I(2)	89.6(6)	C(6)-Cs(1)-I(2)	137.9(8)
O(7)-Cs(1)-I(2)	150.4(6)	C(18)-Cs(1)-I(2)	71.7(7)
C(8)-Cs(1)-I(2)	131.9(10)	C(2)-Cs(1)-I(2)	108.7(7)

Symmetry transformations used to generate equivalent atoms:
1= -x+2,y-1/2,-z+1/2

Table 79.
Anisotropic displacement parameters ($Å^2$ x 10^3) for [Cs(dicyclohexano-18-crown-6)](AuI_2) **(XIV)**

atom	U11	U22	U33	U23	U13	U12
Au(1)	52(2)	54(1)	55(1)	-10(1)	-2(2)	-4(2)
Cs(1)	50(2)	44(2)	44(2)	-2(2)	2(2)	-1(2)
I(2)	111(4)	53(2)	92(3)	8(2)	-1(4)	11(4)
I(4)	103(4)	59(2)	61(2)	-3(2)	-2(3)	-17(3)
O(1)	50(2)	50 (2)	30(2)	0(15)	0(2)	-40(2)
C(2)	70(5)	110(5)	40(3)	-40(4)	10(3)	10(4)
C(3)	190(8)	70(3)	0(2)	10(2)	-40(4)	40(5)
O(4)	80(3)	70(2)	60(2)	-30(2)	0(2)	-100(2)
C(5)	120(5)	60(3)	90(4)	-20(3)	-130(4)	50(4)
C(6)	130(5)	120(4)	60(3)	130(3)	80(4)	0(4)
O(7)	0(2)	80(3)	50(2)	20(2)	-5(19)	-10(2)
C(8)	800(2)	200(7)	80(5)	10(5)	100(8)	480(12)
C(9)	0(2)	180(6)	60(4)	120(4)	20(3)	40(3)
C(10)	40(3)	160(5)	120(4)	-120(4)	120(3)	-150(4)
C(11)	270(9)	90(5)	120(5)	0(4)	210(6)	100(6)
C(12)	120(6)	150(6)	20(3)	30(3)	-30(4)	110(5)
C(13)	40(4)	140(6)	80(5)	70(5)	-80(4)	-40(4)
O(14)	0(2)	100(3)	90(3)	10(2)	30(2)	10(2)
C(15)	0(3)	100(5)	170(7)	-10(5)	30(4)	0(4)
C(16)	30(4)	90(4)	100(5)	30(4)	-80(4)	-40(3)
O(17)	70(3)	50(2)	70(2)	20(2)	0(3)	-40(3)
C(18)	60(4)	20(2)	100(4)	10(3)	-40(4)	-60(3)
C(19)	230(9)	190(7)	0(2)	30(4)	-60(4)	-20(8)
O(20)	120(4)	40(2)	40(2)	4(18)	-80(3)	-10(2)
C(21)	70(4)	60(3)	100(5)	-30(3)	-100(4)	-30(3)
C(22)	130(6)	70(4)	30(3)	20(3)	20(4)	0(4)
C(23)	200(6)	50(3)	40(3)	-30(2)	-10(4)	-160(4)
C(24)	20(3)	30(3)	140(5)	-20(3)	-80(3)	-10(3)
C(25)	160(7)	60(3)	60(4)	20(3)	-70(5)	-100(4)
C(26)	80(4)	160(5)	0(19)	-60(3)	-10(3)	130(4)

The anisotropic displacement factor exponent takes the form:
$-2 \, pi^2 \, [\, h^2 \, a^2 \, {}^*U_{11} + \ldots + 2 \, h \, k \, a^* \, b^* \, U_{12} \,]$

Table 80.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [Cs(dicyclohexano-18-crown-6)](AuI_2) **(XIV)**

atom	x	y	z	U(eq)
H(2A)	11161	7214	-455	80
H(2B)	11684	6736	125	80
H(3A)	9673	8260	14	80
H(3B)	11308	8272	329	80
H(5A)	8578	8646	1051	80
H(5B)	10262	8587	1311	80
H(6A)	8528	8381	2035	80
H(6B)	9332	7412	1922	80
H(8A)	6953	6554	2162	80
H(9A)	7044	7982	2547	80
H(9B)	5731	7466	2904	80
H(10A)	5301	8880	2031	80
H(10B)	4683	9017	2668	80
H(11A)	2503	8648	2092	80
H(11B)	2908	7812	2502	80
H(12A)	4111	7759	1340	80
H(12B)	2496	7282	1506	80
H(13A)	3935	6485	2262	80
H(15A)	3136	5784	1031	80
H(15B)	3057	5308	1648	80
H(16A)	5242	4323	1296	80
H(16B)	3654	4081	984	80
H(18A)	4798	3620	14	80
H(18B)	6377	3620	374	80
H(19A)	6595	3970	-739	80
H(19B)	6069	4938	-495	80
H(21A)	7942	5507	-992	80
H(22A)	9957	4534	-1536	80
H(22B)	8435	3977	-1386	80
H(23A)	10380	3045	-1132	80
H(23B)	9482	3292	-553	80
H(24A)	12321	4315	-969	80
H(24B)	12313	3691	-410	80
H(25A)	12473	5354	-232	80
H(25B)	11103	4811	71	80
H(26A)	10701	5881	-906	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

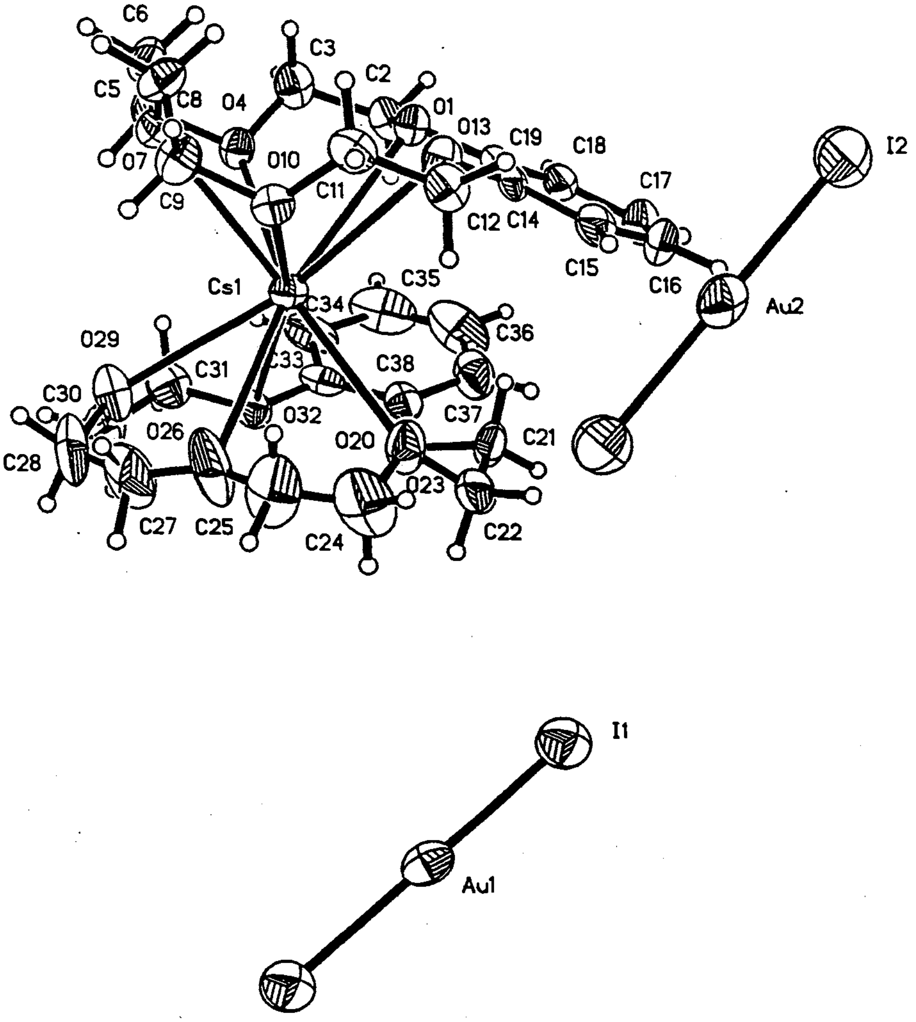


Figure 33. Projection View of [Cs(benzo-15-crown-5)$_2$](AuI$_2$)$_2$ **(XV)**

Table 81.
Crystal data and structure refinement for $[Cs(benzo\text{-}15\text{-}crown\text{-}5)_2](AuI_2)$ **(XV)**

Empirical formula	$C_{28} H_{40} Au I_2 Cs O_{10}$
Formula weight	1120.28
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 11.931(2) Å α = 96.38° b = 13.076(4) Å β = 116.07° c = 13.321(4) Å γ = 103.43°
Volume	1760.8(8) $Å^3$
Z, Calculated density	2, 2.113 Mg/m^3
Absorption coefficient	6.998 mm^{-1}
F(000)	1056.0
Theta range for data collection	1.75 to 30.00 deg.
Index ranges	$-16 \leq h \leq 1$, $-17 \leq k \leq 17$, $-17 \leq l \leq 18$
Reflections collected / unique	11534 / 10166 [R(int) = 0.0500]
Completeness to 2θ = 30.00	98.9%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10166 / 0 / 383
Goodness-of-fit on F^2	0.994
Final R indices [I>2σ(I)]	$R_1 = 0.0769$, $wR_2 = 0.1149$
R indices (all data)	$R_1 = 0.2131$, $wR_2 = 0.1527$
Extinction coefficient	0.00018(10)
Largest diff. peak and hole	0.715 and -0.640 e.$Å^{-3}$

Table 82.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [Cs(benzo-15-crown-5)$_2$](AuI$_2$) **(XV)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Au(1)	0	0	5000	68(1)
Au(2)	0	-5000	0	82(1)
I(1)	-571(1)	-1945(1)	4007(1)	99(1)
I(2)	-379(1)	-6790(1)	-1208(1)	111(1)
Cs(1)	-4345(1)	-1913(1)	-2482(1)	52(1)
O(1)	-5658(6)	-4202(5)	-4332(5)	48(2)
C(2)	-7019(9)	-4337(7)	-4908(9)	55(3)
C(3)	-7208(11)	-3520(8)	-5611(9)	70(3)
O(4)	-6591(7)	-2468(5)	-4889(6)	55(2)
C(5)	-6378(12)	-1652(9)	-5467(10)	72(4)
C(6)	-5153(12)	-1543(9)	-5582(9)	72(4)
O(7)	-4034(7)	-1131(5)	-4471(6)	56(2)
C(8)	-2883(11)	-1126(9)	-4538(9)	69(3)
C(9)	-1739(11)	-734(9)	-3326(10)	68(3)
O(10)	-1776(6)	-1492(5)	-2636(5)	54(2)
C(11)	-1282(10)	-2346(8)	-2808(9)	60(3)
C(12)	-1773(10)	-3246(8)	-2360(9)	61(3)
O(13)	-3159(7)	-3688(5)	-3100(6)	56(2)
C(14)	-3864(10)	-4520(7)	-2875(8)	42(2)
C(15)	-3349(12)	-5066(9)	-2049(9)	66(3)
C(16)	-4130(14)	-5922(10)	-1917(10)	74(4)
C(17)	-5451(14)	-6208(9)	-2567(10)	73(4)
C(18)	-6001(11)	-5665(8)	-3401(9)	55(3)
C(19)	-5204(10)	-4813(7)	-3558(8)	45(2)
O(20)	-5415(8)	-2758(6)	-712(6)	68(2)
C(21)	-4628(12)	-3455(9)	-323(10)	70(3)
C(22)	-3295(14)	-2761(10)	481(11)	84(4)
O(23)	-2762(8)	-2095(6)	-61(7)	81(3)
C(24)	-1657(14)	-1207(12)	697(14)	133(7)
C(25)	-1531(15)	-330(13)	338(14)	140(8)
O(26)	-2489(10)	8(7)	-313(11)	132(5)
C(27)	-264(2)	826(12)	-491(14)	150(9)
C(28)	-365(2)	1127(11)	-1180(2)	123(7)
O(29)	-4801(10)	276(6)	-2012(8)	89(3)
C(30)	-593(2)	305(11)	-1973(12)	93(5)
C(31)	-6923(12)	-751(10)	-2525(11)	78(4)
O(32)	-6489(7)	-1500(6)	-1877(6)	59(2)

Table 82. (cont.)

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($\AA^2$x 10^3) for [Cs(benzo-15-crown-5)$_2$](AuI$_2$) **(XV)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
C(33)	-7243(12)	-2564(10)	-2209(9)	63(3)
C(34)	-8508(13)	-2939(12)	-3143(11)	84(4)
C(35)	-920(2)	-4036(15)	-3386(15)	115(6)
C(36)	-865(2)	-4665(14)	-279(2)	127(7)
C(37)	-739(2)	-4305(10)	-1850(14)	92(4)
C(38)	-6677(12)	-3223(9)	-1569(10)	57(3)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 83.
Bond lengths [A] and angles [deg] for [Cs(benzo-15-crown-5)$_2$](AuI$_2$) **(XV)**

Au(1)-I(1)	2.5176(12)	O(23)-C(24)	1.402(13)
Au(1)-I(1)^{1}	2.5176(12)	C(24)-C(25)	1.29(2)
Au(2)-I(2)	2.5115(12)	C(25)-O(26)	1.31(2)
Au(2)-I(2)^{2}	2.5115(12)	O(26)-C(27)	1.158(15)
Cs(1)-O(4)	3.003(6)	C(27)-C(28)	1.34(2)
Cs(1)-O(23)	3.008(8)	C(28)-O(29)	1.42(2)
Cs(1)-O(7)	3.081(7)	O(29)-C(30)	1.378(15)
Cs(1)-O(29)	3.084(8)	C(30)-C(31)	1.450(15)
Cs(1)-O(10)	3.087(7)	C(31)-O(32)	1.415(12)
Cs(1)-O(26)	3.122(10)	O(32)-C(33)	1.369(12)
Cs(1)-O(32)	3.137(7)	C(33)-C(38)	1.361(14)
Cs(1)-O(13)	3.192(7)	C(33)-C(34)	1.392(15)
Cs(1)-O(1)	3.205(6)	C(34)-C(35)	1.40(2)
Cs(1)-O(20)	3.313(7)	C(35)-C(36)	1.30(2)
Cs(1)-C(33)	3.552(11)	C(36)-C(37)	1.39(2)
Cs(1)-C(14)	3.605(9)	C(37)-C(38)	1.383(15)
O(1)-C(19)	1.374(10)	I(1)-Au(1)-I(1)^{1}	180
O(1)-C(2)	1.414(10)	I(2)-Au(2)-I(2)^{2}	180
C(2)-C(3)	1.488(13)	O(4)-Cs(1)-O(23)	158.9(2)
C(3)-O(4)	1.405(11)	O(4)-Cs(1)-O(7)	57.2(2)
O(4)-C(5)	1.423(12)	O(23)-Cs(1)-O(7)	141.7(2)
C(5)-C(6)	1.51(2)	O(4)-Cs(1)-O(29)	89.3(2)
C(6)-O(7)	1.420(12)	O(23)-Cs(1)-O(29)	100.8(2)
O(7)-C(8)	1.412(12)	O(7)-Cs(1)-O(29)	84.0(2)
C(8)-C(9)	1.512(14)	O(4)-Cs(1)-O(10)	107.9(2)
C(9)-O(10)	1.432(11)	O(23)-Cs(1)-O(10)	86.6(2)
O(10)-C(11)	1.419(11)	O(7)-Cs(1)-O(10)	56.5(2)
C(11)-C(12)	1.492(13)	O(29)-Cs(1)-O(10)	108.7(2)
C(12)-O(13)	1.428(11)	O(4)-Cs(1)-O(26)	142.4(2)
O(13)-C(14)	1.360(11)	O(23)-Cs(1)-O(26)	53.7(3)
C(14)-C(15)	1.372(13)	O(7)-Cs(1)-O(26)	105.0(3)
C(14)-C(19)	1.375(12)	O(29)-Cs(1)-O(26)	54.2(3)
C(15)-C(16)	1.362(15)	O(10)-Cs(1)-O(26)	79.9(3)
C(16)-C(17)	1.35(2)	O(4)-Cs(1)-O(32)	81.5(2)
C(17)-C(18)	1.386(14)	O(23)-Cs(1)-O(32)	89.7(2)
C(18)-C(19)	1.386(13)	O(7)-Cs(1)-O(32)	121.3(2)
O(20)-C(38)	1.360(12)	O(29)-Cs(1)-O(32)	53.1(2)
O(20)-C(21)	1.435(12)	O(10)-Cs(1)-O(32)	160.3(2)
C(21)-C(22)	1.455(15)	O(26)-Cs(1)-O(32)	82.3(3)
C(22)-O(23)	1.403(14)	O(4)-Cs(1)-O(13)	93.3(2)
O(1)-Cs(1)-O(20)	95.8(2)	O(23)-Cs(1)-O(13)	83.1(2)

Table 83. (cont.)
Bond lengths [A] and angles [deg] for
[Cs(benzo-15-crown-5)$_2$](AuI$_2$) **(XV)**

O(4)-Cs(1)-C(33)	74.3(2)	C(24)-C(25)-O(26)	125.9(15)
O(23)-Cs(1)-C(33)	90.3(3)	C(24)-C(25)-Cs(1)	87.5(9)
O(7)-Cs(1)-C(33)	127.1(2)	O(26)-C(25)-Cs(1)	54.6(7)
O(29)-Cs(1)-C(33)	74.9(3)	C(27)-O(26)-C(25)	137.5(14)
O(10)-Cs(1)-C(33)	175.6(3)	C(27)-O(26)-Cs(1)	111.8(10)
O(26)-Cs(1)-C(33)	100.8(3)	C(25)-O(26)-Cs(1)	105.5(9)
O(32)-Cs(1)-C(33)	22.5(2)	O(26)-C(27)-C(28)	135.0(16)
O(13)-Cs(1)-C(33)	123.5(2)	O(26)-C(27)-Cs(1)	51.4(8)
O(1)-Cs(1)-C(33)	86.2(2)	C(28)-C(27)-Cs(1)	87.8(10)
O(20)-Cs(1)-C(33)	39.1(2)	C(27)-C(28)-O(29)	116.2(12)
O(4)-Cs(1)-C(14)	92.5(2)	C(27)-C(28)-Cs(1)	72.1(9)
O(23)-Cs(1)-C(14)	76.3(2)	O(29)-C(28)-Cs(1)	46.0(6)
O(7)-Cs(1)-C(14)	99.9(2)	C(30)-O(29)-C(28)	113.9(12)
O(29)-Cs(1)-C(14)	176.0(2)	C(30)-O(29)-Cs(1)	120.2(7)
O(10)-Cs(1)-C(14)	74.1(2)	C(28)-O(29)-Cs(1)	114.6(8)
O(26)-Cs(1)-C(14)	124.5(3)	O(29)-C(30)-C(31)	110.2(11)
O(32)-Cs(1)-C(14)	123.8(2)	O(32)-C(31)-C(30)	109.1(10)
O(13)-Cs(1)-C(14)	22.0(2)	O(32)-C(31)-Cs(1)	55.4(5)
O(1)-Cs(1)-C(14)	39.6(2)	C(30)-C(31)-Cs(1)	88.8(8)
O(20)-Cs(1)-C(14)	85.8(2)	C(33)-O(32)-C(31)	121.3(9)
C(33)-Cs(1)-C(14)	102.2(3)	C(33)-O(32)-Cs(1)	96.0(6)
C(19)-O(1)-C(2)	118.8(8)	C(31)-O(32)-Cs(1)	102.8(6)
C(19)-O(1)-Cs(1)	96.6(5)	O(32)-C(33)-C(38)	115.8(10)
C(2)-O(1)-Cs(1)	105.1(5)	O(32)-C(33)-C(34)	121.6(12)
O(1)-C(2)-C(3)	107.0(8)	C(38)-C(33)-C(34)	122.6(12)
O(1)-C(2)-Cs(1)	54.0(4)	O(32)-C(33)-Cs(1)	61.4(5)
C(3)-C(2)-Cs(1)	84.0(5)	C(38)-C(33)-Cs(1)	83.5(7)
C(3)-O(4)-C(5)	113.5(8)	C(34)-C(33)-Cs(1)	123.7(8)
C(3)-O(4)-Cs(1)	123.6(5)	C(33)-C(34)-C(35)	116.6(14)
C(5)-O(4)-Cs(1)	110.4(6)	C(36)-C(35)-C(34)	120(2)
O(4)-C(5)-C(6)	112.2(9)	C(35)-C(36)-C(37)	124(2)
O(4)-C(5)-Cs(1)	48.7(4)	C(36)-C(37)-C(38)	117.9(15)
C(6)-C(5)-Cs(1)	85.3(6)	O(20)-C(38)-C(33)	116.3(10)
O(4)-C(3)-C(2)	110.2(8)	O(20)-C(38)-C(37)	125.0(12)
O(7)-C(6)-C(5)	109.0(9)	C(33)-C(38)-C(37)	118.7(12)
C(8)-O(7)-C(6)	110.3(8)	O(20)-C(38)-Cs(1)	64.7(5)
C(8)-O(7)-Cs(1)	118.1(6)	C(33)-C(38)-Cs(1)	74.8(7)
C(6)-O(7)-Cs(1)	116.3(6)	C(37)-C(38)-Cs(1)	129.5(8)
O(7)-C(8)-C(9)	107.8(9)	O(7)-Cs(1)-O(13)	81.9(2)
O(10)-C(9)-C(8)	112.9(8)	O(29)-Cs(1)-O(13)	161.3(2)
O(10)-C(9)-Cs(1)	49.7(5)	O(10)-Cs(1)-O(13)	53.0(2)
C(8)-C(9)-Cs(1)	83.8(6)	O(26)-Cs(1)-O(13)	118.3(2)

Table 83. (cont.)
Bond lengths [A] and angles [deg] for
[Cs(benzo-15-crown-5)$_2$](AuI$_2$) **(XV)**

C(11)-O(10)-C(9)	114.4(8)	O(32)-Cs(1)-O(13)	145.6(2)
C(11)-O(10)-Cs(1)	121.8(5)	O(4)-Cs(1)-O(1)	53.2(2)
C(9)-O(10)-Cs(1)	109.6(6)	O(23)-Cs(1)-O(1)	112.5(2)
O(10)-C(11)-C(12)	108.5(9)	O(7)-Cs(1)-O(1)	81.3(2)
O(13)-C(12)-C(11)	106.9(8)	O(29)-Cs(1)-O(1)	141.7(2)
O(13)-C(12)-Cs(1)	53.8(5)	O(10)-Cs(1)-O(1)	92.0(2)
C(11)-C(12)-Cs(1)	86.7(6)	O(26)-Cs(1)-O(1)	164.0(2)
C(14)-O(13)-C(12)	119.2(8)	O(32)-Cs(1)-O(1)	107.2(2)
C(14)-O(13)-Cs(1)	96.3(5)	O(13)-Cs(1)-O(1)	47.2(2)
C(12)-O(13)-Cs(1)	105.0(5)	O(4)-Cs(1)-O(20)	110.4(2)
O(13)-C(14)-C(15)	125.7(10)	O(23)-Cs(1)-O(20)	51.7(2)
O(13)-C(14)-C(19)	114.9(8)	O(7)-Cs(1)-O(20)	166.3(2)
C(15)-C(14)-C(19)	119.4(10)	O(29)-Cs(1)-O(20)	90.2(2)
O(13)-C(14)-Cs(1)	61.7(4)	O(10)-Cs(1)-O(20)	137.3(2)
C(15)-C(14)-Cs(1)	127.8(7)	O(26)-Cs(1)-O(20)	81.4(3)
C(19)-C(14)-Cs(1)	80.1(5)	O(32)-Cs(1)-O(20)	46.7(2)
C(16)-C(15)-C(14)	121.6(11)	O(13)-Cs(1)-O(20)	106.1(2)
C(17)-C(16)-C(15)	119.6(11)	O(1)-C(19)-C(18)	124.6(9)
C(16)-C(17)-C(18)	120.0(11)	C(14)-C(19)-Cs(1)	78.0(5)
C(17)-C(18)-C(19)	120.4(11)	O(1)-C(19)-Cs(1)	61.3(4)
C(14)-C(19)-O(1)	116.4(8)	C(18)-C(19)-Cs(1)	129.6(6)
C(14)-C(19)-C(18)	118.9(9)	C(38)-O(20)-C(21)	117.6(9)
C(21)-O(20)-Cs(1)	97.5(6)	C(38)-O(20)-Cs(1)	93.5(6)
O(20)-C(21)-C(22)	107.0(9)	C(22)-O(23)-Cs(1)	123.3(7)
O(20)-C(21)-Cs(1)	60.4(5)	C(25)-C(24)-O(23)	116.2(14)
C(22)-C(21)-Cs(1)	86.1(7)	C(25)-C(24)-Cs(1)	72.9(9)
O(23)-C(22)-C(21)	111.5(10)	O(23)-C(24)-Cs(1)	43.8(6)
C(24)-O(23)-C(22)	114.4(11)	C(24)-O(23)-Cs(1)	117.3(8)

Symmetry transformations used to generate equivalent atoms:
1= -x,-y,-z+1   2= -x,-y-1,-z

Table 84.
Anisotropic displacement parameters (Å^2 x 10^3) for [Cs(benzo-15-crown-5)$_2$](AuI$_2$) **(XV)**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au(1)	54(1)	89(1)	58(1)	24(1)	31(1)	11(1)
Au(2)	60(1)	108(1)	70(1)	31(1)	15(1)	41(1)
I(1)	101(1)	93(1)	85(1)	13(1)	37(1)	19(1)
I(2)	101(1)	120(1)	86(1)	18(1)	16(1)	52(1)
Cs(1)	52(1)	57(1)	47(1)	10(1)	24(1)	19(1)
O(1)	33(4)	50(4)	49(4)	16(3)	10(3)	10(3)
C(2)	30(6)	46(6)	62(7)	3(5)	5(5)	9(5)
C(3)	53(7)	65(8)	67(8)	14(6)	7(6)	20(6)
O(4)	52(4)	54(4)	57(4)	19(4)	21(4)	18(4)
C(5)	70(9)	65(8)	58(7)	16(6)	7(7)	27(7)
C(6)	87(10)	57(7)	64(8)	24(6)	33(7)	11(7)
O(7)	54(5)	59(4)	49(4)	15(3)	23(4)	11(4)
C(8)	67(8)	85(9)	55(7)	24(6)	34(7)	13(7)
C(9)	57(7)	67(8)	82(8)	25(7)	39(7)	7(6)
O(10)	43(4)	62(5)	54(4)	11(4)	24(4)	12(4)
C(11)	47(7)	68(7)	70(7)	11(6)	34(6)	22(6)
C(12)	42(7)	66(7)	60(7)	11(6)	8(6)	23(6)
O(13)	47(4)	61(5)	60(4)	20(4)	23(4)	22(4)
C(14)	44(6)	40(6)	51(6)	14(5)	24(5)	27(5)
C(15)	67(8)	72(8)	62(7)	14(6)	24(6)	46(7)
C(16)	102(11)	68(8)	74(8)	42(7)	47(8)	43(8)
C(17)	91(10)	55(7)	81(9)	25(7)	45(8)	24(7)
C(18)	71(8)	40(6)	59(7)	9(5)	37(6)	14(6)
C(19)	54(7)	35(5)	45(6)	5(5)	23(5)	17(5)
O(20)	78(6)	62(5)	69(5)	22(4)	34(5)	29(5)
C(21)	93(10)	63(7)	76(8)	43(7)	49(8)	36(8)
C(22)	108(12)	72(9)	72(8)	16(7)	31(9)	53(9)
O(23)	72(6)	62(5)	77(6)	25(5)	8(5)	21(5)
C(24)	79(12)	97(12)	129(14)	-7(11)	-13(10)	7(10)
C(25)	79(12)	87(12)	127(14)	19(10)	-29(10)	-3(1)
O(26)	84(8)	42(6)	184(12)	13(7)	2(8)	7(6)
C(27)	160(2)	53(10)	120(14)	-14(10)	5(13)	-19(12)
C(28)	16(2)	59(10)	200(2)	69(12)	106(16)	58(12)
O(29)	95(7)	50(5)	123(8)	26(5)	52(6)	24(5)
C(30)	126(14)	89(11)	106(11)	48(9)	64(11)	79(11)

Table 84. (cont.)
Anisotropic displacement parameters (Å^2 x 10^3) for
[Cs(benzo-15-crown-5)$_2$](AuI$_2$) **(XV)**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(31)	77(10)	91(10)	89(9)	25(8)	46(8)	50(9)
O(32)	63(5)	58(5)	56(4)	12(4)	24(4)	27(4)
C(33)	68(9)	66(8)	55(7)	-8(6)	38(7)	16(7)
C(34)	58(8)	102(11)	87(10)	-11(8)	37(8)	29(8)
C(35)	53(10)	130(2)	117(14)	-28(12)	36(10)	-10(11)
C(36)	90(2)	86(13)	180(2)	-17(13)	79(15)	-9(11)
C(37)	119(13)	64(9)	133(13)	35(9)	93(12)	29(9)
C(38)	61(8)	56(7)	75(8)	17(6)	48(7)	22(7)

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 85. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[Cs(benzo\text{-}15\text{-}crown\text{-}5)_2](AuI_2)$ **(XV)**

atom	x	y	z	U(eq)
H(2A)	-7324	-4214	-4362	80
H(2B)	-7502	-5058	-5390	80
H(3A)	-8124	-3627	-6098	80
H(3B)	-6814	-3608	-5048	80
H(5B)	-7130	-1829	-6217	80
H(6A)	-5107	-1067	-6072	80
H(6B)	-5179	-2241	-5921	80
H(8A)	-2759	-647	-5003	80
H(8B)	-2958	-1840	-4884	80
H(9A)	-1731	-53	-2966	80
H(9B)	-935	-616	-3365	80
H(11A)	-339	-2092	-2420	80
H(11B)	-1594	-2611	-3615	80
H(12A)	-1601	-2956	-1594	80
H(12B)	-1348	-3790	-2336	80
H(15A)	-2416	-4842	-1552	80
H(16A)	-3747	-6317	-1360	80
H(17A)	-6004	-6787	-2447	80
H(18A)	-6937	-5876	-3874	80
H(21A)	-4618	-3861	-964	80
H(21B)	-4970	-3956	26	80
H(22A)	-2745	-3195	814	80
H(22B)	-3323	-2318	1089	80
H(24A)	-889	-1436	954	80
H(24B)	-1770	-1005	1353	80
H(25A)	-1171	-484	-158	80
H(25B)	-867	262	972	80
H(27A)	-1978	1093	-706	80
H(27B)	-2340	1295	246	80
H(28A)	-3377	1553	-1623	80
H(28B)	-3874	1582	-726	80
H(30A)	-6252	826	-2376	80
H(30B)	-5754	523	-1193	80
H(31A)	-7059	-989	-3290	80
H(31B)	-7743	-716	-2581	80
H(34A)	-8888	-2467	-3594	80
H(35A)	-10072	-4319	-4026	80
H(36A)	-9142	-5418	-2990	80
H(37A)	-7024	-4779	-1396	80

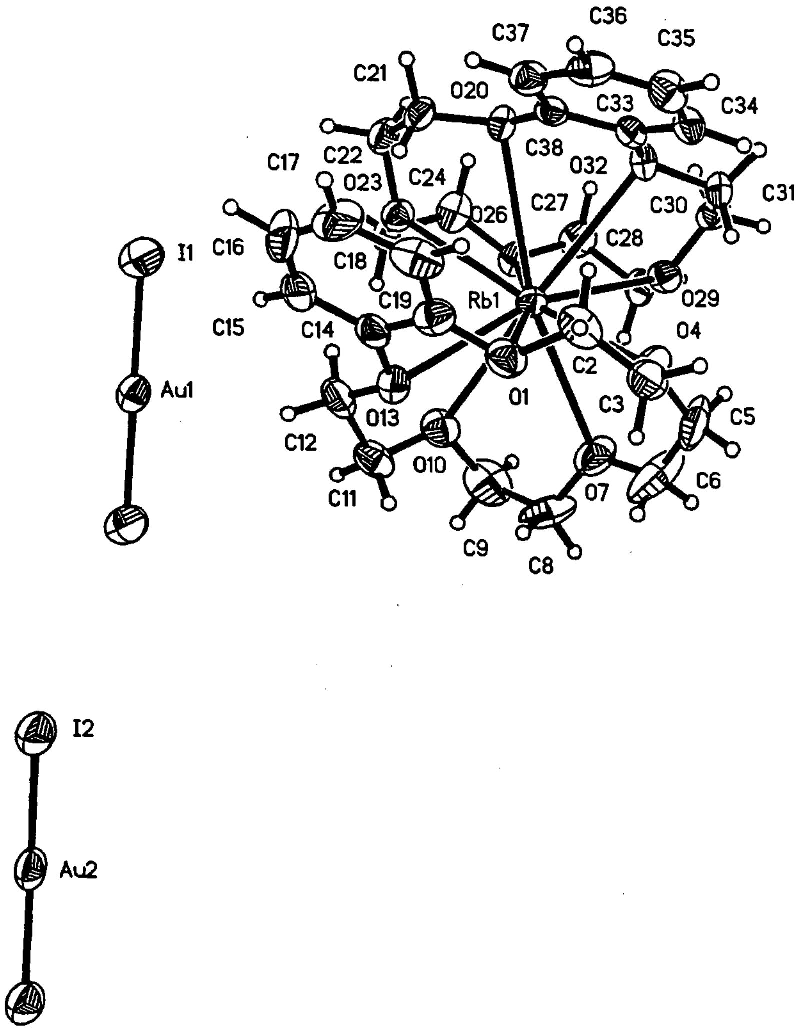


Figure 34. Projection View of [Rb(benzo-15-crown-5)$_2$](AuI$_2$)$_2$ **(XVI)**

Table 86.
Crystal data and structure refinement for
$[Rb(benzo\text{-}15\text{-}crown\text{-}5)_2](AuI_2)$ **(XVI)**

Empirical formula	$C_{28}H_{40}AuI_2O_{10}Rb$	
Formula weight	1072.84	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, $P\bar{1}$	
Unit cell dimensions	a = 11.838(2) Å	α = 97.79(2)°
	b = 13.020(3) Å	β = 115.36(1)°
	c = 13.164(3) Å	γ = 102.45(2)°
Volume	1729.6(6) $Å^3$	
Z, Calculated density	2, 2.060 Mg/m^3	
Absorption coefficient	7.485 mm^{-1}	
F(000)	1020	
Theta range for data collection	1.77 to 30.00°	
Index ranges	$-1 \leq h \leq 16, -17 \leq k \leq 17, -18 \leq l \leq 17$	
Reflections collected / unique	11332 / 9985 [R(int) = 0.0846]	
Completeness to 2θ =30.00°	98.9%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9985 / 0 / 383	
Goodness-of-fit on F^2	0.982	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0801, wR_2 = 0.1422	
R indices (all data)	R_1 = 0.2169, wR_2 = 0.1910	
Extinction coefficient	0.0056(3)	
Largest diff. peak and hole	1.268 and -0.609 e.$Å^{-3}$	

Table 88.
Bond lengths [A] and angles [deg] for [Rb(benzo-15-crown-5)$_2$](AuI$_2$) (**XVI**)

Au(1)-I(1)	2.5170(13)	C(22)-O(23)-C(24)	112.7(8)
Au(1)-I(1)^{1}	2.5170(13)	C(22)-O(23)-Rb(1)	124.1(6)
Au(2)-I(2)^{2}	2.5175(13)	C(24)-O(23)-Rb(1)	108.2(6)
Au(2)-I(2)	2.5175(13)	O(23)-C(24)-C(25)	111.4(9)
Rb(1)-O(4)	2.874(8)	O(23)-C(24)-Rb(1)	49.4(4)
Rb(1)-O(23)	2.891(7)	C(25)-C(24)-Rb(1)	82.5(6)
Rb(1)-O(7)	2.909(9)	O(26)-C(25)-C(24)	111.3(10)
Rb(1)-O(26)	2.913(7)	O(26)-C(25)-Rb(1)	45.3(5)
Rb(1)-O(10)	2.956(8)	C(24)-C(25)-Rb(1)	74.4(6)
Rb(1)-O(29)	2.976(7)	C(25)-O(26)-C(27)	113.5(8)
Rb(1)-O(13)	3.044(7)	C(25)-O(26)-Rb(1)	114.6(6)
Rb(1)-O(32)	3.065(7)	C(27)-O(26)-Rb(1)	117.6(6)
Rb(1)-O(20)	3.104(7)	O(26)-C(27)-C(28)	109.3(9)
Rb(1)-O(1)	3.240(8)	O(29)-C(28)-C(27)	114.2(9)
Rb(1)-C(14)	3.563(11)	O(29)-C(28)-Rb(1)	50.4(5)
Rb(1)-C(38)	3.586(10)	C(27)-C(28)-Rb(1)	82.8(6)
O(1)-C(19)	1.347(14)	C(30)-O(29)-C(28)	114.4(8)
O(1)-C(2)	1.411(13)	C(30)-O(29)-Rb(1)	121.0(6)
C(2)-C(3)	1.49(2)	C(28)-O(29)-Rb(1)	108.1(6)
C(3)-O(4)	1.393(15)	O(29)-C(30)-C(31)	109.7(9)
O(4)-C(5)	1.382(15)	O(32)-C(31)-C(30)	107.4(9)
C(5)-C(6)	1.32(2)	O(32)-C(31)-Rb(1)	51.2(5)
C(6)-O(7)	1.353(15)	C(30)-C(31)-Rb(1)	84.1(6)
O(7)-C(8)	1.367(15)	C(33)-O(32)-C(31)	119.0(8)
C(8)-C(9)	1.44(2)	C(33)-O(32)-Rb(1)	100.8(5)
C(9)-O(10)	1.41(2)	C(31)-O(32)-Rb(1)	107.7(6)
O(10)-C(11)	1.406(13)	C(34)-C(33)-O(32)	124.9(10)
C(11)-C(12)	1.51(2)	C(34)-C(33)-C(38)	122.1(11)
C(12)-O(13)	1.410(13)	O(32)-C(33)-C(38)	112.9(9)
O(13)-C(14)	1.345(13)	C(34)-C(33)-Rb(1)	130.7(7)
C(14)-C(19)	1.36(2)	O(32)-C(33)-Rb(1)	57.0(4)
C(14)-C(15)	1.38(2)	C(38)-C(33)-Rb(1)	78.6(6)
C(15)-C(16)	1.37(2)	C(33)-C(34)-C(35)	118.5(11)
C(16)-C(17)	1.32(2)	C(35)-C(36)-C(37)	120.9(12)
C(17)-C(18)	1.36(2)	C(38)-C(37)-C(36)	118.5(11)
C(18)-C(19)	1.43(2)	O(20)-C(38)-C(33)	117.2(9)
O(20)-C(38)	1.355(11)	O(20)-C(38)-C(37)	124.8(10)
O(20)-C(21)	1.409(11)	C(33)-C(38)-C(37)	118.0(10)
C(21)-C(22)	1.496(14)	O(20)-C(38)-Rb(1)	58.6(5)
C(22)-O(23)	1.401(12)	C(33)-C(38)-Rb(1)	79.0(6)
O(23)-C(24)	1.453(12)	C(37)-C(38)-Rb(1)	133.6(7)
C(24)-C(25)	1.48(2)	C(14)-O(13)-C(12)	118.2(10)

Table 87. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [Rb(benzo-15-crown-5)$_2$](AuI$_2$) **(XVI)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Au(1)	5000	5000	5000	69(1)
Au(2)	5000	0	0	82(1)
I(1)	5548(1)	6959(1)	6016(1)	101(1)
I(2)	5525(1)	1874(1)	1216(1)	105(1)
Rb(1)	-701(1)	6921(1)	2500(1)	50(1)
O(1)	331(9)	7721(6)	737(7)	74(2)
C(2)	-490(13)	8369(10)	302(11)	74(4)
C(3)	-1848(14)	7621(12)	-465(11)	81(4)
O(4)	-2304(8)	7104(7)	206(7)	77(2)
C(5)	-3403(14)	6200(12)	-393(15)	129(7)
C(6)	-324(2)	5229(13)	-395(14)	148(9)
O(7)	-2470(9)	5001(7)	597(8)	94(3)
C(8)	-206(2)	4103(10)	502(12)	102(5)
C(9)	-122(2)	3964(12)	162(2)	109(5)
O(10)	-71(9)	4849(6)	2324(8)	76(2)
C(11)	1013(13)	4759(10)	2172(11)	73(4)
C(12)	2018(13)	5875(11)	2679(11)	77(4)
O(13)	1475(7)	6553(6)	1985(6)	62(2)
C(14)	2224(12)	7582(10)	2233(10)	58(3)
C(15)	3501(13)	8001(12)	3108(13)	81(4)
C(16)	4167(15)	906(2)	326(2)	120(7)
C(17)	361(2)	9671(15)	260(2)	126(8)
C(18)	233(2)	9286(11)	1552(11)	68(3)
O(20)	660(6)	9204(5)	4251(6)	53(2)
C(21)	2180(11)	7450(6)	4772(6)	54(2)
C(24)	1323(11)	6616(9)	5351(10)	67(3)
C(25)	1008(7)	6145(6)	4368(6)	58(2)
C(27)	-2187(12)	6114(10)	4420(10)	71(3)
C(28)	-3301(10)	5779(10)	3219(11)	69(3)
O(29)	-3243(7)	6539(6)	2554(6)	57(2)
C(30)	-3697(10)	7407(9)	2770(10)	63(3)
C(31)	-3205(10)	8315(10)	2348(10)	64(3)
O(32)	-1824(7)	8710(6)	3040(6)	56(2)
C(33)	-1122(10)	9575(8)	2830(9)	50(3)
C(34)	-1660(12)	10114(9)	2022(10)	62(3)
C(35)	-838(14)	10971(10)	1920(11)	69(3)
C(36)	444(14)	11249(9)	2547(10)	69(3)
C(37)	1035(12)	10686(9)	3376(10)	62(3)
C(38)	228(10)	9825(8)	3508(9)	48(2)

Table 88. (cont.)
Bond lengths [A] and angles [deg] for [Rb(benzo-15-crown-5)$_2$](AuI$_2$) (**XVI**)

C(25)-O(26)	1.407(13)	C(14)-O(13)-Rb(1)	101.4(6)
C(27)-C(28)	1.486(15)	C(12)-O(13)-Rb(1)	105.9(6)
C(28)-O(29)	1.417(13)	O(13)-C(14)-C(19)	113.9(11)
O(29)-C(30)	1.398(12)	O(13)-C(14)-C(15)	123.5(12)
C(30)-C(31)	1.484(15)	C(19)-C(14)-C(15)	122.5(12)
C(31)-O(32)	1.415(12)	O(13)-C(14)-Rb(1)	56.8(5)
O(32)-C(33)	1.383(12)	C(19)-C(14)-Rb(1)	82.0(7)
C(33)-C(34)	1.358(14)	C(15)-C(14)-Rb(1)	128.0(8)
C(33)-C(38)	1.390(14)	C(16)-C(15)-C(14)	117.8(15)
C(34)-C(35)	1.38(2)	C(16)-C(17)-C(18)	121(2)
C(35)-C(36)	1.31(2)	C(17)-C(18)-C(19)	119(2)
C(36)-C(37)	1.415(15)	O(1)-C(19)-C(14)	118.4(11)
C(37)-C(38)	1.391(14)	O(1)-C(19)-C(18)	124.3(13)
I(1)-Au(1)-I(1)^1	180	C(14)-C(19)-C(18)	117.2(13)
I(2)^2-Au(2)-I(2)	180	O(1)-C(19)-Rb(1)	62.5(6)
O(4)-Rb(1)-O(23)	158.3(2)	C(14)-C(19)-Rb(1)	76.2(7)
O(4)-Rb(1)-O(7)	58.7(2)	C(18)-C(19)-Rb(1)	134.1(8)
O(23)-Rb(1)-O(7)	138.1(2)	C(38)-O(20)-C(21)	119.2(8)
O(4)-Rb(1)-O(26)	139.2(2)	C(38)-O(20)-Rb(1)	99.5(5)
O(23)-Rb(1)-O(26)	60.4(2)	C(21)-O(20)-Rb(1)	106.9(6)
O(7)-Rb(1)-O(26)	98.3(2)	O(20)-C(21)-C(22)	107.1(9)
O(4)-Rb(1)-O(10)	109.4(2)	O(23)-C(22)-C(21)	109.3(9)
O(23)-Rb(1)-O(10)	81.2(2)	O(13)-Rb(1)-C(38)	103.6(2)
O(7)-Rb(1)-O(10)	58.1(3)	O(32)-Rb(1)-C(38)	39.7(2)
O(26)-Rb(1)-O(10)	77.4(2)	O(20)-Rb(1)-C(38)	21.9(2)
O(4)-Rb(1)-O(29)	81.3(2)	O(1)-Rb(1)-C(38)	78.3(2)
O(23)-Rb(1)-O(29)	113.8(2)	C(14)-Rb(1)-C(38)	81.9(2)
O(7)-Rb(1)-O(29)	75.2(2)	C(19)-O(1)-C(2)	120.3(10)
O(26)-Rb(1)-O(29)	59.2(2)	C(19)-O(1)-Rb(1)	95.8(7)
O(10)-Rb(1)-O(29)	109.2(2)	C(2)-O(1)-Rb(1)	98.7(6)
O(4)-Rb(1)-O(13)	94.4(2)	O(1)-C(2)-C(3)	107.5(10)
O(23)-Rb(1)-O(13)	75.8(2)	O(1)-C(2)-Rb(1)	59.3(5)
O(7)-Rb(1)-O(13)	87.2(3)	C(3)-C(2)-Rb(1)	83.6(7)
O(26)-Rb(1)-O(13)	119.4(2)	O(4)-C(3)-C(2)	109.2(10)
O(10)-Rb(1)-O(13)	55.0(2)	C(5)-O(4)-C(3)	116.3(12)
O(29)-Rb(1)-O(13)	161.5(2)	C(5)-O(4)-Rb(1)	110.3(9)
O(4)-Rb(1)-O(32)	78.6(2)	C(3)-O(4)-Rb(1)	125.7(7)
O(23)-Rb(1)-O(32)	97.1(2)	C(6)-C(5)-O(4)	118.4(13)
O(7)-Rb(1)-O(32)	118.4(2)	C(6)-C(5)-Rb(1)	82.9(9)
O(26)-Rb(1)-O(32)	86.2(2)	O(4)-C(5)-Rb(1)	48.6(6)
O(10)-Rb(1)-O(32)	162.0(2)	C(5)-C(6)-O(7)	121(2)
O(29)-Rb(1)-O(32)	54.9(2)	C(5)-C(6)-Rb(1)	76.3(9)

Table 88. (cont.)
Bond lengths [A] and angles [deg] for
[Rb(benzo-15-crown-5)$_2$](AuI$_2$) **(XVI)**

O(13)-Rb(1)-O(32)	142.1(2)	O(7)-C(6)-Rb(1)	46.4(6)
O(4)-Rb(1)-O(20)	110.2(2)	C(6)-O(7)-C(8)	118.0(13)
O(23)-Rb(1)-O(20)	54.8(2)	C(6)-O(7)-Rb(1)	113.9(8)
O(7)-Rb(1)-O(20)	166.5(2)	C(8)-O(7)-Rb(1)	119.0(8)
O(26)-Rb(1)-O(20)	85.9(2)	O(7)-C(8)-C(9)	112.6(12)
O(10)-Rb(1)-O(20)	135.4(2)	O(10)-C(9)-C(8)	115.0(12)
O(29)-Rb(1)-O(20)	96.3(2)	O(10)-C(9)-Rb(1)	48.3(6)
O(13)-Rb(1)-O(20)	102.1(2)	C(8)-C(9)-Rb(1)	81.4(8)
O(32)-Rb(1)-O(20)	48.8(2)	C(11)-O(10)-C(9)	113.6(11)
O(4)-Rb(1)-O(1)	53.8(2)	C(11)-O(10)-Rb(1)	121.9(7)
O(23)-Rb(1)-O(1)	107.8(2)	C(9)-O(10)-Rb(1)	110.8(8)
O(7)-Rb(1)-O(1)	86.5(3)	O(10)-C(11)-C(12)	107.4(9)
O(26)-Rb(1)-O(1)	166.3(2)	O(13)-C(12)-C(11)	107.2(10)
O(10)-Rb(1)-O(1)	94.6(2)	O(13)-C(12)-Rb(1)	52.6(5)
O(29)-Rb(1)-O(1)	134.4(2)	C(11)-C(12)-Rb(1)	86.0(7)
O(13)-Rb(1)-O(1)	47.8(2)	O(26)-C(27)	1.419(12)
O(32)-Rb(1)-O(1)	102.9(2)	O(13)-Rb(1)-C(14)	21.7(2)
O(20)-Rb(1)-O(1)	92.4(2)	O(32)-Rb(1)-C(14)	120.7(2)
O(4)-Rb(1)-C(14)	93.2(3)	O(20)-Rb(1)-C(14)	82.2(2)
O(23)-Rb(1)-C(14)	70.5(2)	O(1)-Rb(1)-C(14)	39.7(2)
O(7)-Rb(1)-C(14)	105.1(3)	O(4)-Rb(1)-C(38)	88.3(2)
O(26)-Rb(1)-C(14)	126.7(2)	O(23)-Rb(1)-C(38)	75.6(2)
O(10)-Rb(1)-C(14)	75.9(3)	O(7)-Rb(1)-C(38)	146.3(3)
O(29)-Rb(1)-C(14)	173.5(2)	O(26)-Rb(1)-C(38)	103.6(2)
O(29)-Rb(1)-C(38)	94.3(2)	O(10)-Rb(1)-C(38)	152.1(2)

Symmetry transformations used to generate equivalent atoms:
1= -x+1,-y+1,-z+1   2= -x+1,-y,-z

Table 89.
Anisotropic displacement parameters (Å^2 x 10^3) for [Rb(benzo-15-crown-5)$_2$](AuI$_2$) (**XVI**)

atom	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
Au(1)	56(1)	90(1)	60(1)	20(1)	31(1)	12(1)
Au(2)	56(1)	106(1)	70(1)	29(1)	14(1)	32(1)
I(1)	100(1)	94(1)	89(1)	8(1)	35(1)	21(1)
I(2)	88(1)	110(1)	87(1)	18(1)	15(1)	39(1)
Rb(1)	49(1)	56(1)	44(1)	8(1)	22(1)	16(1)
O(1)	88(7)	59(5)	81(6)	21(5)	40(6)	31(5)
C(2)	101(11)	74(8)	84(10)	41(8)	64(9)	43(9)
C(3)	98(11)	94(10)	58(8)	23(8)	31(8)	52(9)
O(4)	73(6)	75(6)	63(5)	26(5)	16(5)	12(5)
C(5)	54(9)	87(11)	15(2)	20(11)	-31(9)	12(9)
C(6)	15(2)	84(12)	80(11)	28(10)	-31(11)	-27(11)
O(7)	88(7)	53(6)	89(7)	6(5)	7(6)	5(5)
C(8)	151(15)	47(8)	61(9)	-2(7)	35(10)	-14(9)
C(9)	133(15)	72(10)	150(2)	51(11)	82(14)	36(11)
O(10)	79(6)	53(5)	99(7)	23(5)	44(6)	20(5)
C(11)	100(11)	66(9)	81(9)	37(7)	50(8)	51(8)
C(12)	74(9)	101(11)	81(9)	28(8)	44(8)	52(9)
O(13)	53(5)	74(5)	60(5)	22(4)	26(4)	22(4)
C(14)	54(7)	61(8)	69(8)	11(6)	40(7)	20(7)
C(15)	53(8)	86(10)	104(11)	1(9)	46(8)	18(8)
C(16)	40(9)	160(2)	12(2)	-3(14)	26(10)	24(11)
C(17)	66(12)	97(13)	170(2)	-48(13)	64(13)	-34(10)
C(18)	120(14)	69(9)	101(12)	23(8)	74(11)	30(9)
C(19)	72(9)	69(9)	65(8)	11(7)	40(7)	13(7)
O(20)	37(4)	59(4)	56(4)	14(4)	16(4)	11(3)
C(21)	40(6)	47(6)	62(7)	6(5)	7(5)	3(5)
C(22)	49(7)	62(7)	53(7)	16(6)	11(6)	16(6)
O(23)	55(5)	52(4)	51(4)	14(4)	21(4)	15(4)
C(24)	49(7)	57(7)	62(7)	18(6)	-2(6)	14(6)
C(25)	68(9)	81(9)	68(9)	34(7)	31(7)	18(7)
O(26)	52(5)	77(5)	48(4)	18(4)	26(4)	15(4)
C(27)	73(9)	85(9)	57(8)	17(7)	39(7)	14(7)
C(28)	35(6)	70(8)	93(10)	10(7)	29(7)	9(6)
O(29)	58(5)	62(5)	56(5)	12(4)	34(4)	15(4)
C(30)	42(6)	74(8)	57(7)	-9(6)	25(6)	1(6)
C(31)	43(7)	80(8)	61(7)	6(6)	15(6)	29(6)

Table 89. (cont.)
Anisotropic displacement parameters (Å^2 x 10^3) for
[Rb(benzo-15-crown-5)$_2$](AuI$_2$) **(XVI)**

O(32)	44(4)	67(5)	60(5)	23(4)	20(4)	27(4)
C(33)	52(7)	43(6)	57(7)	14(5)	25(6)	21(5)
C(34)	66(8)	62(7)	60(7)	20(6)	22(6)	36(7)
C(35)	81(10)	65(8)	71(9)	33(7)	36(8)	33(8)
C(36)	90(10)	47(7)	65(8)	9(6)	41(8)	8(7)
C(37)	63(8)	48(7)	70(8)	8(6)	32(7)	9(6)
C(38)	53(7)	45(6)	47(6)	6(5)	27(5)	16(5)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 90.
Hydrogen coordinates (x 10^4) and isotropic
displacement parameters ($Å^2$ x 10^3) for [Rb(benzo-15-crown-5)$_2$](AuI$_2$) (**XVI**)

atom	x	y	z	U(eq)
H(2A)	-197	8808	-119	80
H(2B)	-477	8840	938	80
H(3A)	-1828	7093	-1037	80
H(3B)	-2424	8016	-862	80
H(5A)	-3864	6242	-1182	80
H(5B)	-3962	6250	-46	80
H(6A)	-2896	5110	-924	80
H(6B)	-4092	4695	-729	80
H(8A)	-1521	4244	134	80
H(8B)	-2785	3456	18	80
H(9A)	-971	3319	1514	80
H(9B)	-1757	3852	1997	80
H(11A)	743	4534	1356	80
H(11B)	1377	4237	2542	80
H(12A)	2188	6146	3463	80
H(15A)	3912	7576	3612	80
H(16A)	5062	9371	3859	80
H(17A)	4103	10402	2699	80
H(18A)	1903	9730	1285	80
H(21A)	2494	10051	5325	80
H(21B)	2324	9186	4284	80
H(22A)	1788	8589	6027	80
H(22B)	3096	8593	6008	80
H(24A)	2056	6795	6116	80
H(24B)	1249	5923	4927	80
H(25A)	162	7255	5811	80
H(25B)	44	6076	5950	80
H(27A)	-2124	6826	4793	80
H(27B)	-2332	5619	4862	80
H(28A)	-4117	5662	3245	80
H(28B)	-3301	5096	2837	80
H(30A)	-3385	7662	3591	80
H(30B)	-4640	7181	2386	80
H(31A)	-3600	8882	2379	80
H(31B)	-3411	8036	1555	80
H(34A)	-2590	9883	1511	80
H(35A)	-1202	11389	1387	80
H(36A)	994	11838	2443	80
H(37A)	1970	10894	3854	80

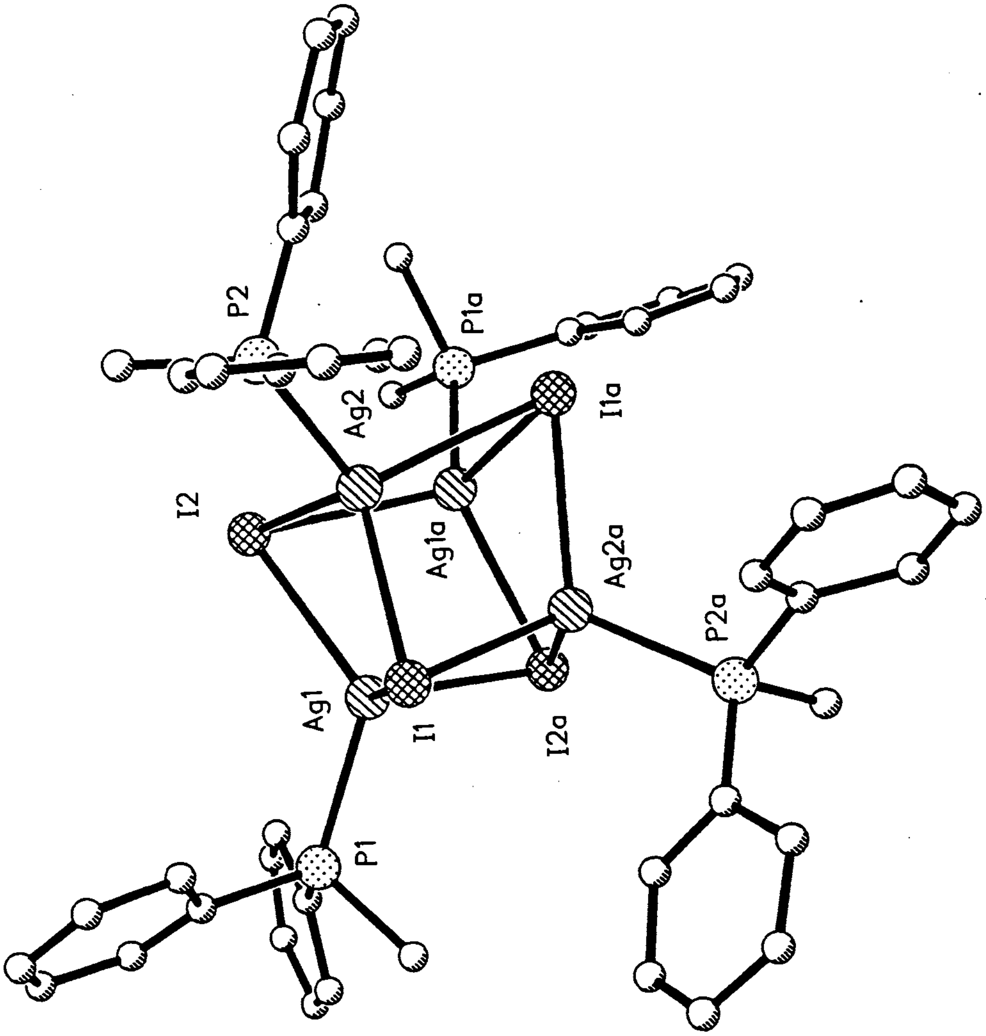


Figure 35. Projection View of $Ag_4I_4(P(Ph)_2Me)_4$ **(XVII)**

Table 91.
Crystal data and structure refinement for
$Ag_4I_4(P(Ph)_2Me)_4$ **(XVII)**

Empirical formula	C_{52} H_{68} Ag_4 I_4 P_4
Formula weight	1756.04
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 13.576(10) Å $\alpha = 90^0$.
	b = 18.018(8) Å $\beta = 90^0$.
	c = 12.368(5) Å $\gamma = 90^0$
Volume	3025(3)Å^2
Z, Calculated density	2, 1.928 Mg/m^3
Absorption coefficient	3.453 mm^{-1}
F(000)	1680
Theta range for data collection	1.88 to 30.24 ^{0}
Index ranges	$-1 \leq h \leq 19$, $-1 \leq k \leq 25$, $-1 \leq l \leq 17$
Reflections collected / unique	6006 / 5769 [R(int) = 0.1347]
Completeness to 2theta =	30.24 98.1%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5769 / 0 / 290
Goodness-of-fit on F^2	1.083
Final R indices [I>2sigma(I)]	R1 = 0.0739, wR2 = 0.1950
R indices (all data)	R1 = 0.1571, wR2 = 0.2624
Absolute structure parameter	-0.13(7)
Extinction coefficient	0.0048(6)
Largest diff. peak and hole	1.594 and -1.786 e.A^{-3}

Table 92.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $Ag_4I_4(P(Ph)_2Me)_4$ (**XVII**)

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Ag(1)	260(2)	931(1)	9054(1)	94(1)
Ag(2)	-1197(1)	145(1)	7206(1)	83(1)
I(1)	243(1)	1293(1)	6665(1)	70(1)
I(2)	-1674(1)	329(1)	9501(1)	83(1)
P(1)	955(4)	2063(3)	9928(4)	67(1)
P(2)	-2764(4)	185(3)	6135(4)	60(1)
C(111)	19(2)	2931(11)	9755(13)	72(5)
C(112)	-5(16)	3397(10)	1060(2)	74(5)
C(113)	-590(2)	4039(13)	10430(2)	107(9)
C(114)	-930(2)	4204(13)	9400(2)	91(7)
C(115)	-780(2)	3721(14)	8620(2)	110(9)
C(116)	-240(2)	3043(14)	8795(15)	90(7)
C(121)	123(2)	2000(10)	11373(14)	68(5)
C(122)	2050(2)	2385(13)	1191(2)	93(7)
C(123)	2180(2)	232(2)	1302(2)	95(8)
C(124)	1550(3)	190(2)	1364(2)	117(12)
C(125)	870(2)	1496(15)	13160(2)	102(9)
C(126)	637(15)	1571(11)	1204(2)	75(5)
C(131)	218(2)	2310(12)	9309(15)	78(6)
C(211)	-2584(15)	577(10)	4759(14)	61(4)
C(212)	-1980(2)	245(12)	408(2)	103(9)
C(213)	-1870(3)	478(13)	2990(2)	114(11)
C(214)	-2390(3)	1010(2)	263(2)	128(12)
C(215)	-3080(4)	1360(2)	3240(3)	18(2)
C(216)	-323(2)	1162(13)	437(2)	88(7)
C(221)	-3261(13)	-719(9)	5858(15)	62(4)
C(222)	-377(2)	-931(11)	4878(13)	76(6)
C(223)	-4183(15)	-1665(11)	479(2)	70(5)
C(224)	-4111(15)	-2185(13)	5570(2)	87(6)
C(225)	-373(2)	-1953(12)	6570(2)	91(7)
C(226)	-324(2)	-1252(11)	669(2)	78(6)
C(231)	-376(2)	700(11)	676(2)	77(5)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 93.
Bond lengths [Å] and angles [°] for
Ag$_4$I$_4$(P(Ph)$_2$Me)$_4$ **(XVII)**

Ag(1)-P(1)	2.495(6)	P(1)-Ag(1)-I(2)	124.53(15)
Ag(1)-I(2)	2.893(3)	P(1)-Ag(1)-I(1)	104.45(13)
Ag(1)-I(1)	3.026(2)	I(2)-Ag(1)-I(1)	105.12(7)
Ag(1)-I(2)^{1}	3.024(3)	P(1)-Ag(1)-I(2)^{1}	107.1(2)
Ag(1)-Ag(2)^{1}	3.257(3)	I(2)-Ag(1)-I(2)^{1}	105.04(8)
Ag(1)-Ag(2)	3.338(3)	I(1)-Ag(1)-I(2)^{1}	110.20(7)
Ag(2)-P(2)	2.506(5)	P(1)-Ag(1)-Ag(2)^{1}	130.0(2)
Ag(2)-I(1)	2.924(2)	I(2)-Ag(1)-Ag(2)^{1}	105.41(7)
Ag(2)-I(2)	2.931(2)	I(1)-Ag(1)-Ag(2)^{1}	56.36(5)
Ag(2)-I(1)^{1}	2.974(2)	I(2)^{1}-Ag(1)-Ag(2)^{1}	55.48(6)
Ag(2)-Ag(1)^{1}	3.257(3)	P(1)-Ag(1)-Ag(2)	150.22(15)
Ag(2)-Ag(2)^{1}	3.293(4)	I(2)-Ag(1)-Ag(2)	55.55(6)
I(1)-Ag(2)^{1}	2.974(2)	I(1)-Ag(1)-Ag(2)	54.45(5)
I(2)-Ag(1)^{1}	3.024(3)	I(2)^{1}-Ag(1)-Ag(2)	100.54(7)
P(1)-C(121)	1.83(2)	Ag(2)^{1}-Ag(1)-Ag(2)	59.90(8)
P(1)-C(111)	1.89(2)	P(2)-Ag(2)-I(1)	115.25(13)
P(1)-C(131)	1.88(2)	P(2)-Ag(2)-I(2)	108.74(13)
P(2)-C(221)	1.80(2)	I(1)-Ag(2)-I(2)	106.79(7)
P(2)-C(231)	1.81(2)	P(2)-Ag(2)-I(1)^{1}	106.01(13)
P(2)-C(211)	1.86(2)	I(1)-Ag(2)-I(1)^{1}	105.90(8)
C(111)-C(116)	1.34(3)	I(2)-Ag(2)-I(1)^{1}	114.36(7)
C(111)-C(112)	1.37(3)	P(2)-Ag(2)-Ag(1)^{1}	136.02(13)
C(112)-C(113)	1.41(3)	I(1)-Ag(2)-Ag(1)^{1}	108.67(8)
C(113)-C(114)	1.40(3)	I(2)-Ag(2)-Ag(1)^{1}	58.24(6)
C(114)-C(115)	1.31(3)	I(1)^{1}-Ag(2)-Ag(1)^{1}	57.90(5)
C(115)-C(116)	1.44(3)	P(2)-Ag(2)-Ag(2)^{1}	147.39(12)
C(121)-C(126)	1.39(3)	I(1)-Ag(2)-Ag(2)^{1}	56.77(6)
C(121)-C(122)	1.47(3)	I(2)-Ag(2)-Ag(2)^{1}	103.64(5)
C(122)-C(123)	1.39(3)	I(1)^{1}-Ag(2)-Ag(2)^{1}	55.35(6)
C(123)-C(124)	1.37(4)	Ag(1)^{1}-Ag(2)-Ag(2)^{1}	61.28(6)
C(124)-C(125)	1.32(4)	P(2)-Ag(2)-Ag(1)	148.48(14)
C(125)-C(126)	1.42(3)	I(1)-Ag(2)-Ag(1)	57.33(5)
C(211)-C(212)	1.32(3)	I(2)-Ag(2)-Ag(1)	54.50(6)
C(211)-C(216)	1.45(3)	I(1)^{1}-Ag(2)-Ag(1)	105.40(8)
C(212)-C(213)	1.42(3)	Ag(1)^{1}-Ag(2)-Ag(1)	62.62(7)
C(213)-C(214)	1.28(4)	Ag(2)'-Ag(2)-Ag(1)	58.82(6)
C(214)-C(215)	1.36(5)	Ag(2)-I(1)-Ag(2)^{1}	67.87(8)
C(215)-C(216)	1.46(3)	Ag(2)-I(1)-Ag(1)	68.23(5)
C(221)-C(226)	1.41(2)	Ag(2)^{1}-I(1)-Ag(1)	65.74(5)
C(221)-C(222)	1.45(3)	Ag(1)-I(2)-Ag(2)	69.94(6)
C(222)-C(223)	1.44(3)	Ag(1)-I(2)-Ag(1)^{1}	70.76(8)

Table 93. (cont.)
Bond lengths [Å] and angles [°] for
$Ag_4I_4(P(Ph)_2Me)_4$ (**XVII**)

C(223)-C(224)	1.35(3)	Ag(2)-I(2)-Ag(1)^1	66.29(6)
C(224)-C(225)	1.41(3)	C(121)-P(1)-C(111)	106.0(8)
C(225)-C(226)	1.43(3)	C(121)-P(1)-C(131)	103.3(10)
C(223)-C(222)-C(221)	120(2)	C(111)-P(1)-C(131)	104.0(9)
C(224)-C(223)-C(222)	124(2)	C(121)-P(1)-Ag(1)	116.7(7)
C(223)-C(224)-C(225)	117(2)	C(111)-P(1)-Ag(1)	114.9(6)
C(224)-C(225)-C(226)	121(2)	C(131)-P(1)-Ag(1)	110.5(7)
C(221)-C(226)-C(225)	121(2)	C(221)-P(2)-C(231)	105.4(9)
C(126)-C(121)-C(122)	116(2)	C(221)-P(2)-C(211)	102.7(8)
C(126)-C(121)-P(1)	120(2)	C(231)-P(2)-C(211)	106.9(9)
C(122)-C(121)-P(1)	125(2)	C(221)-P(2)-Ag(2)	113.2(6)
C(123)-C(122)-C(121)	120(3)	C(231)-P(2)-Ag(2)	115.0(7)
C(124)-C(123)-C(122)	121(3)	C(211)-P(2)-Ag(2)	112.5(7)
C(125)-C(124)-C(123)	120(2)	C(116)-C(111)-C(112)	120(2)
C(124)-C(125)-C(126)	122(2)	C(116)-C(111)-P(1)	117.8(15)
C(121)-C(126)-C(125)	120(2)	C(112)-C(111)-P(1)	121.9(14)
C(212)-C(211)-C(216)	120(2)	C(111)-C(112)-C(113)	120(2)
C(212)-C(211)-P(2)	119.7(14)	C(114)-C(113)-C(112)	120(2)
C(216)-C(211)-P(2)	119.9(14)	C(115)-C(114)-C(113)	119(2)
C(211)-C(212)-C(213)	123(2)	C(114)-C(115)-C(116)	122(2)
C(214)-C(213)-C(212)	119(2)	C(111)-C(116)-C(115)	119(2)
C(213)-C(214)-C(215)	123(2)	C(226)-C(221)-C(222)	116 (2)
C(214)-C(215)-C(216)	121(3)	C(226)-C(221)-P(2)	118.0(14)
C(211)-C(216)-C(215)	114(2)	C(222)-C(221)-P(2)	125.4(13)

Symmetry transformations used to generate equivalent atoms:
1= -x,-y,z

Table 94.
Anisotropic displacement parameters (Å^2 x 10^3) for $Ag_4I_4(P(Ph)_2Me)_4$ (**XVII**)

atom	U11	U22	U33	U23	U13	U12
Ag(1)	117(2)	77(1)	87(1)	-11(1)	-3(1)	-15(1)
Ag(2)	74(1)	92(1)	84(1)	-3(1)	-16(1)	-7(1)
I(1)	83(1)	65(1)	61(1)	8(1)	3(1)	-3(1)
I(2)	89(1)	89(1)	72(1)	-6(1)	21(1)	-1(1)
P(1)	82(4)	64(3)	54(2)	-1(2)	7(2)	2(3)
P(2)	60(3)	65(3)	56(2)	-1(2)	-3(2)	-4(2)
C(111)	92(14)	74(10)	50(8)	-11(8)	-7(10)	-21(12)
C(112)	68(12)	74(11)	81(11)	-23(10)	-19(11)	6(10)
C(113)	150(3)	86(14)	86(14)	-32(13)	0(2)	20(2)
C(114)	86(15)	78(13)	110(2)	-15(13)	-21(14)	22(12)
C(115)	140(2)	94(15)	100(2)	-4(14)	-20(0)	6(2)
C(116)	120(2)	99(14)	54(9)	-16(10)	12(13)	20(2)
C(121)	98(14)	51(8)	56(9)	-2(7)	6(10)	4(10)
C(122)	110(2)	94(15)	71(13)	-13(11)	-10(13)	13(15)
C(123)	83(15)	130(2)	72(13)	-8(14)	-25(13)	20(2)
C(124)	160(3)	150(3)	44(10)	3(14)	-0(2)	90(3)
C(125)	130(2)	100(2)	77(14)	44(13)	20(2)	3(2)
C(126)	60(11)	84(12)	80(12)	16(11)	1(10)	-4(10)
C(131)	90(15)	86(13)	59(10)	11(9)	18(10)	9(12)
C(211)	64(10)	57(9)	61(9)	2(8)	8(9)	7(9)
C(212)	150(2)	67(12)	92(13)	49(11)	40(2)	28(15)
C(213)	180(3)	80(14)	88(14)	29(12)	60(2)	4(2)
C(214)	160(3)	150(3)	77(14)	4(2)	7(2)	-10(2)
C(215)	270(6)	150(3)	110(2)	80(2)	20(3)	60(3)
C(216)	88(15)	10(2)	75(12)	15(11)	26(12)	30(14)
C(221)	54(10)	57(9)	75(10)	3(8)	-7(9)	7(8)
C(222)	11(2)	73(11)	45(8)	-6(8)	15(10)	-23(12)
C(223)	63(12)	76(11)	70(11)	-6(10)	4(10)	-10(10)
C(224)	57(12)	92(14)	11(2)	-19(14)	4(12)	-20(11)
C(225)	82(15)	74(12)	12(2)	39(13)	-15(15)	-6(12)
C(226)	88(15)	76(11)	71(10)	19(11)	-23(12)	-17(12)
C(231)	73(13)	82(12)	76(11)	1(11)	12(11)	5(11)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{2*}U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 95.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $Ag_4I_4(P(Ph)_2Me)_4$ (**XVII**)

atom	x	y	z	U(eq)
H(11A)	244	3280	11308	80
H(11B)	-773	4337	11045	80
H(11C)	-1199	4682	9223	80
H(11E)	-1043	3799	7908	80
H(11F)	-245	2655	8263	80
H(12A)	2506	2681	11499	80
H(12C)	2678	2601	13388	80
H(12D)	1656	1879	14403	80
H(12E)	506	1158	13609	80
H(12F)	86	1308	11741	80
H(13A)	2424	2748	9658	80
H(13B)	2630	1908	9418	80
H(13C)	2106	2402	8548	80
H(21A)	-1568	-141	4355	80
H(21B)	-1398	242	2521	80
H(21C)	-2276	1184	1908	80
H(21D)	-3521	1712	2902	80
H(21E)	-3681	1426	4831	80
H(22A)	-3850	-580	4301	80
H(22B)	-4521	-1803	4136	80
H(22C)	-4343	-2684	5472	80
H(22D)	-3717	-2292	7174	80
H(22E)	-2927	-1125	7364	80
H(23A)	-4323	685	6291	80
H(23B)	-3921	482	7442	80
H(23C)	-3560	1207	6862	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

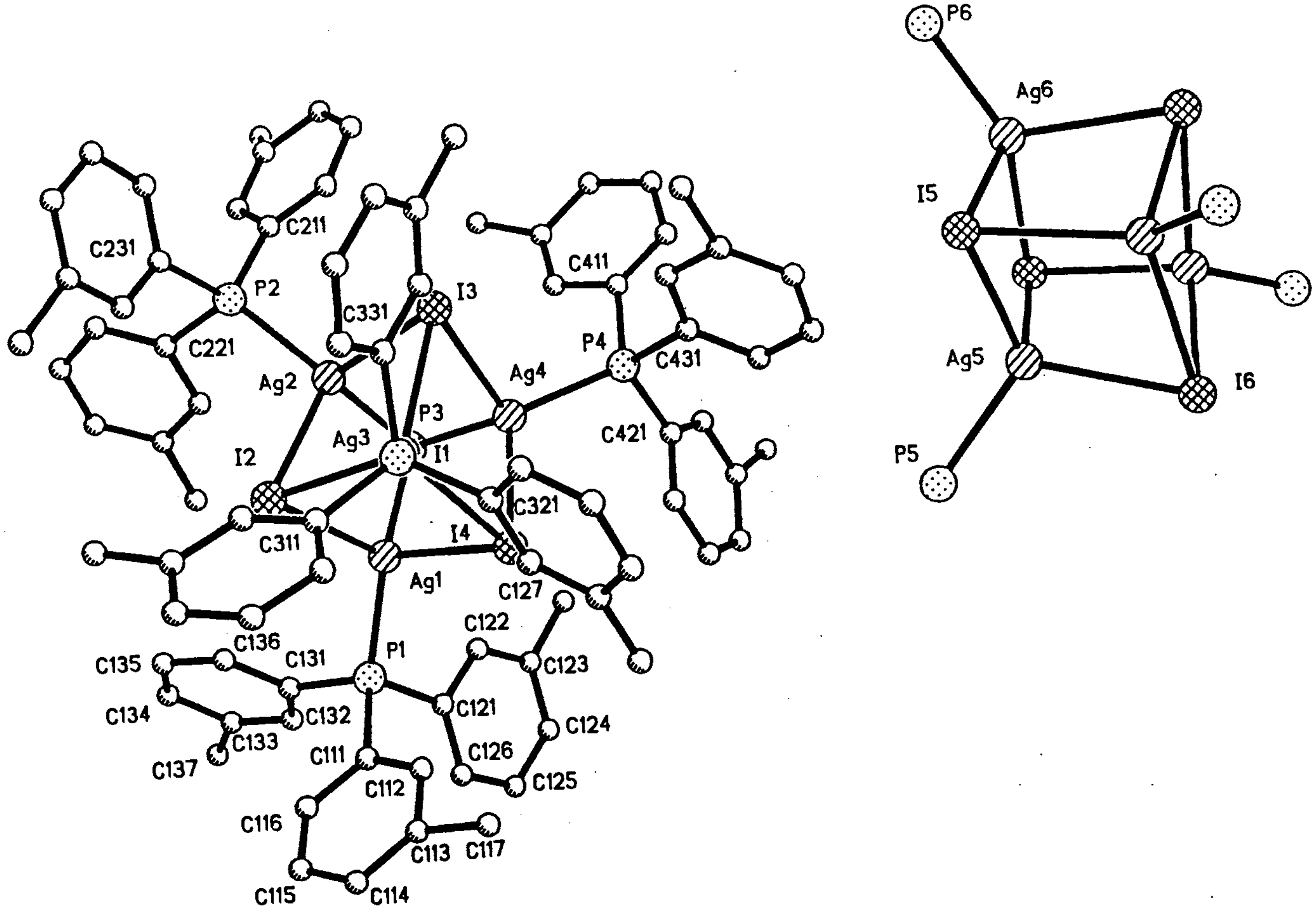


Figure 36. Projection View of $(Ag_4I_4(P(m\text{-tolyl})_3)_4)$ (XVIII)

Table 96.
Crystal data and structure refinement for
($Ag_4I_4(P(m\text{-tolyl})_3)_4$) **(XVIII)**

Empirical formula	$C_{84} H_{84} Ag_4 I_4 P_4$
Formula weight	2156.47
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, R3c
Unit cell dimensions	a = 28.173(8) Å $\alpha = 109.43(1)^{\circ}$
	b = 28.173(8) Å $\beta = 109.43(1)^{\circ}$
	c = 28.173(8) Å $\gamma = 109.43(1)^{\circ}$
Volume	17240(8) Å^3
Z, Calculated density	8, 1.662 Mg/m^3
Absorption coefficient	2.442 mm^{-1}
F(000)	8384
Theta range for data collection	2.34 to 24.71 deg.
Index ranges	$-1 \leq h \leq 31$, $-33 \leq k \leq 1$, $-1 \leq l \leq 31$
Reflections collected / unique	20752 / 10524 [R(int) = 0.2515]
Completeness to $2\theta = 24.71$	93.9%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10524 / 1 / 956
Goodness-of-fit on F^2	0.935
Final R indices [$I>2\sigma(I)$]	R1 = 0.1063, wR2 = 0.2375
R indices (all data)	R1 = 0.2519, wR2 = 0.3269
Absolute structure parameter	-0.16(8)
Extinction coefficient	0.00000(7)
Largest diff. peak and hole	1.180 and -1.219 e.A^{-3}

Table 97.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $(Ag_4I_4(P(m\text{-tolyl})_3)_4)$ **(XVIII)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
I(1)	3036(2)	-1965(2)	-1864(2)	84(1)
I(2)	3322(2)	-2749(2)	-617(2)	89(1)
I(3)	1964(2)	-2248(2)	-904(2)	87(1)
I(4)	3824(2)	-893(2)	169(2)	88(1)
I(5)	1694(1)	904(1)	1977	89(1)
I(6)	2937(2)	2937(2)	2937(2)	86(2)
Ag(1)	3862(2)	-1756(2)	-735(2)	104(2)
Ag(2)	2419(2)	-2791(2)	-1564(2)	105(1)
Ag(3)	3034(2)	-1965(2)	78(2)	88(1)
Ag(4)	2826(2)	-1350(2)	-950(2)	104(2)
Ag(5)	2633(2)	1812(2)	2018(2)	105(2)
Ag(6)	999(3)	999(3)	999(3)	90(2)
P(1)	4850(5)	-1439(6)	-610(6)	76(4)
P(2)	1764(7)	-3787(6)	-2418(7)	90(4)
P(3)	3046(5)	-1959(5)	973(6)	71(3)
P(4)	2481(6)	-693(7)	-1144(6)	85(4)
P(5)	3490(6)	1672(6)	2213(6)	78(4)
P(6)	95(8)	95(8)	95(8)	70(6)
C(112)	5500(2)	-740(2)	680(2)	220(6)
C(113)	5910(2)	-580(2)	1230(2)	150(3)
C(114)	6262(15)	-820(2)	1288(14)	140(3)
C(115)	6204(14)	-1230(2)	800(2)	160(4)
C(116)	5790(2)	-1396(15)	248(15)	110(2)
C(111)	5442(14)	-1150(2)	188(15)	110(3)
C(117)	5820(2)	-110(2)	1640(2)	230(5)
C(122)	4727(14)	-700(2)	-1064(15)	130(3)
C(123)	4900(2)	-230(2)	-1150(2)	170(4)
C(124)	5490(2)	171(15)	-880(2)	160(4)
C(125)	5899(14)	105(14)	-510(2)	150(3)
C(126)	5730(2)	-370(2)	-419(14)	140(3)
C(121)	5140(2)	-769(13)	-696(14)	100(2)
C(127)	4450(3)	-150(3)	-1550(3)	270(7)
C(132)	5240(2)	-1850(2)	-1380(2)	120(2)
C(133)	5230(2)	-2300(2)	-1800(2)	170(4)
C(134)	4920(2)	-2870(2)	-1920(2)	290(8)
C(135)	4630(2)	-2984(14)	-1620(2)	230(6)
C(136)	4640(2)	-2530(2)	-1210(2)	220(5)

Table 97. (cont)
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for ($Ag_4L_4(P(m\text{-tolyl})_3)_4$) **(XVIII)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
C(131)	4950(2)	-1970(2)	-1090(2)	110(2)
C(137)	5500(2)	-2330(4)	-2130(5)	600(2)
C(212)	980(2)	-4160(2)	-3560(2)	190(4)
C(213)	500(2)	-4230(2)	-3995(15)	400(14)
C(214)	195(14)	-3960(2)	-3840(2)	520(2)
C(215)	370(2)	-3630(2)	-3260(2)	160(3)
C(216)	850(2)	-3560(2)	-2830(2)	210(6)
C(211)	1152(12)	-3830(2)	-2983(15)	110(2)
C(217)	250(4)	-4230(4)	-4440(4)	520(15)
C(222)	2560(2)	-3699(10)	-2758(13)	100(2)
C(223)	2872(13)	-3854(13)	-3010(2)	120(3)
C(224)	2703(13)	-4436(15)	-3321(15)	260(8)
C(225)	2219(14)	-4863(10)	-3385(13)	120(2)
C(226)	1906(12)	-4707(13)	-3136(14)	74(14)
C(221)	2075(15)	-4130(2)	-2822(12)	100(2)
C(227)	3340(4)	-3460(3)	-2990(4)	170(4)
C(232)	1801(14)	-4430(2)	-1810(2)	130(3)
C(233)	1550(2)	-4850(2)	-1680(2)	140(2)
C(234)	950(3)	-5200(2)	-1980(2)	150(3)
C(235)	602(14)	-5140(2)	-2410(2)	170(5)
C(236)	850(2)	-4720(2)	-2540(2)	130(3)
C(231)	1450(2)	-4363(14)	-2240(2)	100(2)
C(237)	2090(2)	-4840(2)	-1240(3)	230(5)
C(312)	3384(11)	-2763(12)	862(10)	53(10)
C(313)	3657(15)	-3053(11)	1035(14)	90(2)
C(314)	3983(14)	-2859(15)	1622(15)	110(3)
C(315)	4036(14)	-2375(15)	2036(11)	190(4)
C(316)	3763(15)	-2085(12)	1863(11)	100(2)
C(311)	3437(12)	-2279(12)	1276(13)	68(13)
C(317)	3590(2)	-3580(2)	590(3)	100(2)
C(322)	3824(14)	-773(14)	1681(13)	190(5)
C(323)	4095(13)	-216(11)	2148(15)	280(7)
C(324)	3910(2)	-114(14)	2548(12)	110(3)
C(325)	3440(2)	-570(2)	2480(2)	120(2)
C(326)	3172(14)	-1120(2)	2020(2)	120(2)
C(321)	3362(14)	-1226(10)	1614(12)	63(13)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 97. (cont)
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for ($Ag_4I_4(P(m\text{-tolyl})_3)_4$) **(XVIII)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
C(327)	4600(4)	240(4)	2240(3)	680(2)
C(332)	1829(13)	-2366(11)	445(10)	100(2)
C(333)	1287(10)	-2620(15)	397(14)	100(2)
C(334)	1200(12)	-2902(15)	710(2)	120(2)
C(335)	1660(2)	-2930(13)	1070(2)	140(3)
C(336)	2197(14)	-2676(15)	1115(14)	90(2)
C(331)	2284(10)	-2394(14)	804(14)	73(15)
C(337)	880(3)	-2470(6)	30(3)	440(12)
C(412)	1796(15)	-1485(15)	-2300(2)	90(2)
C(413)	1340(2)	-1780(13)	-2870(2)	100(2)
C(414)	932(15)	-1610(2)	-3016(15)	140(3)
C(415)	971(13)	-1150(2)	-2590(2)	120(3)
C(416)	1420(2)	-851(13)	-2020(2)	110(2)
C(411)	1836(13)	-1021(15)	-1878(13)	120(3)
C(417)	1260(3)	-2240(3)	-3380(2)	330(6)
C(422)	3014(12)	100(2)	-1431(14)	90(2)
C(423)	3460(2)	570(2)	-1370(2)	240(7)
C(424)	4020(14)	840(2)	-900(2)	260(8)
C(425)	4131(13)	660(2)	-500(2)	420(13)
C(426)	3680(2)	200(2)	-561(15)	380(9)
C(421)	3125(15)	-82(15)	-1030(2)	150(3)
C(427)	3180(6)	710(3)	-1860(6)	800(2)
C(432)	1760(2)	-758(12)	-620(2)	200(5)
C(433)	1606(14)	-530(2)	-220(2)	200(5)
C(434)	1870(2)	70(3)	120(2)	610(2)
C(435)	2290(2)	439(14)	65(15)	380(9)
C(436)	2447(14)	207(12)	-337(14)	130(3)
C(431)	2182(15)	-391(14)	-680(12)	120(3)
C(437)	1150(6)	-980(6)	-260(5)	700(2)
C(512)	4600(2)	2400(2)	2540(2)	170(4)
C(513)	5029(15)	2797(15)	2520(2)	160(4)
C(514)	4880(2)	2940(14)	2090(2)	250(7)
C(515)	4300(2)	2680(2)	1670(2)	410(11)
C(516)	3870(2)	2290(2)	1690(2)	410(12)
C(511)	4020(2)	2143(14)	2130(3)	190(4)
C(517)	5610(4)	3160(4)	2890(4)	250(5)
C(522)	3842(11)	2105(12)	3330(2)	140(3)
C(523)	4120(2)	2230(13)	3906(15)	210(5)

Table 97. (cont)
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for ($Ag_4I_4(P(m\text{-tolyl})_3)_4$) **(XVIII)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
C(524)	4420(2)	1950(2)	4054(10)	200(5)
C(525)	4449(14)	1551(13)	3629(14)	150(4)
C(526)	4172(14)	1426(13)	3057(12)	83(15)
C(521)	3869(14)	1703(15)	2910(11)	110(3)
C(527)	4050(3)	2630(3)	4440(2)	150(3)
C(532)	2877(15)	430(2)	1631(14)	110(2)
C(533)	2743(15)	124(13)	1260(2)	130(3)
C(534)	3030(2)	-195(15)	946(13)	240(7)
C(535)	3450(2)	290(2)	1000(2)	800(3)
C(536)	3580(2)	840(2)	1370(2)	120(2)
C(531)	3300(2)	913(12)	1688(14)	110(2)
C(537)	2170(3)	-670(3)	1220(3)	200(5)
C(612)	198(13)	-529(14)	582(15)	120(3)
C(613)	50(2)	-990(2)	696(15)	460(2)
C(614)	-530(2)	-1420(2)	410(2)	110(2)
C(615)	-953(14)	-1400(15)	0(2)	140(3)
C(616)	-807(14)	-940(2)	-110(2)	130(3)
C(611)	-230(2)	-508(14)	180(2)	110(2)
C(617)	370(5)	-1170(4)	950(4)	430(10)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

Table 98.
Bond lengths [Å] and angles [°] for
($Ag_4I_4(P(m\text{-tolyl})_3)_4$) **(XVIII)**

I(1)-Ag(4)	2.953(6)	C(325)-C(326)	1.39
I(1)-Ag(2)	2.958(6)	C(326)-C(321)	1.39
I(1)-Ag(1)	2.966(6)	C(332)-C(333)	1.39
I(2)-Ag(1)	2.894(6)	C(332)-C(331)	1.39
I(2)-Ag(2)	2.947(6)	C(333)-C(334)	1.39
I(2)-Ag(3)	2.957(5)	C(333)-C(337)	1.54(8)
I(3)-Ag(2)	2.903(6)	C(334)-C(335)	1.39
I(3)-Ag(4)	2.940(6)	C(335)-C(336)	1.39
I(3)-Ag(3)	2.962(5)	C(336)-C(331)	1.39
I(4)-Ag(4)	2.913(6)	C(412)-C(413)	1.39
I(4)-Ag(1)	2.939(6)	C(412)-C(411)	1.39
I(4)-Ag(3)	2.964(5)	C(413)-C(414)	1.39
I(5)-Ag(5)^{1}	2.902(5)	C(413)-C(417)	1.47(7)
I(5)-Ag(5)	2.940(6)	C(414)-C(415)	1.39
I(5)-Ag(6)	2.957(4)	C(415)-C(416)	1.39
I(6)-Ag(5)^{2}	2.956(7)	C(416)-C(411)	1.39
I(6)-Ag(5)^{1}	2.956(7)	C(422)-C(423)	1.39
I(6)-Ag(5)	2.956(7)	C(422)-C(421)	1.39
Ag(1)-P(1)	2.480(13)	C(423)-C(424)	1.39
Ag(2)-P(2)	2.49(2)	C(423)-C(427)	1.61(15)
Ag(3)-P(3)	2.503(13)	C(424)-C(425)	1.39
Ag(4)-P(4)	2.488(14)	C(425)-C(426)	1.39
Ag(5)-P(5)	2.485(14)	C(426)-C(421)	1.39
Ag(5)-I(5)^{2}	2.902(5)	C(432)-C(433)	1.39
Ag(6)-P(6)	2.55(2)	C(432)-C(431)	1.39
Ag(6)-I(5)^{1}	2.957(4)	C(433)-C(434)	1.39
Ag(6)-I(5)^{2}	2.957(4)	C(433)-C(437)	1.43(15)
P(1)-C(131)	1.81(3)	C(434)-C(435)	1.39
P(1)-C(121)	1.92(3)	C(435)-C(436)	1.39
P(1)-C(111)	1.97(3)	C(436)-C(431)	1.39
P(2)-C(211)	1.85(3)	C(512)-C(513)	1.39
P(2)-C(221)	1.86(3)	C(512)-C(511)	1.39
P(2)-C(231)	1.88(4)	C(513)-C(517)	1.35(9)
P(3)-C(311)	1.82(2)	C(513)-C(514)	1.39
P(3)-C(321)	1.88(3)	C(514)-C(515)	1.39
P(3)-C(331)	1.88(2)	C(515)-C(516)	1.39
P(4)-C(411)	1.88(3)	C(516)-C(511)	1.39
P(4)-C(421)	1.87(3)	C(522)-C(523)	1.39
P(4)-C(431)	1.90(4)	C(522)-C(521)	1.39
P(5)-C(511)	1.78(4)	C(523)-C(524)	1.39
P(5)-C(521)	1.85(3)	C(523)-C(527)	1.66(6)
P(5)-C(531)	1.91(3)	C(524)-C(525)	1.39

Table 98. (cont.)
Bond lengths [Å] and angles [^{o}] for
(Ag$_4$I$_4$(P(*m*-tolyl)$_3$)$_4$) **(XVIII)**

P(6)-C(611)	1.78(3)	C(525)-C(526)	1.39
P(6)-C(611)'	1.78(5)	C(526)-C(521)	1.39
P(6)-C(611)"	1.78(5)	C(532)-C(533)	1.39
C(112)-C(113)	1.39	C(532)-C(531)	1.39
C(112)-C(111)	1.39	C(533)-C(534)	1.39
C(113)-C(114)	1.39	C(533)-C(537)	1.76(9)
C(113)-C(117)	1.60(6)	C(534)-C(535)	1.39
C(114)-C(115)	1.39	C(535)-C(536)	1.39
C(115)-C(116)	1.39	C(536)-C(531)	1.39
C(116)-C(111)	1.39	C(612)-C(613)	1.39
C(122)-C(123)	1.39	C(612)-C(611)	1.39
C(122)-C(121)	1.39	C(613)-C(617)	1.30(12)
C(123)-C(124)	1.39	C(613)-C(614)	1.39
C(123)-C(127)	1.51(7)	C(614)-C(615)	1.39
C(124)-C(125)	1.39	C(615)-C(616)	1.39
C(125)-C(126)	1.39	C(616)-C(611)	1.39
C(126)-C(121)	1.39	Ag(4)-I(1)-Ag(2)	70.67(15)
C(132)-C(133)	1.39	Ag(4)-I(1)-Ag(1)	70.59(15)
C(132)-C(131)	1.39	Ag(2)-I(1)-Ag(1)	70.73(15)
C(133)-C(134)	1.39	Ag(1)-I(2)-Ag(2)	71.88(15)
C(133)-C(137)	1.39(12)	Ag(1)-I(2)-Ag(3)	81.49(15)
C(134)-C(135)	1.39	Ag(2)-I(2)-Ag(3)	80.81(14)
C(135)-C(136)	1.39	Ag(2)-I(3)-Ag(4)	71.61(15)
C(136)-C(131)	1.39	Ag(2)-I(3)-Ag(3)	81.46(15)
C(212)-C(213)	1.39	Ag(4)-I(3)-Ag(3)	80.73(15)
C(212)-C(211)	1.39	Ag(4)-I(4)-Ag(1)	71.51(15)
C(213)-C(217)	1.20(10)	Ag(4)-I(4)-Ag(3)	81.14(15)
C(213)-C(214)	1.39	Ag(1)-I(4)-Ag(3)	80.63(15)
C(214)-C(215)	1.39	Ag(5)^1-I(5)-Ag(5)	71.3(2)
C(214)-C(217)	1.68(13)	Ag(5)^1-I(5)-Ag(6)	81.0 (2)
C(215)-C(216)	1.39	Ag(5)-I(5)-Ag(6)	80.41(15)
C(216)-C(211)	1.39	Ag(5)^2-I(6)-Ag(5)^1	70.3(2)
C(222)-C(223)	1.39	Ag(5)^2-I(6)-Ag(5)	70.3(2)
C(222)-C(221)	1.39	Ag(5)^1-I(6)-Ag(5)	70.3(2)
C(223)-C(227)	1.37(8)	P(1)-Ag(1)-I(2)	118.9(3)
C(223)-C(224)	1.39	P(1)-Ag(1)-I(4)	112.9(4)
C(224)-C(225)	1.39	I(2)-Ag(1)-I(4)	98.5 (2)
C(225)-C(226)	1.39	P(1)-Ag(1)-I(1)	111.2(4)
C(226)-C(221)	1.39	I(2)-Ag(1)-I(1)	107.5(2)
C(232)-C(233)	1.39	I(4)-Ag(1)-I(1)	106.6 (2)
C(232)-C(231)	1.39	P(2)-Ag(2)-I(3)	119.8(4)
C(233)-C(234)	1.390(1)	P(2)-Ag(2)-I(2)	111.9(4)

Table 98. (cont.)
Bond lengths [Å] and angles [°] for
(Ag$_4$I$_4$(P(*m*-tolyl)$_3$)$_4$) **(XVIII)**

C(233)-C(237)	1.60(7)	I(3)-Ag(2)-I(2)	98.3(2)
C(234)-C(235)	1.39	P(2)-Ag(2)-I(1)	111.6(4)
C(235)-C(236)	1.39	I(3)-Ag(2)-I(1)	107.5(2)
C(236)-C(231)	1.39	I(2)-Ag(2)-I(1)	106.3(2)
C(312)-C(313)	1.39	P(3)-Ag(3)-I(2)	120.2(3)
C(312)-C(311)	1.39	P(3)-Ag(3)-I(3)	121.1(3)
C(313)-C(314)	1.39	I(2)-Ag(3)-I(3)	96.80(2)
C(313)-C(317)	1.50(6)	P(3)-Ag(3)-I(4)	119.8(3)
C(314)-C(315)	1.39	I(2)-Ag(3)-I(4)	96.57(15)
C(315)-C(316)	1.39	I(3)-Ag(3)-I(4)	96.87(15)
C(316)-C(311)	1.39	P(4)-Ag(4)-I(4)	119.5(4)
C(322)-C(323)	1.39	P(4)-Ag(4)-I(3)	111.2(4)
C(322)-C(321)	1.39	I(4)-Ag(4)-I(3)	98.5(2)
C(323)-C(324)	1.39	P(4)-Ag(4)-I(1)	112.0(4)
C(323)-C(327)	1.44(13)	I(4)-Ag(4)-I(1)	107.7(2)
C(324)-C(325)	1.39	C(114)-C(113)-C(117)	138(4)
I(3)-Ag(4)-I(1)	106.7(2)	C(115)-C(114)-C(113)	120
P(5)-Ag(5)-I(5)^{2}	119.2(4)	C(114)-C(115)-C(116)	120
P(5)-Ag(5)-I(5)	111.8(4)	C(111)-C(116)-C(115)	120
I(5)^{2}-Ag(5)-I(5)	98.6(2)	C(116)-C(111)-C(112)	120
P(5)-Ag(5)-I(6)	111.3(4)	C(116)-C(111)-P(1)	116(3)
I(5)-Ag(5)-I(6)	107.9(2)	C(112)-C(111)-P(1)	123(3)
I(5)-Ag(5)-I(6)	106.9(2)	C(123)-C(122)-C(121)	120
P(6)-Ag(6)-I(5)^{1}	120.12(14)	C(122)-C(123)-C(124)	120
P(6)-Ag(6)-I(5)	120.12(14)	C(122)-C(123)-C(127)	120(4)
I(5)^{1}-Ag(6)-I(5)	97.0(2)	C(124)-C(123)-C(127)	120(4)
P(6)-Ag(6)-I(5)^{2}	120.12(14)	C(125)-C(124)-C(123)	120
I(5)^{1}-Ag(6)-I(5)^{2}	7.0(2)	C(124)-C(125)-C(126)	120
I(5)-Ag(6)-I(5)^{2}	7.0(2)	C(125)-C(126)-C(121)	120
C(131)-P(1)-C(121)	105(2)	C(126)-C(121)-C(122)	120
C(131)-P(1)-C(111)	107(2)	C(126)-C(121)-P(1)	124(2)
C(121)-P(1)-C(111)	101(2)	C(122)-C(121)-P(1)	116(2)
C(131)-P(1)-Ag(1)	116.9(15)	C(133)-C(132)-C(131)	120
C(121)-P(1)-Ag(1)	113.0(14)	C(134)-C(133)-C(132)	120
C(111)-P(1)-Ag(1)	112.5(13)	C(134)-C(133)-C(137)	105(5)
C(211)-P(2)-C(221)	104(2)	C(132)-C(133)-C(137)	134(5)
C(211)-P(2)-C(231)	108(2)	C(135)-C(134)-C(133)	120
C(221)-P(2)-C(231)	99(2)	C(134)-C(135)-C(136)	120
C(211)-P(2)-Ag(2)	112.2(14)	C(135)-C(136)-C(131)	120
C(221)-P(2)-Ag(2)	118.5(13)	C(136)-C(131)-C(132)	120
C(231)-P(2)-Ag(2)	114.5(15)	C(136)-C(131)-P(1)	115(3)
C(311)-P(3)-C(321)	103.3(14)	C(132)-C(131)-P(1)	124(3)

Table 98. (cont.)
Bond lengths [Å] and angles [°] for
($Ag_4I_4(P(m\text{-tolyl})_3)_4$) **(XVIII)**

C(311)-P(3)-C(331)	104.8(14)	C(213)-C(212)-C(211)	120
C(321)-P(3)-C(331)	106(2)	C(217)-C(213)-C(214)	81(8)
C(311)-P(3)-Ag(3)	116.0(11)	C(217)-C(213)-C(212)	152(7)
C(321)-P(3)-Ag(3)	116.2(10)	C(214)-C(213)-C(212)	120
C(331)-P(3)-Ag(3)	109.5(11)	C(215)-C(214)-C(213)	120
C(411)-P(4)-C(421)	111(2)	C(215)-C(214)-C(217)	158(3)
C(411)-P(4)-C(431)	98.1(15)	C(213)-C(214)-C(217)	45(5)
C(421)-P(4)-C(431)	110(2)	C(214)-C(215)-C(216)	120
C(411)-P(4)-Ag(4)	116.9(13)	C(215)-C(216)-C(211)	120
C(421)-P(4)-Ag(4)	105.2(15)	C(216)-C(211)-C(212)	120
C(431)-P(4)-Ag(4)	116.3(13)	C(216)-C(211)-P(2)	121(2)
C(511)-P(5)-C(521)	108(2)	C(212)-C(211)-P(2)	119(2)
C(511)-P(5)-C(531)	104(2)	C(213)-C(217)-C(214)	55(5)
C(521)-P(5)-C(531)	99.4(15)	C(223)-C(222)-C(221)	120
C(511)-P(5)-Ag(5)	113(2)	C(227)-C(223)-C(224)	116(4)
C(521)-P(5)-Ag(5)	118.0(13)	C(227)-C(223)-C(222)	124(4)
C(531)-P(5)-Ag(5)	112.8(13)	C(224)-C(223)-C(222)	120
C(611)-P(6)-C(611)^1	101(3)	C(225)-C(224)-C(223)	120
C(611)-P(6)-C(611)^2	101(3)	C(224)-C(225)-C(226)	120
C(611)^1-P(6)-C(611)^2	101(3)	C(221)-C(226)-C(225)	120
C(611)-P(6)-Ag(6)	116.6(15)	C(226)-C(221)-C(222)	120
C(611)^1-P(6)-Ag(6)	117(3)	C(226)-C(221)-P(2)	130(2)
C(611)^2-P(6)-Ag(6)	117(3)	C(222)-C(221)-P(2)	110(2)
C(113)-C(112)-C(111)	120	C(233)-C(232)-C(231)	120.00(6)
C(112)-C(113)-C(114)	120	C(234)-C(233)-C(232)	120
C(112)-C(113)-C(117)	102(4)	C(234)-C(233)-C(237)	135(4)
C(432)-C(431)-P(4)	121(3)	C(232)-C(233)-C(237)	104(5)
C(513)-C(512)-C(511)	120	C(233)-C(234)-C(235)	120
C(517)-C(513)-C(514)	107(5)	C(236)-C(235)-C(234)	120
C(517)-C(513)-C(512)	133(5)	C(235)-C(236)-C(231)	120
C(514)-C(513)-C(512)	120	C(236)-C(231)-C(232)	120
C(513)-C(514)-C(515)	120	C(236)-C(231)-P(2)	118(3)
C(516)-C(515)-C(514)	120	C(232)-C(231)-P(2)	122(3)
C(511)-C(516)-C(515)	120	C(313)-C(312)-C(311)	120
C(516)-C(511)-C(512)	120	C(314)-C(313)-C(312)	120
C(516)-C(511)-P(5)	123(4)	C(314)-C(313)-C(317)	120(3)
C(512)-C(511)-P(5)	117(4)	C(312)-C(313)-C(317)	120(3)
C(523)-C(522)-C(521)	120	C(315)-C(314)-C(313)	120
C(524)-C(523)-C(522)	120	C(316)-C(315)-C(314)	120
C(524)-C(523)-C(527)	114(3)	C(315)-C(316)-C(311)	120
C(522)-C(523)-C(527)	125(3)	C(316)-C(311)-C(312)	120
C(523)-C(524)-C(525)	120	C(316)-C(311)-P(3)	126(2)

Table 98. (cont.)
Bond lengths [Å] and angles [°] for
(Ag_4I_4(P(*m*-tolyl)$_3$)$_4$) **(XVIII)**

C(524)-C(525)-C(526)	120	C(312)-C(311)-P(3)	114(2)
C(525)-C(526)-C(521)	120	C(323)-C(322)-C(321)	120
C(526)-C(521)-C(522)	120	C(322)-C(323)-C(324)	120
C(526)-C(521)-P(5)	131(2)	C(322)-C(323)-C(327)	120(4)
C(522)-C(521)-P(5)	109(2)	C(324)-C(323)-C(327)	120(4)
C(533)-C(532)-C(531)	120	C(325)-C(324)-C(323)	120
C(532)-C(533)-C(534)	120	C(324)-C(325)-C(326)	120
C(532)-C(533)-C(537)	112(3)	C(321)-C(326)-C(325)	120
C(534)-C(533)-C(537)	128(4)	C(326)-C(321)-C(322)	120
C(535)-C(534)-C(533)	120	C(326)-C(321)-P(3)	124(2)
C(534)-C(535)-C(536)	120	C(322)-C(321)-P(3)	116(2)
C(531)-C(536)-C(535)	120	C(333)-C(332)-C(331)	120
C(536)-C(531)-C(532)	120	C(332)-C(333)-C(334)	120
C(536)-C(531)-P(5)	120(3)	C(332)-C(333)-C(337)	110(4)
C(532)-C(531)-P(5)	120(3)	C(334)-C(333)-C(337)	130(4)
C(613)-C(612)-C(611)	120	C(335)-C(334)-C(333)	120
C(617)-C(613)-C(612)	131(4)	C(334)-C(335)-C(336)	120
C(617)-C(613)-C(614)	107(5)	C(331)-C(336)-C(335)	120
C(612)-C(613)-C(614)	120	C(336)-C(331)-C(332)	120
C(615)-C(614)-C(613)	120	C(336)-C(331)-P(3)	118(2)
C(614)-C(615)-C(616)	120	C(332)-C(331)-P(3)	121(2)
C(611)-C(616)-C(615)	120	C(413)-C(412)-C(411)	120
C(616)-C(611)-C(612)	120	C(414)-C(413)-C(412)	120
C(616)-C(611)-P(6)	130(2)	C(414)-C(413)-C(417)	113(4)
C(612)-C(611)-P(6)	109(2)	C(412)-C(413)-C(417)	127(4)
C(424)-C(425)-C(426)	120	C(415)-C(414)-C(413)	120
C(425)-C(426)-C(421)	120	C(414)-C(415)-C(416)	120
C(426)-C(421)-C(422)	120	C(411)-C(416)-C(415)	120
C(426)-C(421)-P(4)	124(2)	C(416)-C(411)-C(412)	120
C(422)-C(421)-P(4)	116(2)	C(416)-C(411)-P(4)	128(2)
C(433)-C(432)-C(431)	120	C(412)-C(411)-P(4)	112(2)
C(434)-C(433)-C(432)	120	C(423)-C(422)-C(421)	120
C(434)-C(433)-C(437)	130(5)	C(424)-C(423)-C(422)	120
C(432)-C(433)-C(437)	110(5)	C(424)-C(423)-C(427)	132(4)
C(435)-C(434)-C(433)	120	C(422)-C(423)-C(427)	108(4)
C(436)-C(435)-C(434)	120	C(425)-C(424)-C(423)	120
C(435)-C(436)-C(431)	120	C(436)-C(431)-C(432)	120
C(436)-C(431)-P(4)	119(3)		

Symmetry transformations used to generate equivalent atoms:
1= y,z,x 2= z,x,y

Table 99.
Anisotropic displacement parameters ($Å^2$ x 10^3) for $(Ag_4I_4(P(m\text{-tolyl})_3)_4)$ **(XVIII)**

atom	U11	U22	U33	U23	U13	U12
I(1)	86(2)	89(2)	84(3)	45(2)	45(2)	47(2)
I(2)	102(3)	87(2)	88(3)	44(2)	48(2)	56(2)
I(3)	80(2)	98(3)	92(3)	53(2)	41(2)	48(2)
I(4)	89(2)	82(2)	86(3)	38(2)	45(2)	37(2)
I(5)	93(3)	91(3)	100(3)	57(2)	49(2)	52(2)
I(6)	85(3)	85(3)	85(3)	42(4)	42(4)	42(4)
Ag(1)	94(3)	109(4)	110(4)	60(3)	52(3)	47(3)
Ag(2)	112(4)	91(3)	102(3)	42(3)	56(3)	47(3)
Ag(3)	89(3)	93(3)	88(3)	49(3)	45(3)	46(3)
Ag(4)	108(3)	114(4)	108(4)	61(3)	51(3)	70(3)
Ag(5)	112(4)	118(4)	105(3)	61(3)	55(3)	72(3)
Ag(6)	90(4)	90(4)	90(4)	45(4)	45(4)	45(4)
P(1)	55(8)	71(9)	74(9)	35(9)	18(8)	18(8)
P(2)	88(10)	74(9)	95(11)	37(10)	46(10)	32(9)
P(3)	48(7)	60(8)	74(9)	30(8)	23(8)	3(7)
P(4)	94(11)	97(11)	85(10)	50(10)	52(10)	57(10)
P(5)	71(10)	71(10)	71(10)	36(12)	36(12)	36(12)
C(112)	540(2)	190(7)	250(9)	200(8)	350(12)	250(10)
C(113)	160(6)	270(10)	170(7)	200(8)	110(6)	120(7)
C(114)	50(4)	150(7)	220(9)	160(7)	30(5)	30(4)
C(115)	60(4)	80(5)	70(4)	-10(4)	-80(4)	-80(4)
C(116)	50(3)	60(4)	60(4)	-10(3)	-20(3)	-40(4)
C(111)	70(4)	140(6)	150(6)	130(6)	40(4)	20(4)
C(117)	170(6)	100(4)	100(4)	-110(4)	120(5)	-160(4)
C(122)	120(5)	190(6)	130(5)	160(6)	50(4)	50(5)
C(123)	200(9)	220(9)	80(5)	70(6)	10(6)	140(9)
C(124)	230(9)	220(8)	80(4)	70(5)	50(5)	210(8)
C(125)	100(5)	80(4)	80(4)	-10(4)	50(5)	-80(4)
C(126)	270(9)	90(4)	210(7)	100(5)	220(8)	120(6)
C(121)	140(5)	60(3)	70(4)	10(3)	90(4)	10(4)
C(127)	220(9)	110(6)	200(9)	100(7)	-110(8)	-20(7)
C(132)	110(5)	80(4)	160(6)	40(5)	80(5)	60(4)
C(133)	0(3)	120(5)	160(7)	-80(6)	20(4)	-30(3)
C(134)	10(4)	240(13)	500(2)	140(14)	40(7)	30(6)
C(135)	40(4)	90(5)	170(8)	-120(6)	-80(6)	-70(5)

Table 99. (cont.)
Anisotropic displacement parameters (Å^2 x 10^3) for (Ag$_4$I$_4$(P(*m*-tolyl)$_3$)$_4$) **(XVIII)**

atom	U11	U22	U33	U23	U13	U12
C(136)	270(10)	110(5)	330(13)	60(7)	190(10)	170(7)
C(131)	50(3)	110(5)	110(5)	40(5)	-20(4)	50(4)
C(137)	0(3)	700(3)	1200(4)	900(3)	20(9)	10(7)
C(212)	90(4)	360(13)	70(4)	80(6)	-20(4)	150(7)
C(213)	50(5)	700(3)	310(14)	400(2)	-20(7)	-10(10)
C(214)	80(7)	600(3)	500(2)	600(2)	-120(10)	160(11)
C(215)	90(4)	190(7)	190(7)	120(6)	-20(5)	120(5)
C(216)	190(8)	130(6)	480(2)	170(9)	250(11)	140(6)
C(211)	60(3)	80(4)	120(5)	70(4)	-10(4)	10(4)
C(217)	270(13)	210(11)	200(14)	0(13)	-180(13)	-40(11)
C(222)	170(6)	140(6)	90(4)	90(4)	90(5)	130(6)
C(223)	90(5)	0(2)	110(5)	-30(3)	30(5)	-60(3)
C(224)	0(2)	350(14)	220(10)	230(11)	-70(4)	-90(5)
C(225)	160(6)	70(4)	60(3)	-20(3)	10(4)	90(5)
C(226)	60(3)	0(18)	50(3)	-40(2)	-10(3)	-20(2)
C(221)	130(5)	190(6)	60(3)	100(4)	70(4)	100(5)
C(227)	240(10)	180(8)	190(8)	90(7)	130(8)	170(8)
C(232)	70(4)	140(7)	90(5)	-20(5)	60(4)	10(5)
C(233)	160(8)	110(6)	120(6)	20(5)	100(6)	60(6)
C(234)	130(6)	150(6)	220(9)	100(7)	150(7)	50(6)
C(235)	70(4)	100(6)	240(11)	0(7)	90(6)	20(5)
C(236)	80(5)	40(3)	100(5)	-20(4)	10(5)	-50(4)
C(231)	100(5)	30(3)	150(7)	-30(5)	-130(5)	-110(4)
C(312)	30(2)	40(2)	30(2)	20(2)	-10(2)	0(2)
C(313)	60(3)	40(3)	30(2)	-20(3)	-40(3)	0(3)
C(314)	140(5)	120(5)	210(8)	100(5)	150(6)	110(5)
C(315)	50(3)	280(10)	250(9)	220(10)	0(5)	70(5)
C(316)	100(4)	40(3)	80(4)	0(3)	10(4)	40(3)
C(311)	30(2)	40(3)	50(3)	-30(3)	10(3)	0(2)
C(317)	110(4)	100(4)	150(5)	110(5)	80(5)	60(4)
C(322)	160(7)	360(12)	350(12)	340(12)	200(8)	190(8)
C(323)	240(9)	0(3)	100(5)	-80(3)	-240(6)	0(5)
C(324)	200(8)	40(3)	20(3)	-10(3)	30(4)	50(5)
C(325)	160(6)	120(5)	180(7)	90(6)	130(6)	110(6)
C(326)	110(5)	120(5)	180(7)	130(6)	100(5)	50(5)

Table 99. (cont.)
Anisotropic displacement parameters (Å^2 x 10^3) for (Ag$_4$L$_4$(P(*m*-tolyl)$_3$)$_4$) **(XVIII)**

atom	U11	U22	U33	U23	U13	U12
C(321)	40(2)	60(3)	60(3)	60(3)	0(2)	-10(2)
C(327)	600(2)	470(2)	200(8)	-300(10)	-410(11)	490(2)
C(332)	60(3)	40(3)	10(2)	-70(2)	-60(2)	0(3)
C(333)	0(2)	50(3)	120(5)	10(4)	-20(3)	-30(2)
C(334)	150(7)	60(4)	80(4)	10(4)	60(5)	10(4)
C(335)	260(9)	70(4)	210(8)	120(5)	190(8)	90(6)
C(336)	50(3)	100(4)	90(4)	30(4)	10(3)	50(3)
C(331)	60(3)	110(4)	110(4)	110(4)	50(3)	40(3)
C(337)	190(9)	1000(4)	220(10)	360(2)	50(8)	350(2)
C(412)	90(4)	80(4)	120(5)	60(4)	80(4)	40(4)
C(413)	30(3)	20(2)	90(4)	-50(3)	-30(3)	-20(3)
C(414)	200(9)	60(4)	80(4)	10(4)	50(6)	20(5)
C(415)	20(2)	70(4)	120(6)	30(5)	-40(3)	-40(3)
C(416)	180(6)	110(5)	220(7)	120(5)	180(7)	120(5)
C(411)	140(5)	210(7)	240(8)	200(7)	180(6)	140(5)
C(417)	190(8)	150(8)	40(4)	-130(5)	-220(5)	-60(8)
C(422)	40(3)	70(4)	50(3)	10(3)	-30(3)	-20(3)
C(423)	340(12)	170(8)	600(2)	310(12)	430(15)	220(9)
C(424)	50(4)	380(16)	80(5)	-30(8)	30(5)	-30(7)
C(425)	600(2)	800(3)	50(4)	150(10)	70(8)	600(2)
C(426)	80(5)	160(8)	150(8)	-210(6)	-130(6)	200(6)
C(421)	220(9)	90(5)	180(7)	50(6)	170(8)	50(6)
C(427)	1200(4)	50(4)	1400(5)	200(13)	1300(4)	260(12)
C(432)	90(5)	60(4)	90(6)	-40(5)	-160(5)	-40(5)
C(433)	150(7)	190(9)	30(4)	50(5)	-120(5)	30(7)
C(434)	900(3)	800(2)	50(5)	-20(10)	-80(10)	800(3)
C(435)	800(3)	230(9)	280(12)	80(9)	400(18)	410(15)
C(436)	0(2)	70(4)	60(3)	-70(3)	-70(3)	-70(3)
C(431)	30(3)	0(2)	60(3)	-90(2)	-110(3)	-30(2)
C(437)	1100(4)	1100(4)	260(14)	300(2)	300(2)	1100(4)
C(512)	150(6)	140(6)	410(13)	200(8)	240(9)	100(5)
C(513)	160(8)	40(4)	70(4)	-100(3)	0(5)	20(5)
C(514)	330(14)	60(4)	470(2)	60(8)	380(15)	90(7)
C(515)	220(11)	100(6)	190(9)	-240(7)	-250(8)	10(8)
C(516)	280(13)	90(6)	270(11)	-230(7)	-210(10)	150(8)
C(511)	160(7)	210(8)	160(7)	0(7)	70(7)	170(7)

Table 99. (cont.)
Anisotropic displacement parameters ($Å^2 \times 10^3$) for $(Ag_4I_4(P(m\text{-tolyl})_3)_4)$ **(XVIII)**

atom	U11	U22	U33	U23	U13	U12
C(522)	40(3)	90(4)	80(4)	50(4)	-30(3)	-110(3)
C(523)	390(11)	130(5)	470(14)	210(8)	420(12)	210(7)
C(524)	400(14)	40(3)	10(2)	-30(3)	60(5)	40(6)
C(525)	50(3)	50(4)	150(6)	40(4)	-100(4)	-30(3)
C(526)	40(3)	60(3)	70(3)	-10(3)	-10(3)	20(3)
C(521)	120(5)	200(7)	20(2)	20(3)	20(3)	130(5)
C(527)	150(6)	120(5)	10(2)	30(3)	-60(3)	30(5)
C(532)	70(4)	70(4)	50(3)	10(4)	-60(3)	-10(4)
C(533)	90(4)	10(2)	70(4)	0(3)	-100(4)	-40(3)
C(534)	380(14)	320(12)	0(2)	-10(4)	20(5)	310(13)
C(535)	240(12)	240(13)	1100(5)	500(2)	-400(2)	-60(10)
C(536)	220(7)	200(7)	140(5)	160(6)	130(6)	170(6)
C(531)	130(5)	100(5)	70(4)	30(4)	0(4)	90(5)
C(537)	180(7)	200(8)	100(5)	-10(6)	-50(5)	180(7)
C(612)	130(6)	40(3)	100(4)	-10(3)	90(5)	-40(3)
C(613)	150(8)	34(2)	400(2)	-200(2)	190(12)	20(11)
C(614)	140(5)	170(6)	160(6)	160(6)	120(5)	110(5)
C(615)	90(4)	130(6)	240(8)	140(6)	90(6)	30(4)
C(616)	90(4)	80(4)	210(8)	50(5)	110(5)	20(4)
C(611)	160(6)	220(7)	120(4)	140(5)	90(4)	180(6)
C(617)	700(2)	200(8)	590(16)	120(10)	68(2)	80(12)

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

Table 100.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for ($Ag_4L_4(P(\textit{m}\text{-tolyl})_3)_4$) **(XVIII)**

atom	x	y	z	U(eq)
H(11A)	5256	-567	637	80
H(11B)	6545	-713	1668	80
H(11C)	6447	-1406	840	80
H(11D)	5755	-1679	-90	80
H(11E)	6087	17	2033	80
H(11F)	5895	225	1589	80
H(11G)	5430	-292	1566	80
H(12A)	4322	-983	-1255	80
H(12B)	5604	496	-940	80
H(12C)	6304	384	-318	80
H(12D)	6012	-410	-166	80
H(12E)	4069	-469	-1704	80
H(12F)	4479	206	-1325	80
H(12G)	4521	-151	-1855	80
H(13A)	5452	-1461	-1299	80
H(13B)	4913	-3180	-2204	80
H(13C)	4415	-3375	-1708	80
H(13D)	4435	-2614	-1008	80
H(13E)	5342	-2746	-2334	80
H(13F)	5380	-2204	-2399	80
H(13G)	5918	-2145	-1921	80
H(21A)	1184	-4350	-3668	80
H(21B)	-135	-4000	-4141	80
H(21C)	164	-3439	-3159	80
H(21D)	973	-3333	-2431	80
H(21E)	427	-4426	-4607	80
H(21F)	-161	-4476	-4660	80
H(21G)	359	-3873	-4441	80
H(22A)	2675	-3297	-2541	80
H(22B)	2919	-4544	-3493	80
H(22C)	2102	-5265	-3602	80
H(22D)	1572	-5002	-3180	80
H(22E)	3497	-3644	-3190	80
H(22F)	3213	-3249	-3150	80
H(22G)	3626	-3205	-2583	80
H(23A)	2215	-4180	-1604	80
H(23B)	777	-5492	-1894	80
H(23C)	188	-5385	-2622	80

Table 100. (cont.)
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for ($Ag_4L_4(P(m\text{-tolyl})_3)_4$) **(XVIII)**

atom	x	y	z	U(eq)
H(23D)	613	-4676	-2841	80
H(23E)	2436	-4500	-1127	80
H(23F)	2070	-4810	-898	80
H(23G)	2106	-5180	-1428	80
H(31A)	3159	-2897	456	80
H(31B)	4172	-3060	1742	80
H(31C)	4261	-2241	2441	80
H(31D)	3800	-1750	2149	80
H(31E)	3810	-3711	800	80
H(31F)	3192	-3884	340	80
H(31G)	3747	-3482	359	80
H(32A)	3955	-844	1404	80
H(32B)	4093	270	2871	80
H(32C)	3312	-496	2758	80
H(32D)	2853	-1436	1969	80
H(32E)	4742	602	2582	80
H(32F)	4902	151	2281	80
H(32G)	4472	286	1906	80
H(33A)	1888	-2171	230	80
H(33B)	826	-3077	674	80
H(33C)	1596	-3125	1281	80
H(33D)	2512	-2695	1363	80
H(33E)	495	-2648	-27	80
H(33F)	1008	-2078	117	80
H(33G)	872	-2685	-326	80
H(41A)	2081	-1603	-2203	80
H(41B)	620	-1814	-3409	80
H(41C)	686	-1028	-2691	80
H(41D)	1450	-529	-1729	80
H(41E)	1573	-2325	-3243	80
H(41F)	902	-2566	-3508	80
H(41G)	1248	-2186	-3703	80
H(42A)	2628	-89	-1752	80
H(42B)	4329	1164	-862	80
H(42C)	4517	851	-179	80
H(42D)	3761	68	-283	80
H(42E)	2785	403	-2131	80

Table 100. (cont.)
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for ($Ag_4I_4(P(m\text{-tolyl})_3)_4$) **(XVIII)**

atom	x	y	z	U(eq)
H(42F)	3182	1064	-1662	80
H(42G)	3384	765	-2069	80
H(43A)	1578	-1171	-857	80
H(43B)	1763	233	402	80
H(43C)	2474	853	301	80
H(43D)	2737	461	-379	80
H(43E)	1089	-1347	-520	80
H(43F)	1217	-964	106	80
H(43G)	804	-957	-423	80
H(51A)	4699	2299	2840	80
H(51B)	5181	3216	2070	80
H(51C)	4201	2784	1373	80
H(51D)	3471	2110	1409	80
H(51E)	5742	3288	2663	80
H(51F)	5608	3473	3171	80
H(51G)	5856	3048	3093	80
H(52A)	3627	2294	3222	80
H(52B)	4611	2052	4450	80
H(52C)	4659	1370	3738	80
H(52D)	4191	1150	2768	80
H(52E)	4291	2667	4799	80
H(52F)	4148	3006	4482	80
H(52G)	3649	2425	4334	80
H(53A)	2679	478	1847	80
H(53B)	2937	-577	690	80
H(53C)	3645	240	786	80
H(53D)	3870	1176	1413	80
H(53E)	2037	-517	1477	80
H(53F)	1852	-879	824	80
H(53G)	2291	-922	1302	80
H(61A)	596	-227	783	80
H(61B)	-626	-1735	484	80
H(61C)	-1351	-1701	-199	80
H(61D)	-1103	-930	-391	80
H(61E)	130	-1506	939	80
H(61F)	592	-1249	770	80
H(61G)	628	-856	1341	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

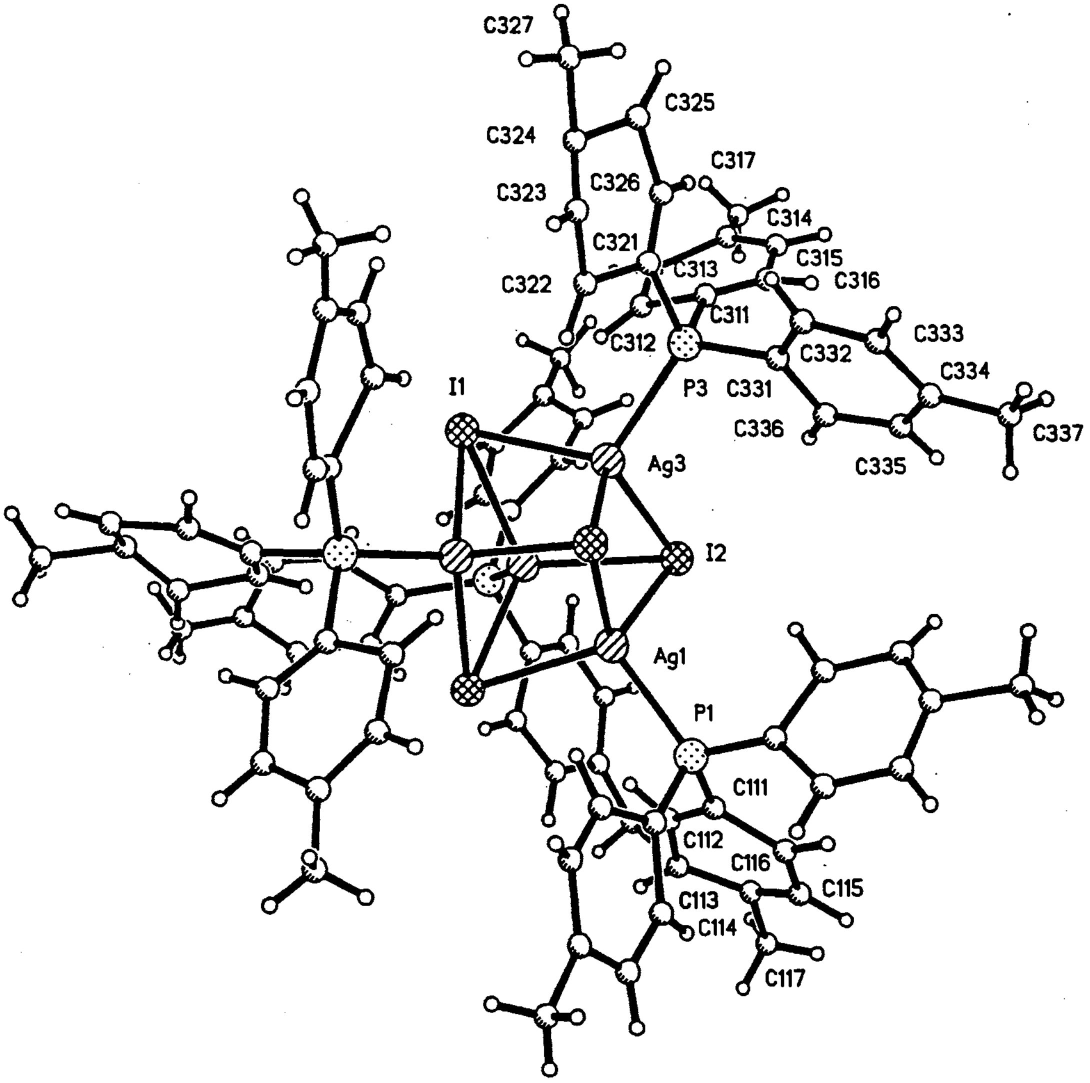


Figure 37. Projection View of $Ag_4I_4(P(p\text{-tolyl})_3)_4$ **(XIX)**

Table 101.
Crystal data and structure refinement for $Ag_4I_4(P(p\text{-tolyl})_3)_4$ **(XIX)**

Empirical formula	C_{84} H_{84} Ag_4 I_4 P_4
Formula weight	2156.47
Temperature	293(2) K
Wavelength	0.71073Å
Crystal system, space group	Trigonal, R-3
Unit cell dimensions	a = 20.486(11) Å α = 50.31(2)°
	b = 20.486(11) Å β = 50.31(2)°
	c = 20.486(11) Å γ = 50.31(2)°
Volume	4688(4) $Å^3$
Z, Calculated density	2, 1.582 Mg/m^3
Absorption coefficient	2.245 mm^{-1}
F(000)	2096
Theta range for data collection	2.34 to 20.81^0.
Index ranges	$-19\leq h\leq 10, -20\leq k\leq 0, -19\leq l\leq 10$
Reflections collected / unique	3919 / 3210 [R(int) = 0.2061]
Completeness to 2θ = 20.81°	97.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3210 / 0 / 294
Goodness-of-fit on F^2	2.276
Final R indices [I>2σ(I)]	R1 = 0.2692, wR2 = 0.5279
R indices (all data)	R1 = 0.3300, wR2 = 0.5914
Extinction coefficient	0.0000(17)
Largest diff. peak and hole	5.814 and -6.109 e. $Å^{-3}$

Table 102.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $Ag_4I_4(P(p\text{-tolyl})_3)_4$ **(XIX)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Ag(1)	3082(1)	3082(1)	3082(1)	71(3)
Ag(3)	3690(3)	1489(3)	2566(3)	76(2)
I(1)	2168(1)	2168(1)	2168(1)	64(2)
I(2)	2902(3)	1310(3)	4435(2)	65(2)
P(1)	3545(4)	3545(4)	3545(4)	51(6)
P(3)	4867(10)	-37(9)	2490(10)	57(4)
C(111)	2900(3)	3550(3)	4590(4)	53(14)
C(112)	1890(3)	3750(4)	5110(3)	60(2)
C(113)	1210(6)	3900(7)	5960(5)	170(5)
C(114)	1720(4)	3500(4)	6500(4)	70(2)
C(115)	2580(4)	3310(3)	6210(4)	70(2)
C(116)	3160(3)	3290(3)	5290(4)	61(15)
C(117)	1070(4)	3580(5)	7510(4)	120(3)
C(311)	4530(4)	-1040(4)	3340(4)	64(16)
C(312)	3300(7)	-800(4)	3780(6)	140(4)
C(313)	3110(5)	-1450(5)	4240(4)	90(2)
C(314)	3690(4)	-2480(7)	4810(6)	120(3)
C(315)	4540(5)	-2590(5)	4590(5)	100(2)
C(316)	4860(4)	-1770(3)	3890(6)	130(4)
C(317)	3390(4)	-3120(5)	5450(4)	84(19)
C(321)	5400(3)	-120(3)	1410(3)	48(13)
C(322)	5230(4)	810(4)	610(3)	70(2)
C(323)	5970(7)	500(7)	-260(4)	170(4)
C(324)	6090(4)	-130(4)	-320(4)	61(14)
C(325)	6270(5)	-1080(8)	500(6)	140(4)
C(326)	5730(5)	-800(4)	1290(4)	90(2)
C(327)	6740(12)	-380(8)	-1130(6)	520(15)
C(331)	5890(3)	-420(4)	2600(3)	53(13)
C(332)	6720(5)	-590(4)	1970(3)	80(2)
C(333)	7470(4)	-780(5)	2060(4)	100(3)
C(334)	7430(3)	-930(3)	2860(4)	60(15)
C(335)	6570(4)	-800(4)	3510(4)	70(2)
C(336)	5630(4)	-550(4)	3580(6)	100(3)
C(337)	8200(5)	-1200(5)	2990(4)	90(2)

Table 103.
Bond lengths [Å] and angles [^{0}] for $Ag_4I_4(P(p\text{-tolyl})_3)_4$ **(XIX)**

Ag(1)-P(1)	2.48(2)	C(324)-C(325)	1.57(11)
Ag(1)-I(2)^{1}	2.924(5)	C(324)-C(327)	1.47(15)
Ag(1)-I(2)^{2}	2.924(5)	C(325)-C(326)	1.50(9)
Ag(1)-I(2)	2.924(5)	C(331)-C(332)	1.30(7)
Ag(1)-Ag(3)^{1}	3.293(7)	C(331)-C(336)	1.59(8)
Ag(1)-Ag(3)^{2}	3.293(7)	C(332)-C(333)	1.44(8)
Ag(1)-Ag(3)	3.293(7)	C(333)-C(334)	1.40(7)
Ag(3)-P(3)	2.475(14)	C(334)-C(335)	1.34(7)
Ag(3)-I(2)^{1}	2.905(6)	C(334)-C(337)	1.46(7)
Ag(3)-I(2)	2.909(6)	C(335)-C(336)	1.56(8)
Ag(3)-I(1)	2.931(6)	P(1)-Ag(1)-I(2)^{1}	111.45(14)
Ag(3)-Ag(3)^{1}	3.320(8)	P(1)-Ag(1)-I(2)^{2}	111.45(14)
Ag(3)-Ag(3)^{2}	3.320(8)	I(2)^{1}-Ag(1)-I(2)^{2}	107.42(15)
I(1)-Ag(3)^{2}	2.931(6)	P(1)-Ag(1)-I(2)	111.45(14)
I(1)-Ag(3)^{1}	2.931(6)	I(2)^{1}-Ag(1)-I(2)	107.42(15)
I(2)-Ag(3)^{2}	2.905(6)	I(2)^{2}-Ag(1)-I(2)	107.42(15)
P(1)-C(111)	1.65(5)	P(1)-Ag(1)-Ag(3)^{1}	144.40(10)
P(1)-C(111)^{2}	1.65(6)	I(2)^{1}-Ag(1)-Ag(3)^{1}	55.41(14)
P(1)-C(111)^{2}	1.65(6)	I(2)^{2}-Ag(1)-Ag(3)^{1}	55.33(14)
P(3)-C(321)	1.81(6)	I(2)-Ag(1)-Ag(3)^{1}	104.1(2)
P(3)-C(331)	1.82(5)	P(1)-Ag(1)-Ag(3)^{2}	144.40(10)
P(3)-C(311)	1.86(6)	I(2)^{1}-Ag(1)-Ag(3)^{2}	104.1(2)
C(111)-C(112)	1.50(6)	I(2)^{2}-Ag(1)-Ag(3)^{2}	55.41(14)
C(111)-C(116)	1.52(7)	I(2)-Ag(1)-Ag(3)^{2}	55.33(14)
C(112)-C(113)	1.46(8)	Ag(3)^{1}-Ag(1)-Ag(3)^{2}	60.6(2)
C(113)-C(114)	1.48(10)	P(1)-Ag(1)-Ag(3)	144.40(10)
C(114)-C(115)	1.30(8)	I(2)^{1}-Ag(1)-Ag(3)	55.33(14)
C(114)-C(117)	1.65(8)	I(2)^{2}-Ag(1)-Ag(3)	104.1(2)
C(115)-C(116)	1.45(8)	I(2)-Ag(1)-Ag(3)	55.41(14)
C(311)-C(316)	1.22(7)	Ag(3)^{1}-Ag(1)-Ag(3)	60.6(2)
C(311)-C(312)	1.87(11)	Ag(3)^{2}-Ag(1)-Ag(3)	60.6(2)
C(312)-C(313)	1.19(9)	P(3)-Ag(3)-I(2)^{1}	113.1(4)
C(313)-C(314)	1.61(11)	P(3)-Ag(3)-I(2)	108.1(4)
C(314)-C(317)	1.28(9)	I(2)^{1}-Ag(3)-I(2)	108.3(2)
C(314)-C(315)	1.38(9)	P(3)-Ag(3)-I(1)	112.9(4)
C(315)-C(316)	1.57(10)	I(2)^{1}-Ag(3)-I(1)	107.1(2)
C(321)-C(326)	1.23(7)	I(2)-Ag(3)-I(1)	107.0(2)
C(321)-C(322)	1.52(7)	P(3)-Ag(3)-Ag(1)	143.4(4)
C(322)-C(323)	1.61(8)	I(2)^{1}-Ag(3)-Ag(1)	55.88(10)
C(323)-C(324)	1.23(9)	I(2)-Ag(3)-Ag(1)	55.85(11)
Ag(1)-Ag(3)-Ag(3)^{1}	59.73(8)	C(326)-C(321)-C(322)	116(5)
P(3)-Ag(3)-Ag(3)^{2}	142.9(4)	C(326)-C(321)-P(3)	127(4)

Table 103. (Cont.)
Bond lengths [Å] and angles [^{0}] for
$Ag_4I_4(P(p\text{-tolyl})_3)_4$ **(XIX)**

I(2)^1-Ag(3)-Ag(3)^2	103.91(14)	C(322)-C(321)-P(3)	115(3)
I(2)-Ag(3)-Ag(3)^2	55.1(2)	C(321)-C(322)-C(323)	101(5)
I(1)-Ag(3)-Ag(3)^2	55.50(9)	C(324)-C(323)-C(322)	126(7)
Ag(1)-Ag(3)-Ag(3)^2	59.73(8)	C(323)-C(324)-C(325)	113(7)
Ag(3)^1-Ag(3)-Ag(3)^2	60.0	C(323)-C(324)-C(327)	126(7)
Ag(3)-I(1)-Ag(3)^2	69.0(2)	C(325)-C(324)-C(327)	103(6)
Ag(3)-I(1)-Ag(3)^1	69.0(2)	C(324)-C(325)-C(326)	102(7)
Ag(3)^2-I(1)-Ag(3)^1	69.0(2)	C(321)-C(326)-C(325)	138(7)
Ag(3)^2-I(2)-Ag(3)	69.7(2)	C(332)-C(331)-C(336)	125(5)
Ag(3)^2-I(2)-Ag(1)	69.0(2)	C(332)-C(331)-P(3)	124(4)
Ag(3)-I(2)-Ag(1)	69.0(2)	C(336)-C(331)-P(3)	111(3)
C(111)-P(1)-C(111)^2	103(2)	C(331)-C(332)-C(333)	121(4)
C(111)-P(1)-C(111)^1	103(2)	C(334)-C(333)-C(332)	125(5)
C(111)^2-P(1)-C(111)^1	103(2)	C(335)-C(334)-C(333)	112(5)
C(111)-P(1)-Ag(1)	115.8(15)	C(335)-C(334)-C(337)	123(6)
C(111)^2-P(1)-Ag(1)	115.8(15)	C(333)-C(334)-C(337)	126(5)
C(111)^1-P(1)-Ag(1)	115.8(15)	C(334)-C(335)-C(336)	134(5)
C(321)-P(3)-C(331)	100(2)	C(335)-C(336)-C(331)	103(5)
C(321)-P(3)-C(311)	103(2)	I(1)-Ag(3)-Ag(1)	103.6(2)
C(331)-P(3)-C(311)	103(2)	P(3)-Ag(3)-Ag(3)^1	148.1(4)
C(321)-P(3)-Ag(3)	116.2(15)	I(2)^1-Ag(3)-Ag(3)^1	55.2(2)
C(331)-P(3)-Ag(3)	114(2)	I(2)-Ag(3)-Ag(3)^1	103.82(15)
C(311)-P(3)-Ag(3)	118(2)	I(1)-Ag(3)-Ag(3)^1	55.50(9)
C(112)-C(111)-C(116)	102(4)	C(311)-C(316)-C(315)	127(5)
C(112)-C(111)-P(1)	127(3)	C(314)-C(315)-C(316)	121(7)
C(116)-C(111)-P(1)	130(3)	C(315)-C(314)-C(313)	114(7)
C(113)-C(112)-C(111)	133(6)	C(317)-C(314)-C(313)	125(6)
C(112)-C(113)-C(114)	108(6)	C(317)-C(314)-C(315)	121(10)
C(115)-C(114)-C(113)	128(6)	C(312)-C(313)-C(314)	126(6)
C(115)-C(114)-C(117)	115(6)	C(313)-C(312)-C(311)	116(6)
C(113)-C(114)-C(117)	115(5)	C(312)-C(311)-P(3)	116(3)
C(114)-C(115)-C(116)	116(5)	C(316)-C(311)-P(3)	130(5)
C(115)-C(116)-C(111)	129(4)	C(316)-C(311)-C(312)	109(6)

Symmetry transformations used to generate equivalent atoms:
1 = z,x,y   2 = y,z,x

Table 104.
Anisotropic displacement parameters ($Å^2 \times 10^3$) for
$Ag_4I_4(P(p\text{-tolyl})_3)_4$ (**XIX**)

atom	U11	U22	U33	U23	U13	U12
Ag(1)	82(4)	82(4)	82(4)	-36(2)	-36(2)	-36(2)
Ag(3)	77(4)	66(3)	93(4)	-39(3)	-41(3)	-15(3)
I(1)	74(3)	74(3)	74(3)	-33(2)	-33(2)	-33(2)
I(2)	80(3)	63(3)	59(3)	-12(2)	-35(2)	-34(2)
P(1)	52(8)	52(8)	52(8)	-21(5)	-21(5)	-21(5)
P(3)	57(9)	49(8)	70(10)	-28(8)	-34(8)	-8(7)
C(111)	40(3)	30(3)	100(4)	0(3)	-60(3)	0(2)
C(112)	10(3)	80(4)	30(3)	-30(3)	-10(2)	10(2)
C(113)	80(5)	300(12)	60(5)	-110(7)	0(4)	-30(7)
C(114)	60(4)	60(4)	60(4)	-30(3)	-30(3)	0(3)
C(115)	80(5)	40(3)	80(4)	0(3)	-80(4)	0(3)
C(116)	40(3)	60(4)	80(4)	-40(3)	-10(3)	-20(3)
C(117)	50(4)	120(6)	60(4)	-50(4)	0(3)	10(4)
C(311)	70(4)	60(4)	60(4)	-30(3)	-50(3)	10(3)
C(312)	270(11)	10(3)	170(8)	20(4)	-220(9)	10(5)
C(313)	70(4)	80(6)	60(4)	30(4)	-40(4)	-60(4)
C(314)	50(4)	210(9)	170(8)	-160(8)	50(5)	-90(6)
C(315)	80(5)	100(6)	120(6)	-80(5)	-60(5)	20(4)
C(316)	90(5)	10(3)	290(10)	0(4)	-180(7)	40(3)
C(317)	90(5)	110(5)	60(4)	-10(4)	-30(4)	-60(5)
C(321)	40(3)	20(3)	80(4)	10(3)	-40(3)	-20(2)
C(322)	110(5)	140(5)	30(3)	-40(3)	40(3)	-120(5)
C(323)	250(12)	170(8)	10(4)	-50(5)	30(5)	-120(8)
C(324)	70(4)	60(4)	50(4)	-30(3)	-10(3)	-20(3)
C(325)	70(5)	260(13)	140(8)	-100(9)	50(5)	-140(7)
C(326)	160(6)	60(4)	30(3)	-10(3)	-40(4)	-30(4)
C(327)	1400(4)	460(2)	280(12)	270(12)	-600(2)	-700(3)
C(331)	40(3)	90(4)	40(3)	-50(3)	-10(3)	-20(3)
C(332)	110(6)	110(5)	20(3)	-40(3)	-10(3)	-40(4)
C(333)	30(3)	200(8)	90(5)	-110(5)	-10(3)	-10(4)
C(334)	20(3)	50(3)	80(4)	-30(3)	-30(3)	10(2)
C(335)	120(5)	60(4)	50(3)	-30(3)	-20(4)	-40(4)
C(336)	90(4)	60(4)	240(9)	-100(5)	-120(5)	40(3)
C(337)	90(5)	90(5)	80(5)	-20(4)	-40(4)	-50(4)

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{2*} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 105.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for $Ag_4L_4(P(p\text{-tolyl})_3)_4$ **(XIX)**

atom	x	y	z	U(eq)
H(11D)	1645	3719	4856	80
H(11E)	568	4298	6104	80
H(11F)	2809	3159	6591	80
H(11G)	3814	3037	5123	80
H(11A)	1427	3249	7857	80
H(11B)	756	4218	7415	80
H(11C)	619	3329	7847	80
H(31D)	2897	-163	3571	80
H(31E)	2500	-1300	4379	80
H(31F)	4882	-3148	4967	80
H(31G)	5443	-1929	3838	80
H(31A)	3885	-3684	5622	80
H(31B)	2939	-2923	5952	80
H(31C)	3116	-3220	5295	80
H(32D)	4872	1379	678	80
H(32E)	6146	997	-800	80
H(32F)	6625	-1693	512	80
H(32G)	5614	-1322	1849	80
H(32A)	6720	135	-1706	80
H(32B)	7340	-660	-1135	80
H(32C)	6632	-822	-1048	80
H(33D)	6841	-581	1427	80
H(33E)	8065	-864	1562	80
H(33F)	6533	-936	4069	80
H(33G)	5035	-465	4069	80
H(33A)	8771	-1245	2460	80
H(33B)	8016	-737	3139	80
H(33C)	8279	-1786	3501	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

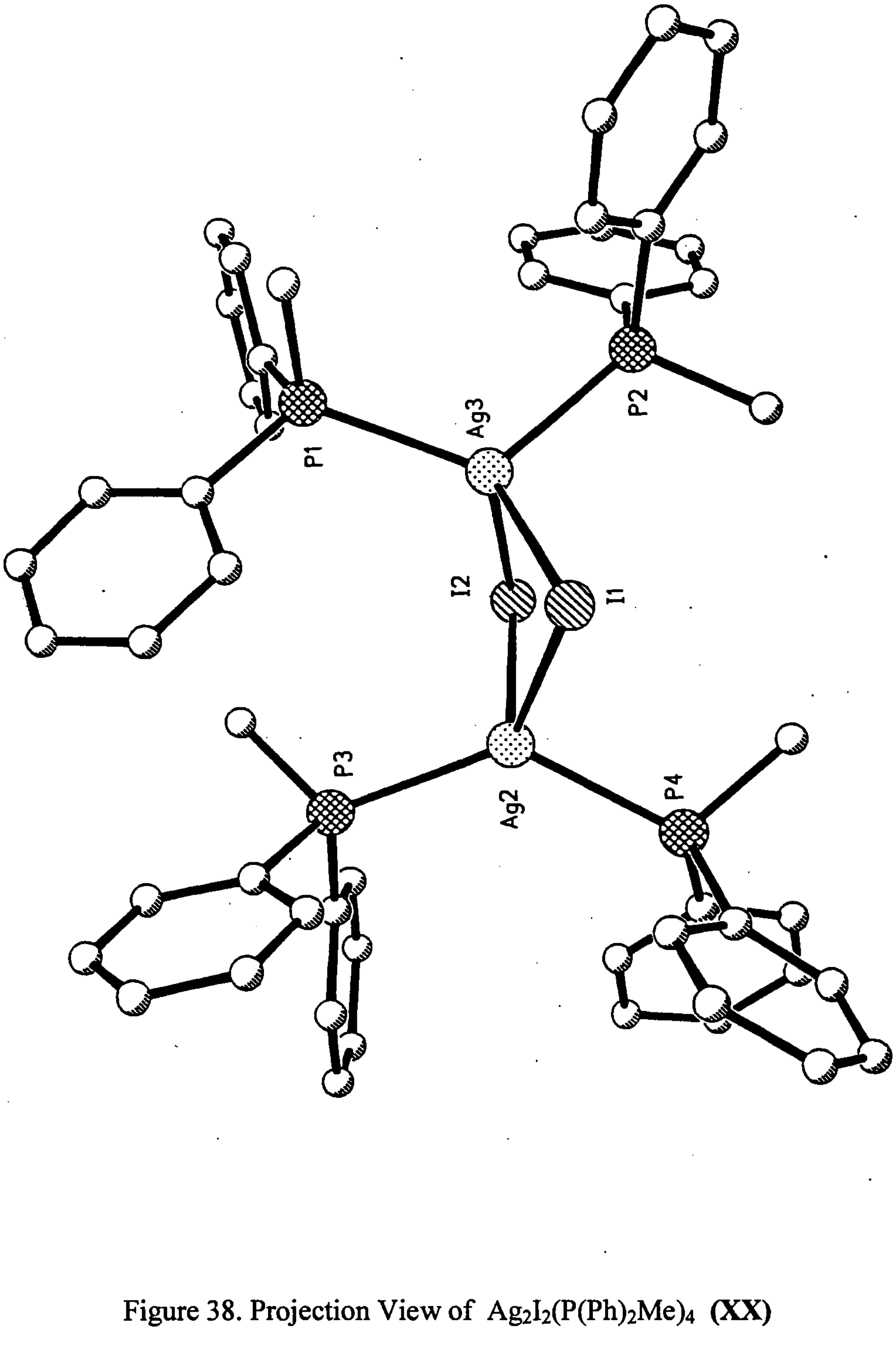


Figure 38. Projection View of $Ag_2I_2(P(Ph)_2Me)_4$ (XX)

Table 106.
Crystal data and structure refinement for $(Ag_2I_2)(P(Ph)_2Me)_4$ **(XX)**

Empirical formula	$C_{52}H_{52}$ Ag_2 I_2 P_4
Formula weight	1270.24
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 10.375(9) Å α = 83.37(2)° b = 14.220(9) Å β = 83.90(4)° c = 18.585(11) Å γ = 79.44(3)°
Volume	2667(3) Å^3
Z, Calculated density	2, 1.588 Mg/m^3
Absorption coefficient	2.043 mm^{-1}
F(000)	1248
Theta range for data collection	1.92 to 30.04 °
Index ranges	$-14 \le h \le 1, -19 \le k \le 19, -26 \le l \le 26$
Reflections collected / unique	17877 / 15500 [R(int) = 0.0690]
Completeness to 2θ =30.04°	99.2%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15500 / 0 / 542
Goodness-of-fit on F^2	1.168
Final R indices [I>2sigma(I)]	R1 = 0.0701, wR2 = 0.1723
R indices (all data)	R1 = 0.1011, wR2 = 0.1923
Extinction coefficient	0.0061(5)
Largest diff. peak and hole	2.625 and -2.409 e.A^{-3}

Table 107.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $(Ag_2I_2)(P(Ph)_2Me)_4$ **(XX)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
I(1)	1562(1)	2069(1)	1374(1)	58(1)
I(2)	2582(1)	2477(1)	3639(1)	61(1)
Ag(2)	3131(1)	1029(1)	2588(1)	55(1)
Ag(3)	1993(1)	3560(1)	2232(1)	54(1)
P(3)	5585(1)	736(1)	2448(1)	43(1)
P(2)	-266(1)	4449(1)	2617(1)	46(1)
P(1)	3713(2)	4489(1)	1642(1)	51(1)
P(4)	1582(2)	-114(1)	3060(1)	53(1)
C(111)	5255(6)	3821(4)	1234(3)	48(1)
C(112)	6504(6)	4056(4)	1253(4)	58(1)
C(113)	7616(6)	3495(5)	932(4)	60(2)
C(114)	7520(7)	2716(5)	581(4)	62(2)
C(115)	6282(7)	2486(4)	536(4)	62(2)
C(116)	5148(6)	3018(4)	867(4)	56(1)
C(121)	4192(6)	5174(5)	2318(5)	68(2)
C(122)	4026(9)	6181(5)	2252(7)	102(3)
C(123)	4265(12)	6667(8)	2840(9)	132(5)
C(124)	4644(13)	6137(10)	3464(9)	134(5)
C(125)	4834(10)	5166(9)	3543(7)	109(4)
C(126)	4610(8)	4667(6)	2969(5)	78(2)
C(131)	3212(8)	5387(5)	882(5)	83(2)
C(211)	-1048(6)	5353(4)	1918(3)	48(1)
C(212)	-2166(7)	6045(4)	2066(4)	60(2)
C(213)	-2693(9)	6707(5)	1521(5)	79(2)
C(214)	-2080(9)	6701(5)	814(5)	81(2)
C(215)	-997(9)	6010(6)	647(5)	80(2)
C(216)	-455(7)	5351(5)	1197(4)	61(2)
C(221)	-403(6)	5136(4)	3407(3)	52(1)
C(222)	-1439(7)	5217(5)	3944(4)	67(2)
C(223)	-1468(9)	5743(6)	4530(4)	76(2)
C(224)	-448(10)	6224(5)	4577(4)	84(3)
C(225)	616(9)	6173(6)	4055(5)	82(2)
C(226)	627(8)	5619(5)	3480(4)	69(2)
C(231)	-1502(7)	3643(5)	2857(4)	67(2)
C(311)	6252(5)	-181(4)	3161(3)	44(1)
C(312)	6182(7)	52(4)	3881(4)	60(2)
C(313)	6634(9)	-630(5)	4436(4)	73(2)

Table 107. (cont.)

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $(Ag_2I_2)(P(Ph)_2Me)_4$ **(XX)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
C(314)	7142(8)	-1571(5)	4284(4)	72(2)
C(315)	7200(8)	-1826(4)	3586(4)	73(2)
C(316)	6745(7)	-1134(4)	3020(4)	60(2)
C(321)	6503(6)	282(4)	1617(3)	49(1)
C(322)	7846(7)	290(5)	1453(4)	65(2)
C(323)	8495(9)	-95(6)	823(5)	83(2)
C(324)	7837(10)	-485(6)	360(5)	84(2)
C(325)	6503(11)	-476(6)	512(5)	91(3)
C(326)	5817(9)	-98(5)	1135(4)	71(2)
C(331)	6333(7)	1776(4)	2595(4)	56(1)
C(411)	1368(6)	-974(4)	2434(4)	53(1)
C(412)	1989(7)	-900(5)	1726(4)	67(2)
C(413)	1792(10)	-1496(5)	1215(5)	84(2)
C(414)	963(8)	-2169(5)	1411(5)	72(2)
C(415)	383(10)	-2261(6)	2088(5)	88(3)
C(416)	579(9)	-1662(5)	2603(5)	79(2)
C(421)	1865(7)	-872(4)	3917(4)	61(2)
C(422)	866(9)	-1148(6)	4429(4)	84(2)
C(423)	1137(12)	-1738(7)	5059(5)	96(3)
C(424)	2425(14)	-2068(7)	5199(5)	104(4)
C(425)	3474(10)	-1806(6)	4718(5)	84(2)
C(426)	3175(8)	-1207(5)	4076(4)	67(2)
C(431)	-118(7)	561(6)	3198(6)	85(3)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 108.
Bond lengths [A] and angles [deg] for
$(Ag_2I_2)(P(Ph)_2Me)_4$ **(XX)**

I(1)-Ag(3)	2.9190(15)	P(3)-Ag(2)-P(4)	129.51(6)
I(1)-Ag(2)	3.009(2)	P(3)-Ag(2)-I(2)	101.19(5)
I(2)-Ag(2)	2.9393(15)	P(4)-Ag(2)-I(2)	103.27(6)
I(2)-Ag(3)	2.940(2)	P(3)-Ag(2)-I(1)	120.98(6)
Ag(2)-P(3)	2.494(3)	P(4)-Ag(2)-I(1)	96.92(7)
Ag(2)-P(4)	2.514(2)	I(2)-Ag(2)-I(1)	100.48(5)
Ag(3)-P(1)	2.498(2)	P(1)-Ag(3)-P(2)	119.36(7)
Ag(3)-P(2)	2.525(2)	P(1)-Ag(3)-I(1)	113.24(6)
P(3)-C(321)	1.845(6)	P(2)-Ag(3)-I(1)	105.84(6)
P(3)-C(331)	1.851(6)	P(1)-Ag(3)-I(2)	115.37(6)
P(3)-C(311)	1.843(6)	P(2)-Ag(3)-I(2)	98.16(6)
P(2)-C(221)	1.835(6)	I(1)-Ag(3)-I(2)	102.61(5)
P(2)-C(211)	1.858(6)	C(321)-P(3)-C(331)	104.5(3)
P(2)-C(231)	1.859(7)	C(321)-P(3)-C(311)	101.9(2)
P(1)-C(111)	1.841(6)	C(331)-P(3)-C(311)	102.1(3)
P(1)-C(121)	1.834(7)	C(321)-P(3)-Ag(2)	121.0(2)
P(1)-C(131)	1.841(8)	C(331)-P(3)-Ag(2)	114.5(2)
P(4)-C(411)	1.840(6)	C(311)-P(3)-Ag(2)	110.6(2)
P(4)-C(421)	1.836(8)	C(221)-P(2)-C(211)	102.7(3)
P(4)-C(431)	1.853(7)	C(221)-P(2)-C(231)	104.2(3)
C(111)-C(112)	1.401(9)	C(211)-P(2)-C(231)	102.8(3)
C(111)-C(116)	1.423(8)	C(221)-P(2)-Ag(3)	116.7(2)
C(112)-C(113)	1.396(9)	C(211)-P(2)-Ag(3)	115.7(2)
C(113)-C(114)	1.372(9)	C(231)-P(2)-Ag(3)	113.0(2)
C(114)-C(115)	1.397(10)	C(111)-P(1)-C(121)	106.0(3)
C(115)-C(116)	1.401(9)	C(111)-P(1)-C(131)	101.3(3)
C(121)-C(122)	1.403(10)	C(121)-P(1)-C(131)	105.1(4)
C(121)-C(126)	1.404(12)	C(111)-P(1)-Ag(3)	118.3(2)
C(122)-C(123)	1.42(2)	C(121)-P(1)-Ag(3)	108.9(2)
C(123)-C(124)	1.36(2)	C(131)-P(1)-Ag(3)	116.0(3)
C(124)-C(125)	1.35(2)	C(411)-P(4)-C(421)	103.3(3)
C(125)-C(126)	1.407(12)	C(411)-P(4)-C(431)	101.4(3)
C(211)-C(212)	1.402(8)	C(421)-P(4)-C(431)	105.2(4)
C(211)-C(216)	1.415(9)	C(411)-P(4)-Ag(2)	115.9(2)
C(212)-C(213)	1.385(10)	C(421)-P(4)-Ag(2)	119.3(2)
C(213)-C(214)	1.398(13)	C(431)-P(4)-Ag(2)	109.9(3)
C(214)-C(215)	1.385(12)	C(112)-C(111)-C(116)	118.5(5)
C(215)-C(216)	1.394(10)	C(112)-C(111)-P(1)	124.8(4)
C(221)-C(222)	1.385(9)	C(116)-C(111)-P(1)	116.7(5)
C(221)-C(226)	1.397(10)	C(111)-C(112)-C(113)	120.2(6)
C(222)-C(223)	1.385(11)	C(114)-C(113)-C(112)	121.5(6)

Table 108. (cont.)
Bond lengths [A] and angles [deg] for
$(Ag_2I_2)(P(Ph)_2Me)_4$ **(XX)**

C(223)-C(224)	1.377(13)	C(113)-C(114)-C(115)	119.3(6)
C(224)-C(225)	1.387(13)	C(116)-C(115)-C(114)	120.7(6)
C(225)-C(226)	1.397(10)	C(115)-C(116)-C(111)	119.7(6)
C(311)-C(316)	1.403(7)	C(122)-C(121)-C(126)	118.3(8)
C(311)-C(312)	1.407(8)	C(122)-C(121)-P(1)	123.5(8)
C(312)-C(313)	1.390(9)	C(126)-C(121)-P(1)	117.7(5)
C(313)-C(314)	1.394(10)	C(121)-C(122)-C(123)	120.2(12)
C(314)-C(315)	1.380(11)	C(124)-C(123)-C(122)	118.7(10)
C(315)-C(316)	1.412(9)	C(123)-C(124)-C(125)	122.7(11)
C(321)-C(326)	1.411(9)	C(124)-C(125)-C(126)	119.8(13)
C(321)-C(322)	1.396(10)	C(121)-C(126)-C(125)	120.2(9)
C(322)-C(323)	1.404(10)	C(212)-C(211)-C(216)	118.3(6)
C(323)-C(324)	1.374(13)	C(212)-C(211)-P(2)	124.1(5)
C(324)-C(325)	1.381(14)	C(216)-C(211)-P(2)	117.6(5)
C(325)-C(326)	1.401(11)	C(213)-C(212)-C(211)	121.2(7)
C(411)-C(416)	1.376(9)	C(212)-C(213)-C(214)	119.5(7)
C(411)-C(412)	1.404(9)	C(215)-C(214)-C(213)	120.5(7)
C(412)-C(413)	1.397(10)	C(216)-C(215)-C(214)	120.0(8)
C(413)-C(414)	1.394(12)	C(215)-C(216)-C(211)	120.3(7)
C(414)-C(415)	1.339(12)	C(222)-C(221)-C(226)	116.6(6)
C(415)-C(416)	1.406(11)	C(222)-C(221)-P(2)	125.7(5)
C(421)-C(422)	1.410(10)	C(226)-C(221)-P(2)	117.6(5)
C(421)-C(426)	1.406(11)	C(223)-C(222)-C(221)	122.5(8)
C(422)-C(423)	1.383(14)	C(222)-C(223)-C(224)	119.3(8)
C(423)-C(424)	1.38(2)	C(223)-C(224)-C(225)	120.9(7)
C(424)-C(425)	1.409(14)	C(224)-C(225)-C(226)	118.3(9)
C(425)-C(426)	1.411(11)	C(221)-C(226)-C(225)	122.4(7)
Ag(3)-I(1)-Ag(2)	74.36(5)	C(316)-C(311)-C(312)	118.2(5)
Ag(2)-I(2)-Ag(3)	75.10(5)	C(316)-C(311)-P(3)	121.9(4)
C(324)-C(323)-C(322)	121.4(8)	C(312)-C(311)-P(3)	119.7(4)
C(325)-C(324)-C(323)	119.0(7)	C(313)-C(312)-C(311)	121.3(6)
C(324)-C(325)-C(326)	121.4(8)	C(314)-C(313)-C(312)	119.7(6)
C(321)-C(326)-C(325)	119.3(8)	C(313)-C(314)-C(315)	120.3(6)
C(416)-C(411)-C(412)	117.3(6)	C(316)-C(315)-C(314)	120.1(6)
C(416)-C(411)-P(4)	124.1(6)	C(315)-C(316)-C(311)	120.3(6)
C(412)-C(411)-P(4)	118.5(5)	C(326)-C(321)-C(322)	119.1(6)
C(411)-C(412)-C(413)	120.8(7)	C(326)-C(321)-P(3)	118.3(5)
C(412)-C(413)-C(414)	119.5(7)	C(322)-C(321)-P(3)	122.7(5)
C(415)-C(414)-C(413)	120.4(7)	C(321)-C(322)-C(323)	119.8(8)
C(414)-C(415)-C(416)	120.2(7)	C(421)-C(422)-C(423)	122.5(10)
C(411)-C(416)-C(415)	121.7(8)	C(424)-C(423)-C(422)	119.2(9)
C(422)-C(421)-C(426)	117.2(8)	C(423)-C(424)-C(425)	121.4(9)

Table 108. (cont.)
Bond lengths [A] and angles [deg] for $(Ag_2I_2)(P(Ph)_2Me)_4$ **(XX)**

C(422)-C(421)-P(4)	124.9(7)	C(426)-C(425)-C(424)	118.4(10)
C(426)-C(421)-P(4)	117.8(5)	C(425)-C(426)-C(421)	121.3(7)

Table 109.
Anisotropic displacement parameters (Å^2 x 10^3) for $(Ag_2I_2)(P(Ph)_2Me)_4$ **(XX)**

atom	U11	U22	U33	U23	U13	U12
I(1)	71(1)	53(1)	54(1)	-12(1)	-15(1)	-9(1)
I(2)	86(1)	55(1)	38(1)	-8(1)	1(1)	-4(1)
Ag(2)	49(1)	54(1)	63(1)	-10(1)	-4(1)	-10(1)
Ag(3)	54(1)	53(1)	54(1)	-9(1)	3(1)	-11(1)
P(3)	46(1)	43(1)	41(1)	-4(1)	-2(1)	-6(1)
P(2)	48(1)	45(1)	44(1)	-4(1)	2(1)	-9(1)
P(1)	48(1)	45(1)	58(1)	-1(1)	2(1)	-8(1)
P(4)	50(1)	55(1)	56(1)	-18(1)	7(1)	-15(1)
C(111)	50(3)	43(2)	49(3)	0(2)	-2(2)	-7(2)
C(112)	65(4)	51(3)	58(4)	-6(3)	4(3)	-16(2)
C(113)	50(3)	67(3)	63(4)	-6(3)	2(3)	-12(3)
C(114)	63(4)	65(3)	54(4)	-8(3)	10(3)	-5(3)
C(115)	81(4)	54(3)	50(4)	-13(3)	7(3)	-16(3)
C(116)	58(3)	55(3)	56(4)	-7(3)	2(3)	-18(2)
C(121)	47(3)	60(3)	99(6)	-31(4)	11(4)	-13(3)
C(122)	78(5)	57(4)	172(11)	-32(5)	-6(6)	-7(4)
C(123)	111(9)	82(6)	22(2)	-82(9)	20(10)	-29(6)
C(124)	105(9)	147(10)	169(13)	-113(10)	17(9)	-25(8)
C(125)	88(7)	147(9)	105(8)	-63(7)	-1(6)	-24(6)
C(126)	69(4)	91(5)	79(6)	-26(4)	1(4)	-21(4)
C(131)	75(5)	67(4)	91(6)	26(4)	0(4)	6(3)
C(211)	52(3)	46(2)	49(3)	-5(2)	-2(3)	-17(2)
C(212)	68(4)	55(3)	57(4)	-3(3)	-8(3)	-7(3)
C(213)	84(5)	63(4)	90(6)	-1(4)	-16(5)	-10(3)
C(214)	107(6)	64(4)	73(5)	17(4)	-29(5)	-18(4)
C(215)	101(6)	88(5)	53(4)	7(4)	-1(4)	-28(4)
C(216)	67(4)	74(4)	43(3)	1(3)	-1(3)	-20(3)
C(221)	57(3)	49(3)	46(3)	-7(2)	0(3)	1(2)
C(222)	67(4)	74(4)	54(4)	-3(3)	7(3)	-6(3)
C(223)	88(6)	76(4)	53(4)	-7(3)	8(4)	11(4)
C(224)	127(8)	63(4)	52(4)	-15(3)	-14(5)	21(4)
C(225)	104(6)	76(4)	70(5)	-27(4)	-12(5)	-9(4)
C(226)	77(5)	69(4)	64(4)	-22(3)	1(4)	-15(3)
C(231)	77(4)	63(3)	63(4)	6(3)	3(4)	-27(3)
C(311)	41(3)	48(2)	40(3)	-1(2)	2(2)	-6(2)
C(312)	73(4)	59(3)	43(3)	-6(3)	0(3)	-1(3)
C(313)	104(6)	76(4)	35(3)	-1(3)	-1(3)	-8(4)
C(314)	89(5)	66(4)	50(4)	11(3)	1(4)	3(3)
C(315)	100(5)	49(3)	58(4)	3(3)	2(4)	9(3)

Table 109. (cont.)
Anisotropic displacement parameters ($Å^2$ x 10^3) for $(Ag_2I_2)(P(Ph)_2Me)_4$ **(XX)**

atom	U11	U22	U33	U23	U13	U12
C(316)	85(4)	46(3)	45(3)	0(2)	-3(3)	-2(3)
C(321)	61(3)	43(2)	39(3)	-3(2)	-6(2)	-3(2)
C(322)	59(4)	79(4)	52(4)	-5(3)	2(3)	-3(3)
C(323)	74(5)	95(5)	64(5)	0(4)	20(4)	5(4)
C(324)	105(7)	76(4)	61(5)	-18(4)	14(5)	6(4)
C(325)	122(8)	95(6)	61(5)	-32(4)	-7(5)	-20(5)
C(326)	85(5)	74(4)	59(4)	-18(3)	-2(4)	-20(3)
C(331)	63(4)	46(3)	60(4)	-4(2)	-3(3)	-17(2)
C(411)	56(3)	50(3)	55(3)	-10(2)	0(3)	-12(2)
C(412)	75(4)	67(3)	61(4)	-20(3)	18(4)	-25(3)
C(413)	125(7)	70(4)	60(5)	-24(4)	13(5)	-24(4)
C(414)	94(5)	52(3)	74(5)	-23(3)	-16(4)	-7(3)
C(415)	120(7)	76(4)	83(6)	-19(4)	-7(5)	-53(5)
C(416)	99(6)	77(4)	68(5)	-12(4)	11(4)	-40(4)
C(421)	73(4)	63(3)	52(4)	-19(3)	15(3)	-31(3)
C(422)	89(6)	118(6)	57(4)	-25(4)	25(4)	-55(5)
C(423)	128(8)	121(7)	55(5)	-21(5)	23(5)	-76(6)
C(424)	186(12)	95(6)	48(4)	-7(4)	7(6)	-76(7)
C(425)	109(7)	78(4)	65(5)	4(4)	-13(5)	-23(4)
C(426)	75(4)	69(4)	59(4)	-11(3)	8(3)	-27(3)
C(431)	59(4)	87(5)	108(7)	-38(5)	5(4)	-4(4)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 110.
Hydrogen coordinates (x 10^{4+}) and isotropic displacement parameters ($Å^2$ x 10^3) for $(Ag_2I_2)(P(Ph)_2Me)_4$ **(XX)**

atom	x	y	z	U(eq)
H(11A)	6584	4602	1493	80
H(11B)	8464	3664	952	80
H(11C)	8291	2323	373	80
H(11D)	6195	1966	267	80
H(11E)	4304	2837	857	80
H(12A)	3747	6553	1814	80
H(12B)	4121	7356	2812	80
H(12C)	4827	6464	3856	80
H(12D)	5120	4803	3983	80
H(12E)	4706	3978	3013	80
H(13A)	3932	5706	692	80
H(13B)	2962	5060	509	80
H(13C)	2477	5852	1045	80
H(21A)	-2569	6065	2555	80
H(21B)	-3471	7164	1634	80
H(21C)	-2430	7175	441	80
H(21D)	-612	5978	156	80
H(21E)	322	4889	1092	80
H(22A)	-2169	4903	3905	80
H(22B)	-2188	5773	4900	80
H(22C)	-483	6605	4975	80
H(22D)	1330	6501	4099	80
H(22E)	1364	5573	3119	80
H(23A)	-2335	4023	2998	80
H(23B)	-1584	3315	2445	80
H(23C)	-1231	3180	3255	80
H(31A)	5803	692	3994	80
H(31B)	6613	-451	4920	80
H(31C)	7446	-2046	4668	80
H(31D)	7557	-2473	3483	80
H(31E)	6767	-1319	2537	80
H(32A)	8316	566	1770	80
H(32B)	9421	-96	713	80
H(32C)	8303	-760	-62	80
H(32D)	6047	-726	174	80
H(32E)	4891	-104	1236	80
H(33A)	7274	1605	2532	80

Table 110. (cont.)
Hydrogen coordinates (x 10^{4+}) and isotropic displacement parameters ($Å^2$ x 10^3) for $(Ag_2I_2)(P(Ph)_2Me)_4$ **(XX)**

atom	x	y	z	U(eq)
H(33B)	6044	2309	2250	80
H(33C)	6071	1953	3079	80
H(41A)	2546	-427	1592	80
H(41B)	2251	-1455	739	80
H(41C)	787	-2550	1050	80
H(41D)	-160	-2744	2222	80
H(41E)	153	-1731	3086	80
H(42A)	-35	-914	4335	80
H(42B)	432	-1916	5395	80
H(42C)	2606	-2483	5635	80
H(42D)	4372	-2031	4822	80
H(42E)	3875	-1014	3744	80
H(43A)	-703	119	3377	80
H(43B)	-147	1017	3544	80
H(43C)	-384	893	2744	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

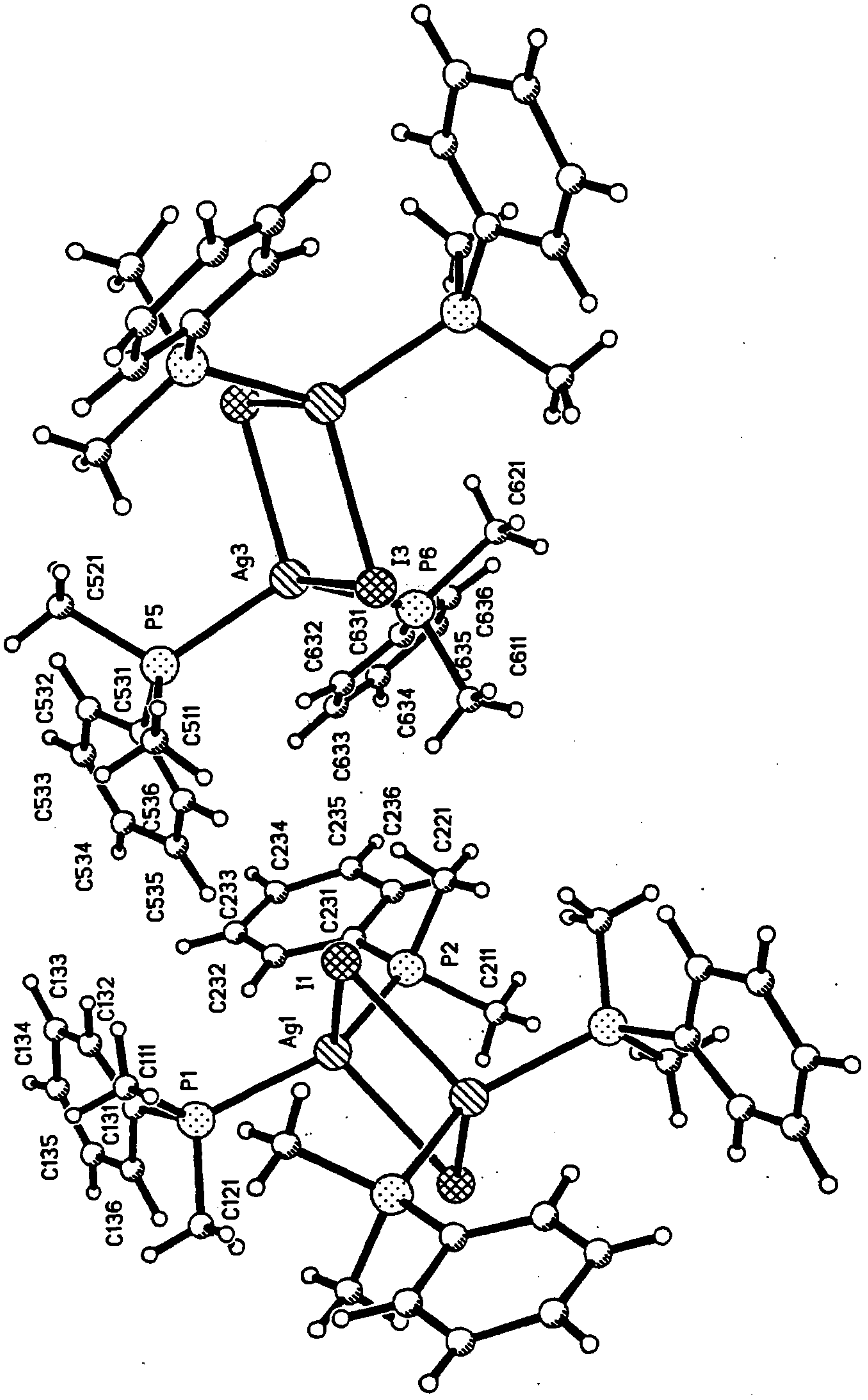


Figure 39. Projection View of $(Ag_2I_2(PPh(Me)_2)_4)_2$ **(XXI)**

Table 111.
Crystal data and structure refinement for $(Ag_2I_2(PPh(Me)_2)_4)_2$ (**XXI**)

Empirical formula	$C_{32} H_{44} Ag_2 I_2 P_4$
Formula weight	1022.09
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 10.346(3) Å α = 103.54(2)°
	b = 12.196(3) Å β= 90.73(3)°
	c = 17.920(8) Å γ = 114.09(2)°
Volume	1991.8(12) $Å^3$
Z, Calculated density	2, 1.704 Mg/m^3
Absorption coefficient	2.713 mm^{-1}
F(000)	992
Theta range for data collection	2.20 to 28.70 deg.
Index ranges	$-13 \leq h \leq 1$, $-1 \leq k \leq 16$, $-24 \leq l \leq 23$
Reflections collected / unique	6343 / 6230 [R(int) = 0.1321]
Completeness to 2θ = 28.70	60.5%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6230 / 0 / 363
Goodness-of-fit on F^2	1.006
Final R indices [$I>2\sigma(I)$]	R_1 = 0.1089, wR_2 = 0.2471
R indices (all data)	R_1 = 0.2088, wR_2 = 0.3167
Extinction coefficient	0.0000(6)
Largest diff. peak and hole	2.638 and -1.531 e. $Å^{-3}$

Table 112. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2x 10^3) for $(Ag_2I_2(PPh(Me)_2)_4)_2$ **(XXI)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
I(3)	4787(2)	4435(1)	1107(1)	70(1)
Ag(3)	6318(2)	6640(2)	507(1)	67(1)
Ag(1)	11086(2)	11297(2)	4537(1)	66(1)
I(1)	9391(3)	8591(2)	3838(1)	77(1)
P(1)	13604(10)	11595(8)	4504(5)	89(3)
P(2)	9645(8)	12299(6)	4141(3)	63(2)
P(5)	8840(9)	7029(6)	663(4)	66(2)
P(6)	5229(9)	7969(6)	1196(4)	67(2)
C(111)	13820(4)	10230(3)	3920(3)	180(2)
C(121)	14450(4)	11760(4)	5400(2)	180(3)
C(131)	14820(3)	12820(2)	4115(13)	57(8)
C(132)	14910(5)	12760(3)	3350(2)	108(15)
C(133)	15580(5)	13670(4)	3050(2)	101(14)
C(134)	16520(5)	14800(4)	3550(3)	120(2)
C(135)	16620(4)	14940(3)	4300(2)	89(12)
C(136)	15830(5)	14050(3)	4630(2)	101(14)
C(211)	9010(4)	13120(3)	4950(15)	90(11)
C(221)	8020(4)	11210(3)	3570(2)	105(14)
C(231)	10450(3)	13480(2)	3625(12)	54(8)
C(232)	11820(3)	13770(3)	3420(14)	62(9)
C(233)	12440(4)	14650(3)	2991(15)	91(14)
C(234)	11630(6)	15270(3)	2790(2)	130(2)
C(235)	10240(4)	14910(3)	2940(2)	76(11)
C(236)	9600(4)	14040(2)	3367(14)	76(10)
C(511)	9280(3)	6250(2)	1330(2)	98(12)
C(521)	9490(4)	6430(3)	-220(2)	103(13)
C(531)	10110(3)	8630(2)	1036(13)	53(7)
C(532)	10860(4)	9350(2)	538(14)	82(12)
C(533)	11730(3)	10620(2)	830(2)	73(10)
C(534)	11940(5)	11210(2)	1600(2)	120(2)
C(535)	11190(3)	10510(2)	2087(13)	66(9)
C(536)	10310(4)	9230(3)	1787(13)	95(14)
C(611)	5280(5)	7980(3)	2210(15)	120(2)
C(621)	3320(5)	7390(4)	920(2)	150(2)
C(631)	6010(3)	9650(2)	1255(15)	55(8)
C(632)	7410(4)	10280(2)	1390(2)	83(13)
C(633)	8030(5)	11570(3)	1493(15)	83(14)
C(634)	7280(5)	12180(2)	1390(2)	93(14)
C(635)	5810(7)	11530(3)	1210(2)	160(3)
C(636)	5140(5)	10230(3)	1090(2)	140(2)

Table 113.
Bond lengths [Å] and angles [°] for $(Ag_2I_2(PPh(Me)_2)_4)_2$ **(XXI)**

I(3)-Ag(3)^{1}	2.882(3)	C(235)-C(236)	1.40(4)
I(3)-Ag(3)	2.970(3)	C(531)-C(536)	1.34(3)
Ag(3)-P(6)	2.451(6)	C(531)-C(532)	1.41(4)
Ag(3)-P(5)	2.454(8)	C(532)-C(533)	1.40(4)
Ag(3)-I(3)^{1}	2.882(3)	C(533)-C(534)	1.37(4)
Ag(1)-P(2)	2.467(5)	C(534)-C(535)	1.38(5)
Ag(1)-P(1)	2.482(9)	C(535)-C(536)	1.41(4)
Ag(1)-I(1)	2.941(3)	C(631)-C(632)	1.32(4)
Ag(1)-I(1)^{2}	2.969(3)	C(631)-C(636)	1.42(3)
I(1)-Ag(1)^{2}	2.941(3)	C(632)-C(633)	1.39(4)
P(1)-C(121)	1.74(3)	C(633)-C(634)	1.32(4)
P(1)-C(131)	1.81(3)	C(634)-C(635)	1.39(6)
P(1)-C(111)	1.85(3)	C(635)-C(636)	1.41(5)
P(2)-C(221)	1.78(4)	Ag(3)^{1}-I(3)-Ag(3)	80.53(8)
P(2)-C(231)	1.82(2)	P(6)-Ag(3)-P(5)	126.9(2)
P(2)-C(211)	1.85(2)	P(6)-Ag(3)-I(3)^{1}	113.4(2)
P(5)-C(531)	1.80(2)	P(5)-Ag(3)-I(3)^{1}	108.9(2)
P(5)-C(521)	1.84(2)	P(6)-Ag(3)-I(3)	98.1(2)
P(5)-C(511)	1.84(2)	P(5)-Ag(3)-I(3)	105.2(2)
P(6)-C(621)	1.82(4)	I(3)^{1}-Ag(3)-I(3)	99.47(8)
P(6)-C(611)	1.81(3)	P(2)-Ag(1)-P(1)	135.6(3)
P(6)-C(631)	1.85(2)	P(2)-Ag(1)-I(1)	102.7(2)
C(131)-C(132)	1.36(4)	P(1)-Ag(1)-I(1)	104.5(2)
C(131)-C(136)	1.50(4)	P(2)-Ag(1)-I(1)^{2}	105.0(2)
C(132)-C(133)	1.30(5)	P(1)-Ag(1)-I(1)	104.3(2)
C(133)-C(134)	1.40(6)	I(1)^{2}-Ag(1)-I(1)	99.56(8)
C(134)-C(135)	1.32(5)	Ag(1)^{2}-I(1)-Ag(1)	80.44(8)
C(135)-C(136)	1.33(5)	C(121)-P(1)-C(131)	107(2)
C(231)-C(232)	1.39(4)	C(121)-P(1)-C(111)	100(2)
C(231)-C(236)	1.44(3)	C(131)-P(1)-C(111)	100.8(15)
C(232)-C(233)	1.41(4)	C(121)-P(1)-Ag(1)	113.4(13)
C(233)-C(234)	1.43(5)	C(131)-P(1)-Ag(1)	119.4(7)
C(234)-C(235)	1.38(6)	C(111)-P(1)-Ag(1)	114.3(14)
C(231)-P(2)-C(211)	101.8(10)	C(221)-P(2)-C(231)	105.7(12)
C(221)-P(2)-Ag(1)	112.7(10)	C(221)-P(2)-C(211)	102(2)
C(231)-P(2)-Ag(1)	118.6(9)	C(531)-C(536)-C(535)	124(3)
C(211)-P(2)-Ag(1)	114.5(8)	C(632)-C(631)-C(636)	120(2)
C(531)-P(5)-C(521)	105.7(13)	C(632)-C(631)-P(6)	119(2)
C(531)-P(5)-C(511)	102.8(13)	C(636)-C(631)-P(6)	121(3)
C(521)-P(5)-C(511)	100.6(13)	C(631)-C(632)-C(633)	121(3)
C(531)-P(5)-Ag(3)	116.4(7)	C(634)-C(633)-C(632)	122(4)

Table 113. (cont.)
Bond lengths [Å] and angles [°] for
$(Ag_2I_2(PPh(Me)_2)_4)_2$ **(XXI)**

C(521)-P(5)-Ag(3)	114.7(11)	C(633)-C(634)-C(635)	118(3)
C(511)-P(5)-Ag(3)	114.7(10)	C(636)-C(635)-C(634)	121(3)
C(621)-P(6)-C(611)	101(2)	C(635)-C(636)-C(631)	116(4)
C(621)-P(6)-C(631)	106.7(14)	C(235)-C(234)-C(233)	120(3)
C(611)-P(6)-C(631)	101.6(12)	C(234)-C(235)-C(236)	123(3)
C(621)-P(6)-Ag(3)	114.7(11)	C(235)-C(236)-C(231)	117(3)
C(611)-P(6)-Ag(3)	110.0(11)	C(536)-C(531)-C(532)	116(2)
C(631)-P(6)-Ag(3)	120.6(9)	C(536)-C(531)-P(5)	123(2)
C(132)-C(131)-C(136)	112(3)	C(532)-C(531)-P(5)	121(2)
C(132)-C(131)-P(1)	126(3)	C(531)-C(532)-C(533)	121(2)
C(136)-C(131)-P(1)	122(2)	C(534)-C(533)-C(532)	122(3)
C(133)-C(132)-C(131)	127(3)	C(533)-C(534)-C(535)	118(3)
C(132)-C(133)-C(134)	117(3)	C(534)-C(535)-C(536)	120(2)
C(135)-C(134)-C(133)	120(4)	C(232)-C(231)-C(236)	120(2)
C(134)-C(135)-C(136)	123(4)	C(232)-C(231)-P(2)	120.7(15)
C(135)-C(136)-C(131)	119(3)	C(236)-C(231)-P(2)	119(2)
C(232)-C(233)-C(234)	118(4)	C(233)-C(232)-C(231)	122(2)

Symmetry transformations used to generate equivalent atoms:
1= -x+1,-y+1,-z   2= -x+2,-y+2,-z+1

Table 114. Anisotropic displacement parameters (A^2 x 10^3) for $(Ag_2I_2(PPh(Me)_2)_4)_2$ **(XXI)**

atom	U11	U22	U33	U23	U13	U12
I(3)	84(2)	52(1)	71(1)	19(1)	0(1)	24(1)
Ag(3)	59(2)	54(1)	89(1)	10(1)	0(1)	30(2)
Ag(1)	58(2)	63(1)	88(1)	24(1)	8(1)	35(2)
I(1)	97(2)	57(1)	71(1)	13(1)	5(1)	29(2)
P(1)	62(8)	90(5)	144(6)	59(5)	20(5)	45(7)
P(2)	63(7)	62(4)	76(3)	18(3)	3(4)	38(5)
P(5)	59(7)	56(4)	90(4)	10(3)	0(4)	35(5)
P(6)	59(8)	52(4)	91(4)	6(3)	7(4)	29(5)
C(111)	100(4)	120(3)	370(7)	100(4)	50(4)	90(4)
C(121)	50(4)	340(7)	260(5)	250(5)	60(3)	90(5)
C(131)	40(2)	64(14)	81(14)	35(12)	21(14)	30(2)
C(132)	100(5)	110(3)	110(2)	10(2)	-30(2)	50(4)
C(133)	100(5)	110(3)	120(2)	60(2)	10(3)	60(4)
C(134)	90(5)	120(3)	210(4)	110(3)	70(4)	60(4)
C(135)	60(4)	51(15)	140(3)	10(2)	10(3)	20(2)
C(136)	160(5)	110(2)	90(2)	20(2)	30(2)	100(3)
C(211)	110(4)	100(2)	110(2)	50(2)	50(2)	70(3)
C(221)	90(5)	100(2)	120(2)	50(2)	0(3)	10(3)
C(231)	50(3)	34(10)	72(12)	6(10)	1(14)	10(2)
C(232)	30(3)	82(2)	90(2)	52(15)	40(2)	20(3)
C(233)	70(4)	120(3)	80(2)	20(2)	20(2)	40(4)
C(234)	210(8)	90(3)	100(2)	50(2)	10(3)	40(5)
C(235)	50(4)	70(2)	120(2)	60(2)	40(2)	20(3)
C(236)	70(3)	70(2)	110(2)	34(15)	10(2)	40(2)
C(511)	60(3)	80(2)	180(3)	70(2)	20(2)	40(2)
C(521)	70(3)	80(2)	130(2)	-40(2)	0(2)	40(3)
C(531)	20(2)	33(10)	97(15)	12(11)	1(14)	6(15)
C(532)	90(4)	70(2)	76(15)	-8(13)	-20(2)	40(3)
C(533)	0(3)	58(15)	130(2)	60(2)	-30(2)	-30(2)
C(534)	130(5)	42(14)	120(2)	-30(15)	-90(3)	10(3)
C(535)	60(3)	80(2)	65(13)	5(13)	10(2)	40(2)
C(536)	130(5)	120(2)	46(12)	5(14)	20(2)	80(3)
C(611)	160(6)	70(2)	90(2)	-8(15)	10(2)	40(3)
C(621)	130(6)	120(3)	210(4)	-10(3)	-40(4)	80(4)
C(631)	20(3)	30(11)	90(2)	4(11)	10(2)	-0(2)
C(632)	100(4)	46(14)	107(19)	6(14)	-10(2)	40(2)
C(633)	60(5)	60(2)	100(2)	10(15)	20(2)	-10(3)
C(634)	140(4)	41(14)	120(2)	21(15)	50(3)	50(3)
C(635)	230(8)	70(2)	170(3)	10(2)	-60(4)	80(4)
C(636)	120(4)	60(2)	230(4)	0(2)	-50(3)	60(3)

Table 115.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $(Ag_2I_2(PPh(Me)_2)_4)_2$ **(XXI)**

atom	x	y	z	U(eq)
H(11A)	14807	10374	3915	80
H(11B)	13315	9516	4107	80
H(11C)	13412	10096	3404	80
H(12A)	15424	11883	5400	80
H(12B)	14396	12471	5744	80
H(12C)	13906	11028	5563	80
H(13A)	14306	11973	2999	80
H(13B)	15495	13567	2499	80
H(13C)	17131	15480	3355	80
H(13D)	17240	15730	4643	80
H(13E)	15906	14172	5176	80
H(21A)	8455	13492	4759	80
H(21B)	8420	12529	5213	80
H(21C)	9806	13759	5303	80
H(22A)	7487	11635	3426	80
H(22B)	8274	10795	3108	80
H(22C)	7438	10605	3825	80
H(23A)	12363	13397	3611	80
H(23B)	13385	14812	2864	80
H(23C)	11996	15855	2483	80
H(23D)	9713	15340	2805	80
H(23E)	8654	13872	3505	80
H(51A)	10274	6415	1377	80
H(51B)	9027	6545	1821	80
H(51C)	8717	5366	1139	80
H(52A)	10480	6610	-122	80
H(52B)	8947	5543	-413	80
H(52C)	9369	6831	-598	80
H(53A)	10749	8951	-3	80
H(53B)	12219	11108	480	80
H(53C)	12548	12081	1794	80
H(53D)	11289	10893	2630	80
H(53E)	9823	8744	2129	80
H(61A)	4843	8496	2479	80
H(61B)	4773	7150	2259	80
H(61C)	6254	8309	2429	80
H(62A)	2942	7930	1212	80
H(62B)	3209	7348	384	80
H(62C)	2823	6567	996	80

Table 115. (cont.)
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $(Ag_2I_2(PPh(Me)_2)_4)_2$ (**XXI**)

atom	x	y	z	U(eq)
H(63A)	7975	9828	1403	80
H(63B)	9049	12040	1604	80
H(63C)	7670	13075	1563	80
H(63D)	5371	11962	995	80
H(63E)	4118	9786	1029	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

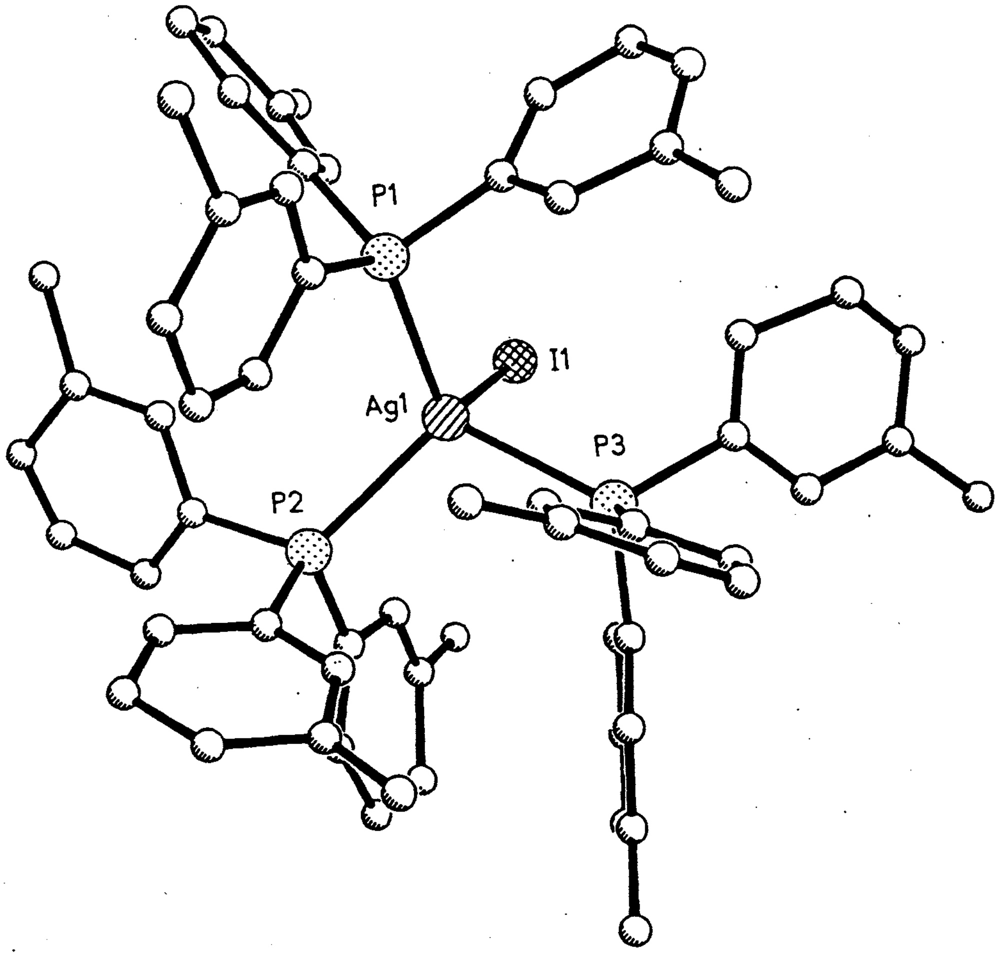


Figure 40. Projection View of AgI(P(*m*-tolyl)$_3$)$_3$ **(XXII)**

Table 116.
Crystal data and structure refinement for $AgI(P(m\text{-tolyl})_3)_3$ (**XXII**)

Empirical formula	$C_{63} H_{63} Ag I P_3$
Formula weight	1147.81
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 20.34(2) Å α = 90°
	b = 22.92(3) Å β = 90°
	c = 24.64(3) Å γ = 90°
Volume	11486(25) $Å^3$
Z, Calculated density	8, 1.327 Mg/m^3
Absorption coefficient	1.009 mm^{-1}
F(000)	4688
Theta range for data collection	2.13° to 23.26°.
Index ranges	$-1 \leq h \leq 22$, $-25 \leq k \leq 1$, $-1 \leq l \leq 27$
Reflections collected / unique	9742 / 8228 [R(int) = 0.0881]
Completeness to 2θ= 23.26	91.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8228 / 0 / 614
Goodness-of-fit on F^2	1.000
Final R indices [I>2σ(I)]	$R_1 = 0.0891$, $wR_2 = 0.1364$
R indices (all data)	$R_1 = 0.2228$, $wR_2 = 0.1809$
Extinction coefficient	0.00001(3)
Largest diff. peak and hole	0.532 and -0.491 $e.Å^{-3}$

Table 117 .
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for AgI(P(*m*-tolyl)$_3$)$_3$ (**XXII**)

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Ag(1)	4168(1)	3191(1)	1135(1)	50(1)
I(1)	4512(1)	3025(1)	13(1)	68(1)
P(1)	5342(2)	3198(2)	1539(2)	48(1)
P(2)	3546(2)	4148(2)	1257(2)	46(1)
P(3)	3555(2)	2263(2)	1428(2)	48(1)
C(112)	6090(8)	3610(8)	2438(7)	83(6)
C(113)	6163(9)	3852(9)	2942(7)	96(7)
C(114)	5629(9)	4012(7)	3245(7)	77(6)
C(115)	5000(10)	3940(7)	3042(7)	73(5)
C(116)	4929(8)	3692(6)	2522(6)	59(4)
C(117)	4398(10)	4133(9)	3358(7)	134(9)
C(111)	5452(8)	3523(6)	210(6)	51(4)
C(122)	6597(7)	3297(7)	990(5)	60(4)
C(123)	7076(8)	3618(8)	690(6)	62(5)
C(124)	6936(9)	4189(7)	545(6)	66(5)
C(125)	6342(9)	4460(7)	692(6)	70(5)
C(126)	5867(9)	4132(7)	969(6)	73(5)
C(127)	7701(8)	3335(7)	527(7)	105(7)
C(121)	5994(7)	3569(6)	1133(6)	49(4)
C(132)	5814(7)	2201(7)	2120(6)	60(4)
C(133)	5992(8)	1618(7)	2171(9)	70(5)
C(134)	6011(10)	1285(8)	1715(11)	97(7)
C(135)	5877(9)	1506(8)	1214(9)	93(6)
C(136)	5680(7)	2085(7)	1154(7)	69(5)
C(137)	6164(8)	1359(7)	2717(8)	104(7)
C(131)	5637(7)	2450(6)	1611(7)	55(4)
C(212)	2965(8)	4037(7)	258(7)	73(5)
C(213)	2527(9)	4134(7)	-191(6)	69(5)
C(214)	1984(8)	4507(7)	-77(8)	75(5)
C(215)	1910(9)	4741(8)	427(9)	96(7)
C(216)	2351(9)	4645(7)	858(7)	79(6)
C(217)	2666(10)	3885(10)	-733(7)	160(11)
C(211)	2903(8)	4296(6)	753(6)	56(4)
C(222)	2961(7)	4828(7)	2096(6)	58(4)
C(223)	2640(7)	4915(7)	2566(7)	54(4)
C(224)	2534(8)	4437(9)	2920(6)	68(5)

Table 117 . (cont.)
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for (AgI(P(*m*-tolyl)$_3$)$_3$) (**XXII**)

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
C(225)	2757(8)	3899(8)	2773(7)	74(5)
C(226)	3061(7)	3798(6)	2263(6)	56(4)
C(227)	2370(8)	5492(7)	2757(6)	103(7)
C(221)	3158(6)	4283(6)	1921(5)	41(4)
C(232)	4177(7)	5045(6)	670(6)	54(4)
C(233)	4656(7)	5484(6)	597(6)	53(4)
C(234)	5043(7)	5645(6)	1032(6)	56(4)
C(235)	4994(8)	5370(6)	1532(6)	56(4)
C(236)	4500(7)	4946(6)	1606(6)	54(4)
C(237)	5435(8)	5525(7)	1994(7)	102(6)
C(231)	4106(7)	4775(5)	1170(6)	49(4)
C(312)	2362(8)	2588(7)	976(7)	73(5)
C(313)	1718(10)	2498(8)	746(7)	80(6)
C(314)	1487(9)	1941(10)	707(8)	96(6)
C(315)	1834(9)	1465(8)	884(7)	81(6)
C(316)	2461(8)	1560(7)	1106(7)	74(5)
C(317)	1319(8)	3001(8)	559(7)	117(8)
C(311)	2720(7)	2121(6)	1155(6)	54(4)
C(322)	4172(7)	1505(6)	710(5)	51(4)
C(323)	4479(9)	998(7)	526(6)	65(5)
C(324)	4582(9)	558(7)	897(7)	74(5)
C(325)	4404(9)	609(7)	1428(8)	84(6)
C(326)	4100(8)	1121(6)	1617(6)	62(5)
C(327)	4696(8)	935(7)	-64(7)	99(6)
C(321)	3975(6)	1571(6)	1246(6)	49(4)
C(332)	4011(7)	2277(6)	2498(6)	56(4)
C(333)	3988(10)	2276(7)	3057(6)	66(5)
C(334)	3362(11)	2211(8)	3292(7)	86(6)
C(335)	2808(10)	2170(8)	2979(9)	93(7)
C(336)	2845(8)	2181(6)	2422(7)	68(5)
C(337)	4593(9)	2343(7)	3403(6)	95(6)
C(331)	3452(7)	2224(6)	2161(6)	46(4)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 118.
Bond lengths [Å] and angles [°] for (AgI(P(*m*-tolyl)$_3$)$_3$) **(XXII)**

Ag(1)-P(2)	2.550(5)	C(212)-C(211)	1.36(2)
Ag(1)-P(3)	2.567(5)	C(212)-C(213)	1.44(2)
Ag(1)-P(1)	2.589(4)	C(213)-C(214)	1.43(2)
Ag(1)-I(1)	2.877(4)	C(213)-C(217)	1.48 (2)
P(1)-C(131)	1.824(14)	C(214)-C(215)	1.36(2)
P(1)-C(111)	1.827(14)	C(215)-C(216)	1.41(2)
P(1)-C(121)	1.866(14)	C(216)-C(211)	1.40(2)
P(2)-C(211)	1.84(2)	C(222)-C(223)	1.34 (2)
P(2)-C(221)	1.841(14)	C(222)-C(221)	1.38(2)
P(2)-C(231)	1.848(13)	C(223)-C(224)	1.42(2)
P(3)-C(331)	1.820(14)	C(223)-C(227)	1.51(2)
P(3)-C(311)	1.857(15)	C(224)-C(225)	1.36(2)
P(3)-C(321)	1.857(13)	C(225)-C(226)	1.42(2)
C(112)-C(113)	1.37(2)	C(226)-C(221)	1.41(2)
C(112)-C(111)	1.43(2)	C(232)-C(231)	1.39(2)
C(113)-C(114)	1.37(2)	C(232)-C(233)	1.41 (2)
C(114)-C(115)	1.38(2)	C(233)-C(234)	1.38(2)
C(115)-C(116)	1.41(2)	C(234)-C(235)	1.39(2)
C(115)-C(117)	1.52(2)	C(235)-C(236)	1.41(2)
C(116)-C(111)	1.37(2)	C(235)-C(237)	1.49(2)
C(122)-C(121)	1.42(2)	C(236)-C(231)	1.40(2)
C(122)-C(123)	1.43(2)	C(312)-C(311)	1.37(2)
C(123)-C(124)	1.39(2)	C(312)-C(313)	1.44(2)
C(123)-C(127)	1.48(2)	C(313)-C(314)	1.36(2)
C(124)-C(125)	1.41(2)	C(313)-C(317)	1.48(2)
C(125)-C(126)	1.40(2)	C(314)-C(315)	1.37(2)
C(126)-C(121)	1.38(2)	C(315)-C(316)	1.41(2)
C(132)-C(133)	1.39(2)	C(316)-C(311)	1.39(2)
C(132)-C(131)	1.43(2)	C(322)-C(321)	1.39(2)
C(133)-C(134)	1.36(2)	C(322)-C(323)	1.40(2)
C(133)-C(137)	1.51(2)	C(323)-C(324)	1.38(2)
C(134)-C(135)	1.36(2)	C(323)-C(327)	1.53(2)
C(135)-C(136)	1.39(2)	C(324)-C(325)	1.36(2)
C(136)-C(131)	1.41(2)	C(325)-C(326)	1.41(2)
C(332)-C(331)	1.42(2)	C(326)-C(321)	1.40(2)
C(333)-C(334)	1.41(2)	C(332)-C(333)	1.38(2)
C(333)-C(337)	1.51(2)	C(112)-C(113)-C(114)	121(2)
C(334)-C(335)	1.37(2)	C(113)-C(114)-C(115)	120(2)
C(335)-C(336)	1.37(2)	C(114)-C(115)-C(116)	118(2)
C(336)-C(331)	1.40(2)	C(114)-C(115)-C(117)	122(2)
P(2)-Ag(1)-P(3)	116.03(15)	C(116)-C(115)-C(117)	120(2)

Table 118. (cont.)
Bond lengths [Å] and angles [°] for
(AgI(P(*m*-tolyl)$_3$)$_3$) **(XXII)**

P(2)-Ag(1)-P(1)	114.03(13)	C(111)-C(116)-C(115)	123(2)
P(3)-Ag(1)-P(1)	110.21(13)	C(116)-C(111)-C(112)	116.5(14)
P(2)-Ag(1)-I(1)	110.32(9)	C(116)-C(111)-P(1)	121.9(12)
P(3)-Ag(1)-I(1)	106.19(10)	C(112)-C(111)-P(1)	121.6(12)
P(1)-Ag(1)-I(1)	98.35(11)	C(121)-C(122)-C(123)	119.5(14)
C(131)-P(1)-C(111)	104.8(7)	C(124)-C(123)-C(122)	118.7(15)
C(131)-P(1)-C(121)	104.2(6)	C(124)-C(123)-C(127)	121(2)
C(111)-P(1)-C(121)	102.3(6)	C(122)-C(123)-C(127)	120.1(15)
C(131)-P(1)-Ag(1)	109.5(5)	C(123)-C(124)-C(125)	121.7(15)
C(111)-P(1)-Ag(1)	117.6(5)	C(126)-C(125)-C(124)	118.8(15)
C(121)-P(1)-Ag(1)	116.9(5)	C(121)-C(126)-C(125)	121(2)
C(211)-P(2)-C(221)	105.4(7)	C(126)-C(121)-C(122)	120.1(14)
C(211)-P(2)-C(231)	102.5(7)	C(126)-C(121)-P(1)	116.8(12)
C(221)-P(2)-C(231)	103.7(6)	C(122)-C(121)-P(1)	123.2(11)
C(211)-P(2)-Ag(1)	115.7(5)	C(133)-C(132)-C(131)	122(2)
C(221)-P(2)-Ag(1)	117.5(4)	C(134)-C(133)-C(132)	118(2)
C(231)-P(2)-Ag(1)	110.5(4)	C(134)-C(133)-C(137)	121(2)
C(331)-P(3)-C(311)	104.1(7)	C(132)-C(133)-C(137)	121(2)
C(331)-P(3)-C(321)	104.5(7)	C(133)-C(134)-C(135)	122(2)
C(311)-P(3)-C(321)	100.6(6)	C(134)-C(135)-C(136)	121(2)
C(331)-P(3)-Ag(1)	112.1(5)	C(135)-C(136)-C(131)	120(2)
C(311)-P(3)-Ag(1)	119.2(5)	C(136)-C(131)-C(132)	116.8(13)
C(321)-P(3)-Ag(1)	114.6(5)	C(136)-C(131)-P(1)	120.2(12)
C(113)-C(112)-C(111)	121(2)	C(132)-C(131)-P(1)	123.0(12)
C(231)-C(236)-C(235)	120.3(14)	C(211)-C(212)-C(213)	124.4(15)
C(232)-C(231)-C(236)	120.0(13)	C(214)-C(213)-C(212)	114.9(14)
C(232)-C(231)-P(2)	120.9(11)	C(214)-C(213)-C(217)	124(2)
C(236)-C(231)-P(2)	118.9(11)	C(212)-C(213)-C(217)	121(2)
C(311)-C(312)-C(313)	119.9(15)	C(215)-C(214)-C(213)	120(2)
C(314)-C(313)-C(312)	118(2)	C(214)-C(215)-C(216)	124(2)
C(314)-C(313)-C(317)	121(2)	C(211)-C(216)-C(215)	117(2)
C(312)-C(313)-C(317)	121(2)	C(212)-C(211)-C(216)	119(2)
C(313)-C(314)-C(315)	123(2)	C(212)-C(211)-P(2)	117.4(13)
C(314)-C(315)-C(316)	118(2)	C(216)-C(211)-P(2)	123.4(13)
C(311)-C(316)-C(315)	121(2)	C(223)-C(222)-C(221)	123.1(15)
C(312)-C(311)-C(316)	119.5(14)	C(222)-C(223)-C(224)	119.3(14)
C(312)-C(311)-P(3)	117.8(11)	C(222)-C(223)-C(227)	125(2)
C(316)-C(311)-P(3)	122.6(12)	C(224)-C(223)-C(227)	115(2)
C(321)-C(322)-C(323)	121.9(14)	C(225)-C(224)-C(223)	119.0(15)
C(324)-C(323)-C(322)	117.6(14)	C(224)-C(225)-C(226)	122(2)
C(324)-C(323)-C(327)	121.3(15)	C(221)-C(226)-C(225)	117.5(14)
C(322)-C(323)-C(327)	121.2(14)	C(222)-C(221)-C(226)	119.1(14)

Table 118. (cont.)
Bond lengths [Å] and angles [°] for
(AgI(P(*m*-tolyl)$_3$)$_3$) (**XXII**)

C(325)-C(324)-C(323)	122(2)	C(222)-C(221)-P(2)	123.7(11)
C(324)-C(325)-C(326)	120(2)	C(226)-C(221)-P(2)	117.3(11)
C(321)-C(326)-C(325)	118.6(14)	C(231)-C(232)-C(233)	120.2(14)
C(322)-C(321)-C(326)	119.2(13)	C(234)-C(233)-C(232)	119.1(14)
C(322)-C(321)-P(3)	117.0(11)	C(233)-C(234)-C(235)	121.7(14)
C(326)-C(321)-P(3)	123.7(11)	C(234)-C(235)-C(236)	118.6(15)
C(333)-C(332)-C(331)	124.0(15)	C(234)-C(235)-C(237)	121.7(15)
C(332)-C(333)-C(334)	116(2)	C(236)-C(235)-C(237)	119.7(14)
C(332)-C(333)-C(337)	123(2)	C(334)-C(335)-C(336)	121(2)
C(334)-C(333)-C(337)	121(2)	C(335)-C(336)-C(331)	121(2)
C(335)-C(334)-C(333)	121(2)	C(336)-C(331)-P(3)	124.3(12)
C(336)-C(331)-C(332)	116.5(13)	C(332)-C(331)-P(3)	119.1(11)

Table 119.
Anisotropic displacement parameters (Å^2 x 10^3) for
(AgI(P(*m*-tolyl)$_3$)$_3$) (**XXII**)

atom	U11	U22	U33	U23	U13	U12
Ag(1)	48(1)	53(1)	48(1)	1(1)	1(1)	0(1)
I(1)	77(1)	77(1)	48(1)	4(1)	16(1)	7(1)
P(1)	38(2)	55(2)	50(2)	0(2)	-3(2)	-1(2)
P(2)	47(3)	47(2)	45(2)	-1(2)	-1(2)	2(2)
P(3)	45(3)	51(2)	48(3)	1(2)	-3(2)	-7(2)
C(112)	46(11)	140(2)	59(12)	-30(12)	8(10)	-35(11)
C(113)	54(13)	170(2)	60(13)	-26(13)	5(11)	-26(13)
C(114)	90(2)	82(12)	62(12)	-16(10)	-11(12)	-19(12)
C(115)	90(2)	76(12)	53(12)	-26(9)	2(12)	40(12)
C(116)	46(11)	69(11)	63(11)	-5(9)	3(10)	-3(9)
C(117)	140(2)	180(2)	84(16)	-37(15)	1(17)	0(2)
C(111)	52(10)	53(9)	49(9)	8(7)	8(10)	0(9)
C(122)	55(10)	78(11)	47(10)	4(9)	3(8)	18(10)
C(123)	55(12)	83(13)	48(11)	1(9)	15(10)	-3(11)
C(124)	59(13)	83(13)	56(11)	19(10)	11(10)	-24(11)
C(125)	82(15)	69(11)	59(12)	12(9)	9(11)	-12(11)
C(126)	85(13)	73(11)	61(12)	14(9)	19(11)	9(12)
C(127)	79(15)	110(2)	120(2)	30(13)	33(13)	-1(13)
C(121)	49(10)	49(9)	48(9)	-10(8)	-11(9)	-9(8)
C(132)	26(9)	80(12)	74(12)	8(9)	11(10)	-7(9)
C(133)	33(10)	59(12)	120(2)	21(12)	-3(11)	4(9)
C(134)	90(2)	58(13)	150(2)	8(15)	10(2)	-1(12)
C(135)	76(14)	80(14)	120(2)	-34(14)	10(2)	11(12)
C(136)	58(12)	69(11)	81(12)	-19(10)	-19(10)	22(9)
C(137)	64(13)	94(14)	160(2)	59(14)	8(14)	26(11)
C(131)	40(10)	52(9)	73(11)	11(9)	3(9)	-5(8)
C(212)	69(13)	64(11)	85(14)	9(10)	-4(12)	25(10)
C(213)	84(14)	81(12)	43(10)	-6(9)	-3(11)	11(11)
C(214)	47(11)	98(14)	80(15)	10(12)	-10(11)	3(10)
C(215)	69(15)	95(15)	120(2)	-3(15)	18(15)	37(12)
C(216)	88(15)	83(13)	66(13)	-4(11)	-9(12)	16(12)
C(217)	110(2)	300(3)	74(15)	-70(2)	-19(15)	70(2)
C(211)	64(12)	39(9)	63(12)	-6(8)	5(10)	2(9)
C(222)	53(11)	64(11)	56(11)	-3(9)	16(9)	-7(9)
C(223)	27(9)	67(11)	66(12)	-22(10)	-17(9)	14(8)
C(224)	42(10)	119(15)	42(10)	-12(12)	-4(10)	20(11)

Table 119. (cont.)
Anisotropic displacement parameters (Å^2 x 10^3) for
$(AgI(P(m\text{-tolyl})_3)_3)$ (**XXII**)

atom	U11	U22	U33	U23	U13	U12
C(225)	59(12)	98(15)	63(13)	20(11)	20(11)	-19(11)
C(226)	50(11)	61(10)	56(11)	3(9)	-1(9)	-10(9)
C(227)	110(2)	140(2)	68(12)	-32(12)	19(13)	-22(14)
C(221)	28(8)	40(8)	55(9)	10(8)	-11(7)	4(7)
C(232)	43(10)	51(9)	69(11)	2(8)	8(10)	-13(9)
C(233)	33(10)	72(11)	53(10)	-4(8)	2(8)	2(9)
C(234)	55(11)	46(9)	67(11)	2(9)	0(10)	-2(8)
C(235)	59(11)	54(10)	55(11)	-3(9)	-8(10)	2(9)
C(236)	56(11)	51(9)	54(10)	-4(8)	0(10)	-6(9)
C(237)	62(12)	114(15)	130(2)	-8(13)	2(14)	-19(12)
C(231)	62(10)	34(7)	50(9)	-3(8)	-5(10)	0(8)
C(312)	61(12)	58(11)	100(15)	2(10)	-29(11)	-7(10)
C(313)	90(2)	71(13)	81(14)	9(11)	-34(12)	15(12)
C(314)	62(14)	120(2)	110(2)	-1(15)	-4(12)	5(14)
C(315)	66(14)	77(13)	100(2)	-27(12)	-9(12)	-37(11)
C(316)	62(12)	67(11)	93(14)	-4(10)	-2(12)	-18(9)
C(317)	71(14)	150(2)	130(2)	16(15)	-59(13)	-34(14)
C(311)	64(11)	55(9)	44(9)	-10(8)	-11(9)	-18(9)
C(322)	55(10)	59(9)	41(9)	-11(7)	7(9)	-5(9)
C(323)	91(14)	62(10)	43(10)	-20(9)	14(11)	-7(11)
C(324)	80(14)	72(12)	69(12)	-10(11)	-5(12)	-1(11)
C(325)	110(2)	48(10)	93(15)	0(10)	-17(14)	12(11)
C(326)	93(13)	53(9)	41(9)	8(8)	-5(10)	13(10)
C(327)	130(2)	91(12)	78(14)	5(11)	28(14)	9(12)
C(321)	35(9)	63(9)	48(10)	-21(8)	-18(8)	-6(7)
C(332)	38(10)	66(10)	62(11)	10(9)	19(9)	-1(8)
C(333)	86(15)	73(11)	40(10)	4(9)	-6(11)	6(11)
C(334)	10(2)	97(14)	51(12)	5(11)	30(14)	14(14)
C(335)	65(15)	120(2)	100(2)	-1(14)	41(13)	-15(13)
C(336)	72(14)	81(12)	51(12)	6(9)	17(10)	-23(10)
C(337)	140(2)	116(14)	30(9)	17(9)	-8(12)	-21(14)
C(331)	42(10)	45(9)	52(10)	-1(7)	10(9)	-1(8)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 120.
Hydrogen coordinates (x 10^4) and isotropic
displacement parameters (Å^2 x 10^3) for
(AgI(P(*m*-tolyl)$_3$)$_3$) **(XXII)**

atom	x	y	z	U(eq)
H(11A)	6469	3497	2231	80
H(11B)	6594	3926	3085	80
H(11C)	5689	4168	3603	80
H(11D)	4493	3651	2378	80
H(11H)	4530	4293	3701	80
H(11I)	4164	4424	3155	80
H(11J)	4118	3802	3417	80
H(11E)	4516	4291	3705	80
H(11F)	4163	4421	3152	80
H(11G)	4124	3796	3408	80
H(12A)	6683	2901	1095	80
H(12B)	7258	4401	338	80
H(12C)	6259	4858	594	80
H(12D)	5468	4315	1089	80
H(12E)	7964	3613	332	80
H(12F)	7937	3203	841	80
H(12G)	7606	3009	296	80
H(13A)	5777	2445	2435	80
H(13B)	6091	874	1746	80
H(13C)	5968	1277	896	80
H(13D)	5538	2228	807	80
H(13J)	6467	1642	2859	80
H(13E)	6138	1652	2995	80
H(13F)	5852	1056	2792	80
H(13G)	6599	1198	2710	80
H(13H)	5806	1367	2970	80
H(13I)	6351	992	2823	80
H(21A)	3324	3771	206	80
H(21B)	1665	4572	-358	80
H(21C)	1552	5008	478	80
H(21D)	2270	4806	1211	80
H(21E)	3055	3649	-732	80
H(21F)	2296	3652	-841	80
H(21G)	2720	4202	-985	80
H(22G)	3070	5162	1879	80
H(22A)	2308	4492	3259	80
H(22B)	2708	3581	3023	80

Table 120. (cont.)
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for (AgI(P(*m*-tolyl)$_3$)$_3$) **(XXII)**

atom	x	y	z	U(eq)
H(22C)	3194	3413	2155	80
H(22D)	2475	5772	2481	80
H(22E)	1901	5464	2794	80
H(22F)	2559	5612	3096	80
H(23A)	3884	4944	379	80
H(23B)	4721	5660	247	80
H(23D)	5354	5956	985	80
H(23C)	4427	4772	1955	80
H(23J)	5901	5463	1999	80
H(23E)	5756	5812	1893	80
H(23F)	5166	5675	2283	80
H(23G)	5654	5177	2114	80
H(23H)	5120	5317	2210	80
H(23I)	5215	5867	2128	80
H(31A)	2528	2978	1008	80
H(31B)	1063	1874	549	80
H(31C)	1640	1082	885	80
H(31D)	2745	1237	1187	80
H(31E)	908	2882	402	80
H(31F)	1237	3243	870	80
H(31G)	1568	3216	295	80
H(32A)	4091	1815	457	80
H(32B)	4826	226	771	80
H(32C)	4477	283	1666	80
H(32D)	3974	1154	1991	80
H(32F)	4889	556	-108	80
H(32G)	4328	974	-304	80
H(32H)	5017	1229	-147	80
H(33A)	4426	2316	2317	80
H(33B)	3310	2189	3679	80
H(33C)	2386	2124	3147	80
H(33D)	2455	2171	2203	80
H(33E)	4965	2383	3166	80
H(33F)	4559	2683	3629	80
H(33G)	4648	2003	3626	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

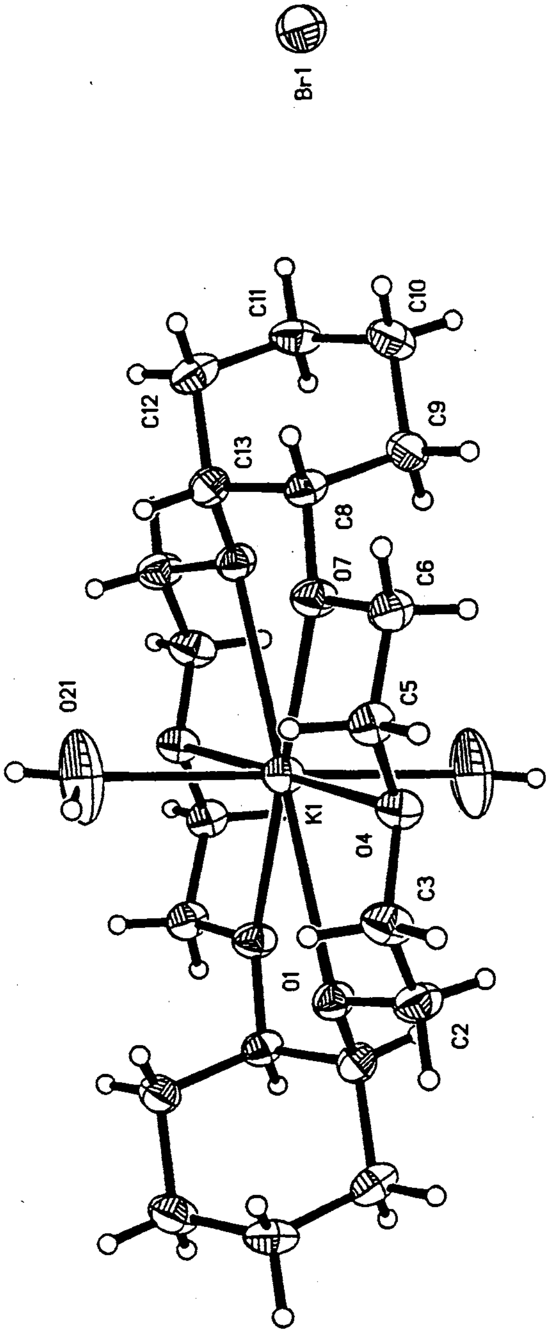


Figure 41. Projection View of [K(dicyclohexano-18-crown-6)(H_2O)$_2$]Br **(XXIII)**

Table 121.
Crystal data and structure refinement for
[K(dicyclohexano-18-crown-6)(H_2O)$_2$]Br **(XXIII)**

Empirical formula	$C_{20} H_{40} Br K O_8$	
Formula weight	527.53	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, $P\overline{1}$	
Unit cell dimensions	a = 6.890(3) Å	$\alpha = 109.83^\circ$
	b = 10.283(4) Å	$\beta = 106.99^\circ$
	c = 10.293(5) Å	$\gamma = 99.76(1)^\circ$
Volume	626.1(5) $Å^3$	
Z, Calculated density	1, 1.399 Mg/m^3	
Absorption coefficient	1.847 mm^{-1}	
F(000)	278	
Theta range for data collection	2.43 to 30.00 deg.	
Index ranges	$-9 \leq h \leq 1, -13 \leq k \leq 13, -14 \leq l \leq 14$	
Reflections collected / unique	4272 / 3487 [R(int) = 0.0758]	
Completeness to 2 θ =30.00	95.2%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3487 / 0 / 140	
Goodness-of-fit on F^2	0.989	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0618, wR2 = 0.1184	
R indices (all data)	R1 = 0.1461, wR2 = 0.1490	
Extinction coefficient	0.000(4)	
Largest diff. peak and hole	0.730 and -0.382 e.$Å^{-3}$	

Table 122.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [K(dicyclohexano-18-crown-6)$(H_2O)_2$]Br (**XXIII**)

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Br(1)	0	0	0	65(1)
K(1)	5000	10000	5000	41(1)
O(1)	5615(4)	12851(3)	7265(3)	41(1)
C(2)	4212(7)	12682(4)	8002(5)	53(1)
C(3)	4430(7)	11493(4)	8489(4)	51(1)
O(4)	3439(4)	10139(3)	7226(3)	43(1)
C(5)	3574(6)	8949(4)	7614(4)	44(1)
C(6)	2433(6)	7578(4)	6253(4)	47(1)
O(7)	3536(4)	7486(3)	5261(3)	45(1)
C(8)	2936(6)	6084(4)	4087(4)	40(1)
C(9)	695(6)	5617(4)	2971(4)	48(1)
C(10)	195(7)	4129(5)	1749(5)	58(1)
C(11)	1809(7)	4077(4)	1005(5)	57(1)
C(12)	4050(7)	4573(4)	2170(5)	53(1)
C(13)	4545(6)	6088(4)	3347(4)	42(1)
O(21)	8805(6)	9862(6)	6548(5)	123(2)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 123.
Bond lengths [Å] and angles [°] for [K(dicyclohexano-18-crown-6)(H$_2$O)$_2$]Br (**XXIII**)

K(1)-O(21)	2.696(4)	O(21)-K(1)-O(21)^1	180
K(1)-O(21)^1	2.696(4)	O(21)-K(1)-O(7)	82.63(12)
K(1)-O(7)	2.742(3)	O(21)^1-K(1)-O(7)	97.37(12)
K(1)-O(7)^1	2.742(3)	O(21)-K(1)-O(7)^1	97.37(12)
K(1)-O(4)	2.774(2)	O(21)^1-K(1)-O(7)^1	82.63(12)
K(1)-O(4)^1	2.774(2)	O(7)-K(1)-O(7)^1	180
K(1)-O(1)^1	2.928(3)	O(21)-K(1)-O(4)	93.83(10)
K(1)-O(1)	2.928(3)	O(21)^1-K(1)-O(4)	86.17(10)
K(1)-C(5)^1	3.540(4)	O(7)-K(1)-O(4)	61.42(7)
K(1)-C(5)	3.540(4)	O(7)^1-K(1)-O(4)	118.58(7)
O(1)-C(2)	1.415(4)	O(21)-K(1)-O(4)^1	86.17(10)
O(1)-C(13)^1	1.438(4)	O(21)^1-K(1)-O(4)^1	93.83(10)
C(2)-C(3)	1.484(6)	O(7)-K(1)-O(4)^1	118.58(7)
C(3)-O(4)	1.424(5)	O(7)^1-K(1)-O(4)^1	61.42(7)
O(4)-C(5)	1.420(4)	O(4)-K(1)-O(4)^1	180
C(5)-C(6)	1.486(5)	O(21)-K(1)-O(1)^1	87.55(12)
C(6)-O(7)	1.429(4)	O(21)^1-K(1)-O(1)^1	92.45(13)
O(7)-C(8)	1.426(4)	O(7)-K(1)-O(1)^1	57.94(7)
C(8)-C(9)	1.508(5)	O(7)^1-K(1)-O(1)^1	122.06(7)
C(8)-C(13)	1.517(5)	O(4)-K(1)-O(1)^1	118.58(7)
C(9)-C(10)	1.518(6)	O(4)^1-K(1)-O(1)^1	61.42(7)
C(10)-C(11)	1.522(5)	O(21)-K(1)-O(1)	92.45(12)
C(11)-C(12)	1.522(6)	O(21)^1-K(1)-O(1)	87.55(13)
C(12)-C(13)	1.519(5)	O(7)-K(1)-O(1)	122.06(7)
C(13)-O(1)^1	1.438(4)	O(7)^1-K(1)-O(1)	57.94(7)
O(4)-K(1)-O(1)	61.42(7)	O(4)-C(3)-C(2)	109.2(3)
O(4)^1-K(1)-O(1)	118.58(7)	C(5)-O(4)-C(3)	112.3(3)
O(1)^1-K(1)-O(1)	180	C(5)-O(4)-K(1)	111.0(2)
O(21)-K(1)-C(5)^1	98.63(11)	C(3)-O(4)-K(1)	112.1(2)
O(21)^1-K(1)-C(5)^1	81.37(11)	O(4)-C(5)-C(6)	109.1(3)
O(7)-K(1)-C(5)^1	138.07(8)	O(4)-C(5)-K(1)	47.03(14)
O(7)^1-K(1)-C(5)^1	41.93(8)	C(6)-C(5)-K(1)	80.6(2)
O(4)-K(1)-C(5)^1	158.01(8)	O(7)-C(6)-C(5)	108.6(3)
O(4)^1-K(1)-C(5)^1	21.99(8)	C(8)-O(7)-C(6)	114.4(3)
O(1)^1-K(1)-C(5)^1	80.18(8)	C(8)-O(7)-K(1)	123.2(2)
O(1)-K(1)-C(5)^1	99.82(8)	C(6)-O(7)-K(1)	116.2(2)
O(21)-K(1)-C(5)	81.37(11)	O(7)-C(8)-C(9)	113.7(3)
O(21)^1-K(1)-C(5)	98.63(11)	O(7)-C(8)-C(13)	107.7(3)
O(7)-K(1)-C(5)	41.93(8)	C(9)-C(8)-C(13)	111.6(3)
O(7)^1-K(1)-C(5)	138.07(8)	C(8)-C(9)-C(10)	110.4(3)
O(4)-K(1)-C(5)	21.99(8)	C(9)-C(10)-C(11)	111.9(3)
O(4)^1-K(1)-C(5)	158.01(8)	C(10)-C(11)-C(12)	110.2(3)

Table 123. (cont.)
Bond lengths [Å] and angles [°] for [K(dicyclohexano-18-crown-6)(H_2O)$_2$]Br (**XXIII**)

O(1)^1-K(1)-C(5)	99.82(8)	C(13)-C(12)-C(11)	111.0(3)
O(1)-K(1)-C(5)	80.18(8)	O(1)^1-C(13)-C(8)	106.5(3)
C(5)^1-K(1)-C(5)	180.000(1)	O(1)^1-C(13)-C(12)	113.0(3)
C(2)-O(1)-C(13)^1	114.9(3)	C(8)-C(13)-C(12)	108.9(3)
C(2)-O(1)-K(1)	108.2(2)	O(1)-C(2)-C(3)	109.6(3)
C(13)^1-O(1)-K(1)	112.(2)		

Symmetry transformations: 1= -x+1,-y+2,-z+1

Table 124.
Anisotropic displacement parameters ($Å^2$ x 10^3) for [K(dicyclohexano-18-crown-6)$(H_2O)_2$]Br (**XXIII**)

atom	U11	U22	U33	U23	U13	U12
Br(1)	70(1)	59(1)	77(1)	29(1)	41(1)	21(1)
K(1)	48(1)	39(1)	40(1)	16(1)	22(1)	11(1)
O(1)	47(2)	37(1)	47(1)	18(1)	26(1)	14(1)
C(2)	68(3)	38(2)	59(2)	15(2)	40(2)	16(2)
C(3)	65(3)	45(2)	36(2)	9(2)	25(2)	5(2)
O(4)	52(2)	38(1)	36(1)	15(1)	17(1)	10(1)
C(5)	54(2)	44(2)	39(2)	19(2)	23(2)	16(2)
C(6)	57(2)	41(2)	54(2)	21(2)	33(2)	16(2)
O(7)	55(2)	37(1)	43(1)	13(1)	26(1)	10(1)
C(8)	52(2)	34(2)	43(2)	19(2)	23(2)	17(2)
C(9)	44(2)	42(2)	50(2)	13(2)	19(2)	6(2)
C(10)	57(3)	43(2)	58(3)	11(2)	19(2)	-1(2)
C(11)	73(3)	33(2)	51(2)	5(2)	23(2)	8(2)
C(12)	75(3)	44(2)	60(3)	26(2)	41(3)	31(2)
C(13)	46(2)	42(2)	43(2)	21(2)	17(2)	17(2)
O(21)	58(2)	231(6)	107(3)	100(4)	24(2)	57(3)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 125.

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [K(dicyclohexano-18-crown-6)(H_2O)$_2$]Br **(XXIII)**

atom	x	y	z	U(eq)
H(2A)	2776	12456	7335	80
H(2B)	4539	13571	8849	80
H(3A)	3782	11525	9204	80
H(3B)	5912	11603	8952	80
H(5A)	2972	8987	8353	80
H(5B)	5038	8990	8022	80
H(6A)	1009	7580	5780	80
H(6B)	2362	6758	6504	80
H(8A)	3035	5398	4526	80
H(9A)	550	6297	2527	80
H(9B)	-291	5608	3465	80
H(10A)	-1209	3862	1018	80
H(10B)	223	3440	2186	80
H(11A)	1701	4698	487	80
H(11B)	1516	3107	292	80
H(12A)	5069	4570	1703	80
H(12B)	4172	3908	2635	80
H(13A)	5946	6371	4087	80
H(21B)	10003	9811	6503	50
H(21A)	9202	10187	7491	50

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

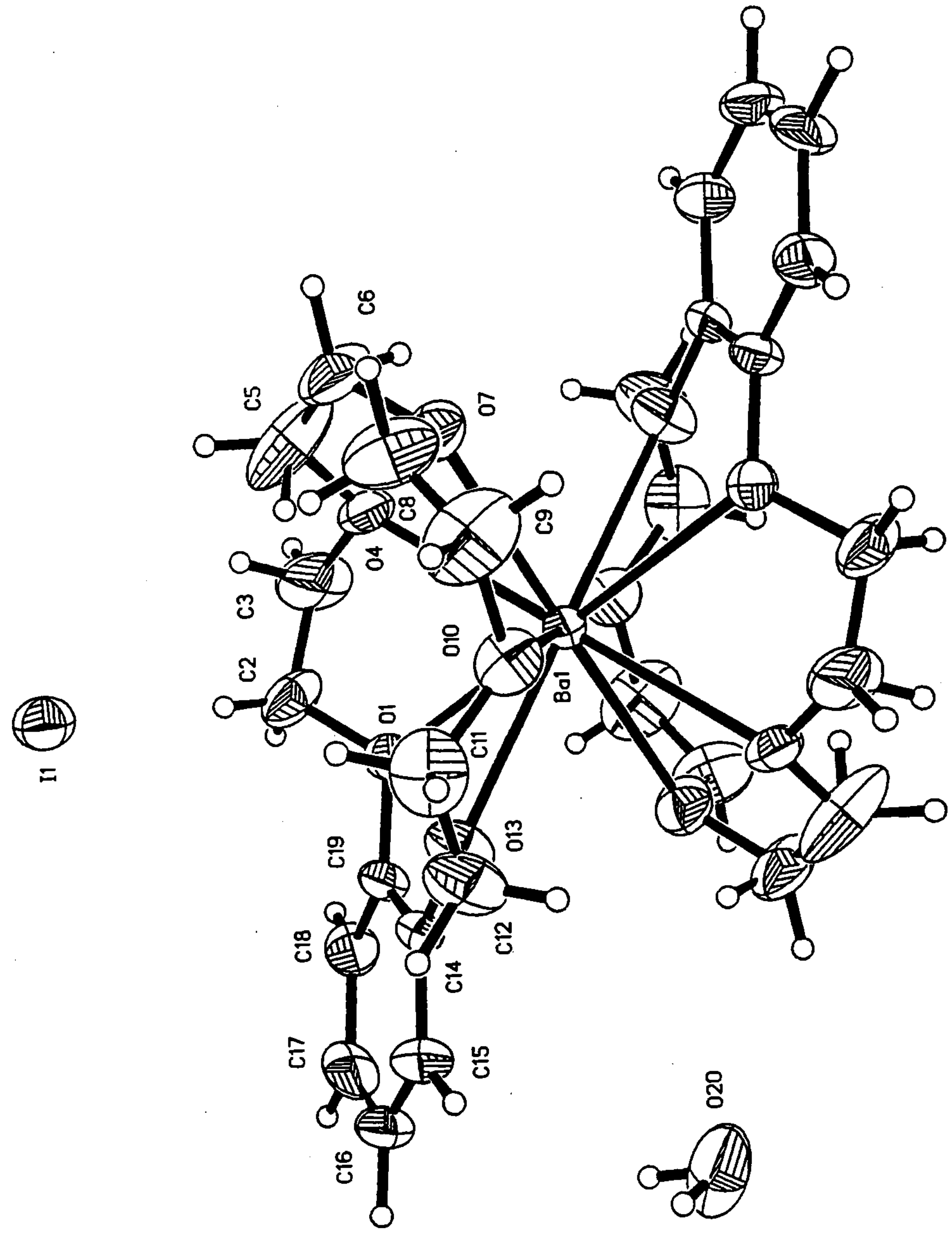


Figure 42. Projection View of [Ba(benzo-15-crown-5)$_2$](H$_2$O)$_2$(I$_2$) **(XXIV)**

Table 126.
Crystal data and structure refinement for $[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2](I_2)$ **(XXIV)**

Empirical formula	$C_{28} H_{44} Ba I_2 O_{10}$
Formula weight	927.74
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 9.846(5) Å $\alpha = 90^\circ$
	b = 10.899(4) Å $\beta = 105.38(3)^\circ$
	c = 17.350(7) Å $\gamma = 90^\circ$
Volume	1795.2(13) $Å^3$
Z, Calculated density	2, 1.716 Mg/m^3
Absorption coefficient	2.872 mm^{-1}
F(000)	900
Theta range for data collection	2.79 to 26.37 deg.
Index ranges	$-12 \leq h \leq 1, -13 \leq k \leq 1, -21 \leq l \leq 21$
Reflections collected / unique	4710 / 3635 [R(int) = 0.0824]
Completeness to 2θ =26.37	93.7%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2628 / 0 / 187
Goodness-of-fit on F^2	1.028
Final R indices [$I>2\sigma(I)$]	R1 = 0.0677, wR2 = 0.1587
R indices (all data)	R1 = 0.1083, wR2 = 0.1781
Largest diff. peak and hole	2.087 and -1.465 $e.Å^{-3}$

Table 127.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2](I_2)$ **(XXIV)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Ba(1)	0	0	0	43(1)
I(1)	2697(1)	-4134(1)	1910(1)	68(1)
O(1)	-752(8)	-1072(6)	1310(4)	57(2)
C(2)	128(13)	-936(16)	2114(7)	86(4)
C(3)	1030(2)	60(2)	2166(9)	144(9)
O(4)	1721(8)	294(8)	1572(5)	70(2)
C(5)	3080(2)	-110(2)	1720(12)	156(10)
C(6)	3783(14)	-60(2)	1110(10)	114(7)
O(7)	2967(9)	-274(8)	306(5)	78(2)
C(8)	3460(2)	-1340(2)	19(13)	120(6)
C(9)	2630(2)	-1820(2)	-689(12)	127(7)
O(10)	1141(8)	-1975(7)	-712(5)	69(2)
C(11)	800(2)	-3199(13)	-550(10)	97(5)
C(12)	-660(2)	-3272(12)	-523(10)	93(5)
O(13)	-963(9)	-2413(7)	31(5)	71(2)
C(14)	-1898(11)	-2697(9)	491(6)	53(3)
C(15)	-2920(15)	-3600(11)	281(8)	78(4)
C(16)	-3822(15)	-3756(14)	792(13)	96(6)
C(17)	-3706(13)	-3062(15)	1457(11)	89(5)
C(18)	-2706(11)	-2144(12)	1652(8)	70(3)
C(19)	-1784(11)	-2000(9)	1161(7)	53(3)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 128.
Bond lengths [Å] and angles [°] for [Ba(benzo-15-crown-5)$_2$](I$_2$) **(XXIV)**

Ba(1)-O(13)	2.801(8)	O(13)-Ba(1)-O(13)^{1}	180
Ba(1)-O(13)^{1}	2.801(8)	O(13)-Ba(1)-O(4)^{1}	78.0(2)
Ba(1)-O(4)^{1}	2.821(7)	O(13)^{1}-Ba(1)-O(4)^{1}	102.0(2)
Ba(1)-O(4)	2.821(7)	O(13)-Ba(1)-O(4)	102.0(2)
Ba(1)-O(1)^{1}	2.823(7)	O(13)^{1}-Ba(1)-O(4)	78.0(2)
Ba(1)-O(1)	2.824(7)	O(4)^{1}-Ba(1)-O(4)	180
Ba(1)-O(7)	2.843(8)	O(13)-Ba(1)-O(1)^{1}	124.5(2)
Ba(1)-O(7)^{1}	2.843(8)	O(13)^{1}-Ba(1)-O(1)^{1}	55.5(2)
Ba(1)-O(10)	2.856(7)	O(4)^{1}-Ba(1)-O(1)^{1}	59.1(2)
Ba(1)-O(10)^{1}	2.856(7)	O(4)-Ba(1)-O(1)^{1}	120.9(2)
O(1)-C(19)	1.409(11)	O(13)-Ba(1)-O(1)	55.5(2)
O(1)-C(2)	1.441(13)	O(13)^{1}-Ba(1)-O(1)	124.5(2)
C(2)-C(3)	1.39(2)	O(4)^{1}-Ba(1)-O(1)	120.9(2)
C(3)-O(4)	1.40(2)	O(4)-Ba(1)-O(1)	59.1(2)
O(4)-C(5)	1.37(2)	O(1)^{1}-Ba(1)-(1)	180
C(5)-C(6)	1.41(3)	O(13)-Ba(1)-O(7)	103.5(3)
C(6)-O(7)	1.43(2)	O(13)^{1}-Ba(1)-O(7)	76.5(3)
O(7)-C(8)	1.40(2)	O(4)-Ba(1)-O(7)	119.5(3)
C(8)-C(9)	1.39(2)	O(4)-Ba(1)-O(7)	60.5(3)
C(9)-O(10)	1.46(2)	O(1)^{1}-Ba(1)-O(7)	73.6(2)
O(10)-C(11)	1.42(2)	O(1)-Ba(1)-O(7)	106.4(2)
C(11)-C(12)	1.45(2)	O(13)-Ba(1)-O(7)^{1}	76.5(3)
C(12)-O(13)	1.429(15)	O(13)^{1}-Ba(1)-O(7)^{1}	103.5(3)
O(13)-C(14)	1.403(13)	O(4)^{1}-Ba(1)-O(7)^{1}	60.5(3)
C(14)-C(19)	1.368(15)	O(4)-Ba(1)-O(7)^{1}	119.5(3)
C(14)-C(15)	1.386(15)	O(1)^{1}-Ba(1)-O(7)^{1}	106.4(2)
C(15)-C(16)	1.42(2)	O(1)-Ba(1)-O(7)^{1}	73.6(2)
C(16)-C(17)	1.36(2)	O(7)-Ba(1)-O(7)^{1}	180
C(17)-C(18)	1.38(2)	O(13)-Ba(1)-O(10)	58.3(2)
C(18)-C(19)	1.41(2)	O (13)^{1}-Ba(1)-O(10)	121.7(2)
O(4)^{1}-Ba(1)-O(10)	72.6(2)	C(17)-C(16)-C(15)	122.5(12)
O(4)-Ba(1)-O(10)	107.4(2)	C(16)-C(17)-C(18)	120.3(13)
O(1)^{1}-Ba(1)-O(10)	75.3(2)	C(17)-C(18)-C(19)	117.7(13)
O(1)-Ba(1)-O(10)	104.7(2)	C(14)-C(19)-O(1)	116.6(9)
O(7)-Ba(1)-O(10)	59.9(3)	C(14)-C(19)-C(18)	122.1(10)
O(7)^{1}-Ba(1)-O(10)	120.1(3)	O(1)-C(19)-C(18)	121.2(10)
O(13)-Ba(1)-O(10)^{1}	121.7(2)	O(10)-C(11)-C(12)	110.0(12)
O(13)^{1}-Ba(1)-O(10)^{1}	58.3(2)	O(13)-C(12)-C(11)	111.9(11)
O(4)^{1}-Ba(1)-O(10)^{1}	107.4(2)	C(14)-O(13)-C(12)	121.7(9)
O(4)-Ba(1)-O(10)^{1}	72.6(2)	C(14)-O(13)-Ba(1)	119.6(6)
O(1)^{1}-Ba(1)-O(10)^{1}	104.7(2)	C(12)-O(13)-Ba(1)	118.0(7)

Table 128. (cont.)
Bond lengths [Å] and angles [°] for
[Ba(benzo-15-crown-5)$_2$](I$_2$) **(XXIV)**

O(1)-Ba(1)-O(10)^1	75.3(2)	C(19)-C(14)-C(15)	120.5(12)
O(7)-Ba(1)-O(10)^1	120.1(3)	C(19)-C(14)-O(13)	116.3(8)
O(7)^1-Ba(1)-O(10)^1	59.9(3)	C(15)-C(14)-O(13)	123.2(11)
O(10)-Ba(1)-O(10)^1	180	C(14)-C(15)-C(16)	116.9(13)
C(19)-O(1)-C(2)	118.1(9)	C(5)-C(6)-O(7)	117.6(12)
C(19)-O(1)-Ba(1)	118.7(6)	C(8)-O(7)-C(6)	108.7(13)
C(2)-O(1)-Ba(1)	121.2(7)	C(8)-O(7)-Ba(1)	117.1(8)
C(3)-C(2)-O(1)	110.6(12)	C(6)-O(7)-Ba(1)	116.7(9)
C(3)-C(2)-H(2A)	108.1	C(9)-C(8)-O(7)	116.5(15)
C(2)-C(3)-O(4)	121.3(15)	C(8)-C(9)-O(10)	115.0(14)
C(5)-O(4)-C(3)	116(2)	C(11)-O(10)-C(9)	112.7(14)
C(5)-O(4)-Ba(1)	116.9(9)	C(11)-O(10)-Ba(1)	118.9(8)
C(3)-O(4)-Ba(1)	114.0(7)	C(9)-O(10)-Ba(1)	114.0(10)
O(4)-C(5)-C(6)	120(2)		

Symmetry transformations used to generate equivalent atoms:
1= -x,-y,-z

Table 129.
Anisotropic displacement parameters ($Å^2 \times 10^3$) for
$[Ba(benzo\text{-}15\text{-}crown\text{-}5)_2](I_2)$ **(XXIV)**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba(1)	37(1)	44(1)	47(1)	6(1)	9(1)	-1(1)
I(1)	60(1)	76(1)	67(1)	0(1)	17(1)	-12(1)
O(1)	58(4)	68(4)	44(4)	4(3)	10(3)	-12(4)
C(2)	56(7)	156(13)	42(6)	-3(7)	6(5)	-18(9)
C(3)	160(2)	200(2)	49(8)	-2(11)	-15(10)	-110(2)
O(4)	44(4)	97(6)	60(5)	4(4)	2(4)	-23(4)
C(5)	89(12)	240(3)	102(13)	-70(2)	-32(11)	30(2)
C(6)	42(7)	210(2)	85(10)	22(12)	6(7)	-20(10)
O(7)	51(5)	98(6)	86(6)	11(5)	17(4)	9(5)
C(8)	49(8)	160(2)	160(2)	-17(14)	50(11)	9(10)
C(9)	82(11)	190(2)	128(15)	-39(14)	51(11)	37(13)
O(10)	59(5)	77(5)	79(5)	-11(4)	30(4)	15(4)
C(11)	133(15)	79(10)	82(10)	-28(8)	35(9)	25(10)
C(12)	132(14)	56(7)	100(11)	-33(7)	44(10)	-28(9)
O(13)	99(6)	57(4)	69(5)	-14(4)	43(5)	-17(5)
C(14)	55(6)	48(5)	51(6)	10(5)	7(5)	-17(5)
C(15)	78(9)	61(7)	83(9)	-2(6)	1(7)	-29(7)
C(16)	54(8)	71(8)	144(15)	35(10)	-8(9)	-26(7)
C(17)	46(7)	103(11)	129(13)	55(10)	43(8)	0(8)
C(18)	45(6)	84(8)	86(8)	19(7)	28(6)	4(6)
C(19)	47(6)	44(5)	67(7)	8(5)	16(5)	-11(5)

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 130.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [Ba(benzo-15-crown-5)$_2$](H$_2$O)$_2$(I$_2$) **(XXIV)**

atom	x	y	z	U(eq)
H(2A)	693	-1663	2244	80
H(2B)	-444	-880	2483	80
H(3B)	1809	-445	2432	80
H(3A)	1193	579	2630	80
H(5B)	2688	-867	1469	80
H(5A)	3509	-554	2202	80
H(6B)	3411	755	1037	80
H(6A)	4722	259	1226	80
H(8A)	3432	-1960	410	80
H(8B)	4424	-1224	14	80
H(9A)	2994	-2583	-826	80
H(9B)	2703	-1221	-1079	80
H(11A)	1343	-3437	-26	80
H(11B)	1035	-3732	-937	80
H(12A)	-946	-4092	-442	80
H(12B)	-1191	-2992	-1039	80
H(15A)	-3045	-4059	-205	80
H(16A)	-4520	-4393	670	80
H(17A)	-4327	-3210	1791	80
H(18A)	-2643	-1598	2094	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

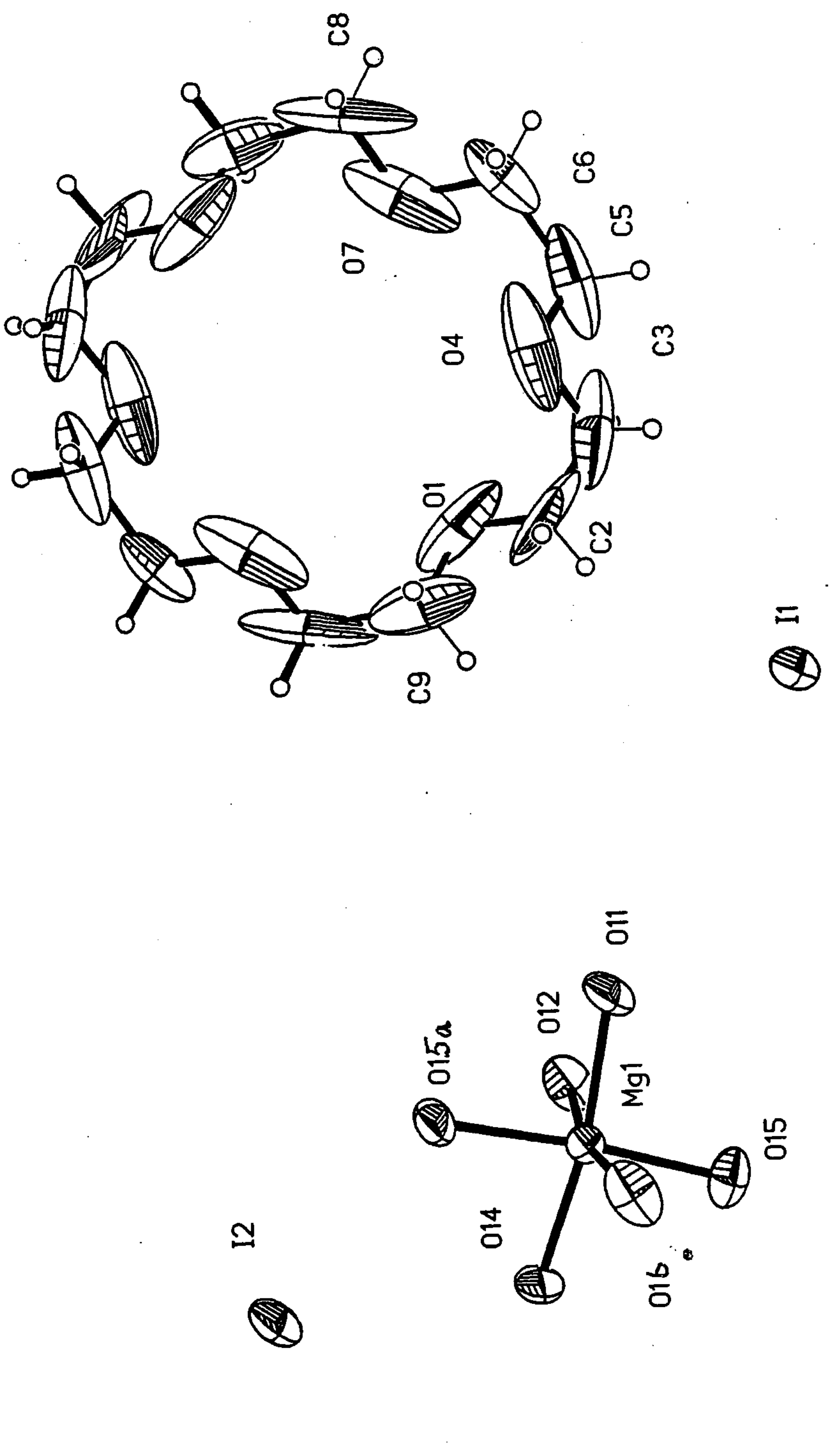


Figure 43. Projection View of $[Mg(18\text{-crown-6})(H_2O)_6](I)_2$ **(XXV)**

Table 131.
Crystal data and structure refinement for $[Mg(18\text{-crown-}6)(H_2O)_6](I)_2$ **(XXV)**

Empirical formula	$C_{12} H_{36} I_2 Mg O_{12}$
Formula weight	650.5
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pnma
Unit cell dimensions	a = 10.322(2) Å α = 90°
	b = 13.692(2) Å β = 90°
	c = 18.044(2) Å γ = 90°
Volume	2550.1(7) $Å^3$
Z, Calculated density	4, 1.694 Mg/m^3
Absorption coefficient	2.537 mm^{-1}
F(000)	1288
Theta range for data collection	2.26 to 30.00 deg.
Index ranges	$-1 \leq h \leq 14$, $-1 \leq k \leq 19$, $-25 \leq l \leq 1$
Reflections collected / unique	4804 / 3853 [R(int) = 0.0309]
Completeness to 2θ = 30.00°	92.7%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3853 / 0 / 134
Goodness-of-fit on F^2	1.012
Final R indices [I>2σ(I)]	$R_1 = 0.0633$, $wR_2 = 0.1327$
R indices (all data)	$R_1 = 0.1503$, $wR_2 = 0.1681$
Extinction coefficient	0.0000(2)
Largest diff. peak and hole	0.837 and -0.684 e. $Å^{-3}$

Table 132.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Mg(18-crown-6)(H_2O)$_6$](I)$_2$ **(XXV)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
I(1)	5882(1)	2500	6563(1)	66(1)
I(2)	313(1)	2500	11848(1)	85(1)
Mg(1)	4039(3)	2500	10288(2)	47(1)
O(1)	3101(13)	-391(7)	11009(9)	214(6)
C(2)	3680(2)	-868(12)	11614(9)	206(11)
C(3)	5000(3)	-246(12)	11865(8)	252(2)
O(4)	5730(2)	-292(9)	11369(6)	244(10)
C(5)	6810(2)	319(13)	11637(10)	250(2)
C(6)	7930(2)	337(12)	10927(13)	250(2)
O(7)	7383(11)	781(7)	10477(13)	240(9)
C(8)	8330(2)	780(2)	9865(15)	270(2)
C(9)	2160(2)	-760(2)	10907(14)	370(3)
O(11)	4085(8)	2500	9139(4)	96(3)
O(12)	2054(7)	2500	10204(4)	118(4)
O(13)	3708(7)	2500	11406(3)	77(2)
O(14)	5990(7)	2500	10463(6)	84(2)
O(15)	4212(6)	1026(3)	10223(3)	92(2)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 133.
Bond lengths [Å] and angles [°] for
[Mg(18-crown-6)(H$_2$O)$_6$](I)$_2$ **(XXV)**

Mg(1)-O(15)^1	2.029(5)	O(13)-Mg(1)-O(12)	84.6(3)
Mg(1)-O(15)	2.029(5)	O(15)^1-Mg(1)-O(11)	86.6(2)
Mg(1)-O(14)	2.039(8)	O(15)-Mg(1)-O(11)	86.6(2)
Mg(1)-O(13)	2.047(6)	O(14)-Mg(1)-O(11)	97.6(4)
Mg(1)-O(12)	2.054(8)	O(13)-Mg(1)-O(11)	171.7(4)
Mg(1)-O(11)	2.074(8)	O(12)-Mg(1)-O(11)	87.1(3)
O(1)-C(9)	1.12(2)	C(9)-O(1)-C(2)	107(2)
O(1)-C(2)	1.41(2)	O(1)-C(2)-C(3)	108.8(13)
C(2)-C(3)	1.66(3)	O(1)-C(2)-C(9)	31.7(8)
C(2)-C(9)	2.03(3)	C(3)-C(2)-C(9)	140.0(12)
C(3)-O(4)	1.18(3)	O(4)-C(3)-C(2)	106.9(16)
O(4)-C(5)	1.47(3)	C(3)-O(4)-C(5)	102.0(14)
C(5)-C(6)	1.73(3)	O(4)-C(5)-C(6)	105.7(14)
C(6)-O(7)	1.16(2)	O(7)-C(6)-C(5)	101(2)
O(7)-C(8)	1.47(3)	C(6)-O(7)-C(8)	101.5(14)
C(8)-C(9)^2	1.48(3)	O(7)-C(8)-C(9)^2	119(2)
O(15)^1-Mg(1)-O(15)	117(2)	O(1)-C(9)-C(8)^2	167.9(4)
O(15)^1-Mg(1)-O(14)	85.5(2)	O(1)-C(9)-C(2)	41.5(12)
O(15)-Mg(1)-O(14)	85.5(2)	C(8)^2-C(9)-C(2)	148(2)
O(15)^1-Mg(1)-O(13)	94.11(2)	O(15)^1-Mg(1)-O(12)	94.8(2)
O(15)-Mg(1)-O(13)	94.11(2)	O(15)-Mg(1)-O(12)	94.8(2)
O(14)-Mg(1)-O(13)	90.7(4)	O(14)-Mg(1)- O(12)	175.3(4)

Symmetry transformations used to generate equivalent atoms:
1= x,-y+1/2,z 2= -x+1,-y,-z+2

Table 134.
Anisotropic displacement parameters (Å^2 x 10^3) for [Mg(18-crown-6)(H_2O)$_6$](I)$_2$ **(XXV)**

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I(1)	74(1)	70(1)	53(1)	0	7(1)	0
I(2)	90(1)	109(1)	57(1)	0	27(1)	0
Mg(1)	47(2)	47(2)	46(2)	0	4(1)	0
O(1)	181(10)	127(7)	340(2)	81(9)	153(11)	4(7)
C(2)	350(3)	105(11)	164(15)	71(11)	150(2)	80(2)
C(3)	610(5)	81(9)	62(8)	1(7)	-70(2)	70(2)
O(4)	470(3)	172(10)	92(6)	-67(7)	-117(11)	188(15)
C(5)	460(4)	111(11)	169(15)	-29(13)	-220(2)	60(2)
C(6)	170(2)	78(9)	490(4)	-60(2)	-230(3)	29(11)
O(7)	123(9)	98(6)	500(3)	-79(11)	-179(15)	56(7)
C(8)	57(9)	160(2)	580(5)	-180(3)	-60(2)	12(10)
C(9)	320(3)	400(4)	400(4)	-130(3)	270(3)	-270(3)
O(11)	73(5)	173(8)	40(4)	0	17(4)	0
O(12)	52(5)	268(13)	33(3)	0	2(3)	0
O(13)	72(5)	131(6)	29(3)	0	4(3)	0
O(14)	48(4)	56(4)	148(8)	0	-15(5)	0
O(15)	128(5)	44(3)	103(4)	-11(3)	50(4)	-18(3)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 141.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [Mg(18-crown-6)(H_2O)$_6$](I)$_2$ **(XXV)**

atom	x	y	z	U(eq)
H(2A)	3977	-1490	11434	80
H(2B)	3035	-972	11987	80
H(3A)	5318	-530	12316	80
H(3B)	4733	414	11963	80
H(5A)	7127	34	12088	80
H(5B)	6481	960	11743	80
H(6A)	8233	-311	10817	80
H(6B)	8649	701	11123	80
H(8B)	9076	1076	10089	80
H(8C)	8450	87	9838	80
H(9B)	2353	-1409	10733	80
H(9C)	1536	-802	11303	80
H(12A)	1615	2500	9805	50
H(12B)	1571	2500	10586	50
H(15A)	4135	518	10490	50
H(11A)	3406	2500	8872	50
H(15B)	4270	872	9768	50
H(11B)	4649	2500	8795	50
H(14A)	6393	1982	10582	50
H(13A)	3239	2275	11754	50

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

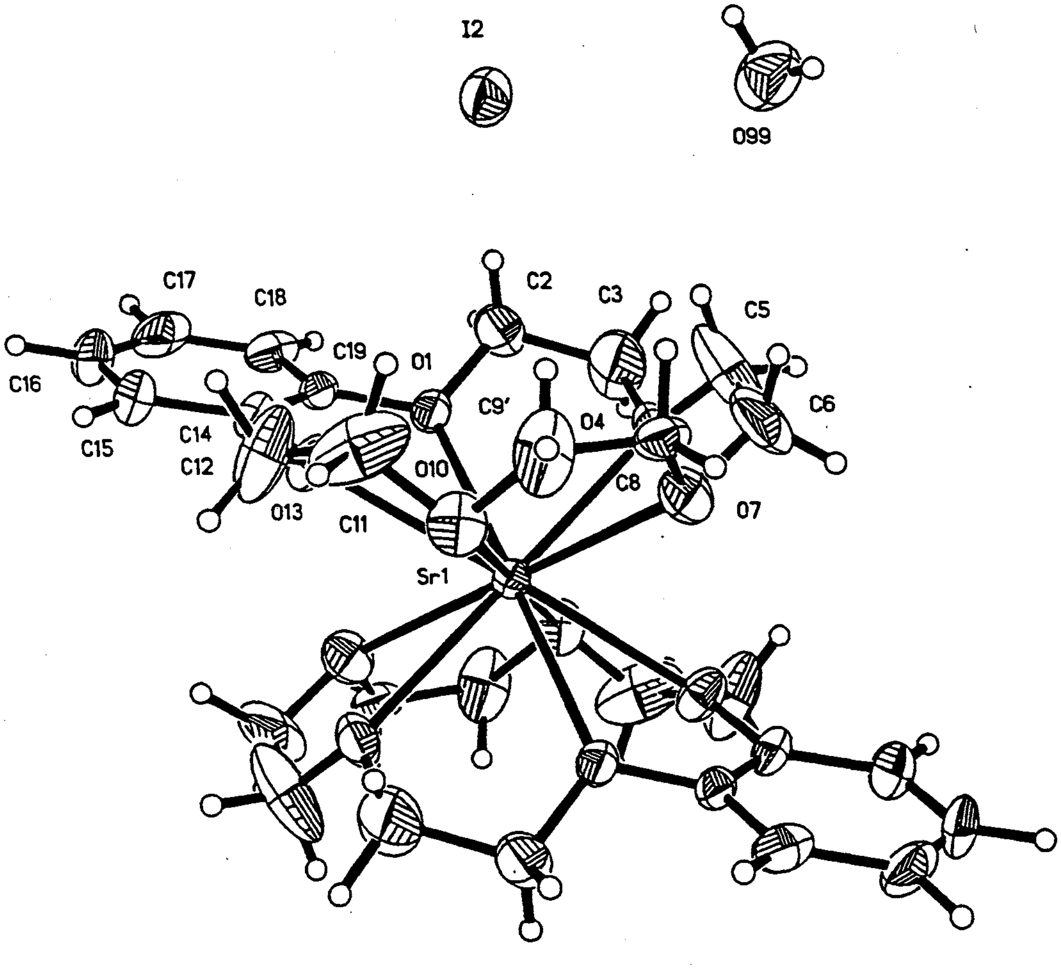


Figure 44. Projection View of [Sr(benzo-15-crown-5)$_2$ (H$_2$O)$_2$](I)$_2$ **(XXVI)**

Table 136.
Crystal data and structure refinement for
[Sr(benzo-15-crown-5)$_2$ (H$_2$O)$_2$](I)$_2$ (**XXVI**)

Empirical formula	$C_{28} H_{44} I_2 O_{12} Sr$
Formula weight	914.05
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic,$P2_1/c$
Unit cell dimensions	a = 9.8290(10) Å alpha = 90°
	b = 10.5670(10) Å beta = 106.010(10)°
	c = 17.287(2) Å gamma = 90°
Volume	1725.8(3) Å^3
Z, Calculated density	2, 1.759 Mg/m^3
Absorption coefficient	3.41 mm^{-1}
F(000)	904
Theta range for data collection	2.28° to 26.37°
Index ranges	$-1 \leq h \leq 12$, $-13 \leq k \leq 1$, $-21 \leq l \leq 21$
Reflections collected / unique	4569 / 3498 [R(int) = 0.0404]
Completeness to 2θ = 26.37°	93.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3498 / 5 / 216
Goodness-of-fit on F^2	0.989
Final R indices [$I>2\sigma(I)$]	R1 = 0.0606, wR2 = 0.1351
R indices (all data)	R1 = 0.1186, wR2 = 0.1624
Extinction coefficient	0.0002(6)
Largest diff. peak and hole	0.728 and -0.663 e. Å^{-3}

Table 137.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Sr(benzo-15-crown-5)$_2$ (H$_2$O)$_2$](I)$_2$ (**XXVI**)

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
Sr(1)	0	0	0	38(1)
I(2)	2728(1)	-4057(1)	1915(1)	68(1)
O(1)	- 766(6)	-975(5)	1259(3)	48(1)
C(2)	52(10)	-844(10)	2068(5)	70(3)
C(3)	1106(17)	193(16)	2144(7)	39(7)
O(4)	1640(6)	398(7)	1504(4)	64(2)
C(5)	3015(12)	130(2)	1708(8)	147(8)
C(6)	3675(11)	10(2)	1033(7)	136(7)
O(7)	2846(6)	-238(7)	291(4)	69(2)
C(8)	3430(2)	-1343(13)	106(12)	60(7)
C(8')	3230(3)	-1100(3)	-340(3)	93(12)
C(9)	2580(3)	-1690(3)	-723(11)	76(9)
C(9')	2550(3)	-2240(3)	-420(2)	91(10)
O(10)	1090(7)	-1945(7)	-692(4)	68(2)
C(11)	704(13)	-3144(11)	-610(9)	128(6)
C(12)	-742(13)	-3265(11)	-501(9)	116(5)
O(13)	-1046(7)	-2345(5)	-15(3)	62(2)
C(14)	-1949(9)	-2621(8)	450(5)	53(2)
C(15)	-3006(12)	-3544(10)	268(7)	81(3)
C(16)	-3871(11)	-3686(13)	758(9)	93(4)
C(17)	-3704(11)	-2958(12)	1428(9)	87(4)
C(18)	-2693(10)	-2024(10)	1617(6)	65(3)
C(19)	-1796(8)	-1873(8)	1124(5)	46(2)
O(99)	4821(18)	-1658(14)	3354(8)	114(8)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 138.
Bond lengths [Å] and angles [deg] for [Sr(benzo-15-crown-5)$_2$(H$_2$O)$_2$](I)$_2$ (**XXVI**)

Sr(1)-O(13)	2.680(6)	C(15)-C(16)	1.36(2)
Sr(1)-O(13)^1	2.680(6)	C(16)-C(17)	1.36(2)
Sr(1)-O(4)^1	2.687(6)	C(17)-C(18)	1.374(15)
Sr(1)-O(4)	2.687(6)	C(17)-H(17A)	0.96
Sr(1)-O(1)	2.695(5)	C(18)-C(19)	1.394(11)
Sr(1)-O(1)^1	2.695(5)	O(13)-Sr(1)-O(13)^1	180
Sr(1)-O(7)	2.714(6)	O(13)-Sr(1)-O(4)^1	73.70(2)
Sr(1)-O(7)^1	2.714(6)	O(13)^1-Sr(1)-O(4)^1	106.3(2)
Sr(1)-O(10)^1	2.740(6)	O(13)-Sr(1)-O(4)	106.3(2)
Sr(1)-O(10)	2.740(6)	O(13)^1-Sr(1)-O(4)	73.7(2)
O(1)-C(19)	1.360(9)	O(4)^1-Sr(1)-O(4)	180
O(1)-C(2)	1.415(10)	O(13)-Sr(1)-O(1)	57.5(2)
C(2)-C(3)	1.4894(10)	O(13)^1-Sr(1)-O(1)	122.5(2)
C(3)-O(4)	1.367(13)	O(4)^1-Sr(1)-O(1)	119.6(2)
O(4)-C(5)	1.329(13)	O(4)-Sr(1)-O(1)	60.4(2)
C(5)-C(6)	1.4895(10)	O(13)-Sr(1)-O(1)^1	122.5(2)
C(6)-O(7)	1.342(13)	O(13)^1-Sr(1)-O(1)^1	57.5(2)
O(7)-C(8)	1.3750(10)	O(4)^1-Sr(1)-O(1)^1	60.4(2)
O(7)-C(8)^1	1.54(4)	O(4)-Sr(1)-O(1)^1	119.6(2)
C(8)-C(8)^1	0.78(4)	O(1)-Sr(1)-O(1)^1	180
C(8)-C(9)^1	1.42(4)	O(13)-Sr(1)-O(7)	106.8(2)
C(8)-C(9)	1.4900(11)	O(13)^1-Sr(1)-O(7)	73.2(2)
C(8)^1-C(9)	1.00(4)	O(4)^1-Sr(1)-O(7)	118.5(2)
C(8)^1-C(9)^1	1.36(4)	O(4)-Sr(1)-O(7)	61.5(2)
C(9)-C(9)^1	0.79(3)	O(1)-Sr(1)-O(7)	108.6(2)
C(9)-O(10)	1.51(3)	O(1)^1-Sr(1)-O(7)	71.4(2)
C(9)^1-O(10)	1.42(3)	O(13)-Sr(1)-O(7)^1	73.2(2)
C(9)^1-C(11)	2.00(3)	O(13)^1-Sr(1)-O(7)^1	106.8(2)
O(10)-C(11)	1.341(13)	O(4)^1-Sr(1)-O(7)^1	61.5(2)
C(11)-C(12)	1.4896(10)	O(4)-Sr(1)-O(7)^1	118.5(2)
C(12)-O(13)	1.371(11)	O(1)-Sr(1)-O(7)^1	71.4(2)
O(13)-C(14)	1.383(10)	O(1)^1-Sr(1)-O(7)^1	108.6(2)
C(14)-C(19)	1.382(12)	O(7)-Sr(1)-O(7)^1	180
C(14)-C(15)	1.396(13)	O(13)-Sr(1)-O(10)^1	120.19(2)
O(13)^1-Sr(1)-O(10)^1	59.83(2)	O(7)-C(8)-C(9)	106.1(2)
O(4)^1-Sr(1)-O(10)^1	109.7(2)	C(9)^1-C(8)-C(9)	31.3(14)
O(4)-Sr(1)-O(10)^1	70.3(2)	C(8)-C(8)^1-C(9)	113(4)
O(1)-Sr(1)-O(10)^1	72.83(2)	C(8)-C(8)^1-C(9)^1	78(4)
O(1)^1-Sr(1)-O(10)^1	107.19(2)	C(9)-C(8)^1-C(9)^1	35.3(2)
O(7)-Sr(1)-O(10)^1	119.7(2)	C(8)-C(8)^1-O(7)	63(3)
O(7)^1-Sr(1)-O(10)^1	60.3(2)	C(9)-C(8)^1-O(7)	127(3)

Table 138. (cont.)
Bond lengths [Å] and angles [deg] for
[Sr(benzo-15-crown-5)$_2$(H$_2$O)$_2$](I)$_2$ **(XXVI)**

O(13)-Sr(1)-O(10)	59.8(2)	C(9)^1-C(8)^1-O(7)	113(3)
O(13)$_1$-Sr(1)-O(10)	120.2(2)	C(9^1)-C(9)-C(8^1)	98(3)
O(4)^1-Sr(1)-O(10)	70.3(2)	C(9^1)-C(9)-O(10)	68(3)
O(4)-Sr(1)-O(10)	109.7(2)	C(8^1)-C(9)-O(10)	122(3)
O(1)-Sr(1)-O(10)	107.2(2)	C(9^1)-C(9)-C(8)	69(3)
O(1)^1-Sr(1)-O(10)	72.8(2)	C(8^1)-C(9)-C(8)	29(2)
O(7)-Sr(1)-O(10)	60.3(2)	O(10)-C(9)-C(8)	107(2)
O(7)^1-Sr(1)-O(10)	119.7(2)	C(9)-C(9^1)-C(8^1)	47(3)
O(10)^1-Sr(1)-O(10)	180	C(9)-C(9^1)-C(8)	79(3)
C(19)-O(1)-C(2)	115.5(6)	C(8^1)-C(9^1)-C(8)	32(2)
C(19)-O(1)-Sr(1)	119.3(4)	C(9)-C(9^1)-O(10)	81(4)
C(2)-O(1)-Sr(1)	123.5(4)	C(8^1)-C(9)^1-O(10)	105(2)
O(1)-C(2)-C(3)	110.5(8)	C(8)-C(9)^1-O(10)	117(2)
O(4)-C(3)-C(2)	117.3(10)	C(9)-C(9)^1-C(11)	116(4)
C(5)-O(4)-C(3)	109.9(11)	C(8)^1-C(9)^1-C(11)	147(2)
C(5)-O(4)-Sr(1)	121.2(6)	C(8)-C(9)^1-C(11)	142(2)
C(3)-O(4)-Sr(1)	119.8(6)	O(10)-C(9)^1-C(11)	42.0(8)
O(4)-C(5)-C(6)	116.2(11)	C(11)-O(10)-C(9)^1	93.0(14)
O(7)-C(6)-C(5)	119.0(9)	C(11)-O(10)-C(9)	118.7(14)
C(6)-O(7)-C(8)	102.0(13)	C(9)^1-O(10)-C(9)	31.1(14)
C(6)-O(7)-C(8)^1	126(2)	C(11)-O(10)-Sr(1)	120.4(6)
C(8)-O(7)-C(8)^1	30.2(12)	C(9)^1-O(10)-Sr(1)	119.9(12)
C(6)-O(7)-Sr(1)	118.8(7)	C(9)-O(10)-Sr(1)	112.5(12)
C(8)-O(7)-Sr(1)	120.5(11)	O(10)-C(11)-C(12)	113.7(9)
C(8)^1-O(7)-Sr(1)	111.3(13)	O(10)-C(11)-C(9)^1	45.1(10)
C(8)^1-C(8)-O(7)	87(3)	C(12)-C(11)-C(9)^1	151.0(11)
C(8)^1-C(8)-C(9)^1	69(3)	O(13)-C(12)-C(11)	113.2(9)
O(7)-C(8)-C(9)^1	120(2)	C(14)-O(13)-C(12)	119.3(7)
C(8)^1-C(8)-C(9)	38(3)	C(14)-O(13)-Sr(1)	119.7(5)
C(16)-C(15)-C(14)	119.3(11)	C(12)-O(13)-Sr(1)	120.9(6)
C(15)-C(16)-C(17)	121.1(10)	O(13)-C(14)-C(19)	115.6(7)
C(16)-C(17)-C(18)	121.1(10)	O(13)-C(14)-C(15)	125.0(9)
C(17)-C(18)-C(19)	118.4(10)	C(19)-C(14)-C(15)	119.4(9)
O(1)-C(19)-C(14)	116.5(7)	C(14)-C(19)-C(18)	120.6(8)
O(1)-C(19)-C(18)	122.8(8)		

Symmetry transformations used to generate equivalent atoms:
1= -x,-y,-z

Table 139.
Anisotropic displacement parameters (A^2 x 10^3) for $[Sr(benzo\text{-}15\text{-}crown\text{-}5)_2(H_2O)_2](I)_2$ **(XXVI)**

atom	U11	U22	U33	U23	U13	U12
Sr(1)	36(1)	37(1)	42(1)	2(1)	11(1)	-3(1)
I(2)	64(1)	70(1)	71(1)	3(1)	21(1)	-14(1)
O(1)	55(3)	45(3)	43(3)	0(3)	11(3)	-13(3)
C(2)	56(6)	105(8)	51(5)	7(6)	16(4)	-11(6)
C(3)	178(15)	180(2)	47(6)	1(8)	3(8)	-89(14)
O(4)	48(4)	86(5)	51(3)	-1(3)	1(3)	-20(3)
C(5)	55(8)	230(2)	132(13)	-81(14)	-22(8)	27(10)
C(6)	36(6)	260(2)	100(10)	67(12)	-7(6)	-22(10)
O(7)	45(4)	76(5)	81(5)	4(4)	13(3)	10(3)
C(8)	51(13)	70(2)	67(14)	29(12)	24(12)	8(11)
C(8')	40(2)	90(2)	160(4)	40(3)	50(2)	23(15)
C(9)	80(2)	70(2)	90(2)	20(2)	40(2)	-0(2)
C(9')	45(14)	80(0)	170(3)	-30(2)	62(19)	11(14)
O(10)	62(4)	65(4)	84(4)	-11(4)	28(3)	6(3)
C(11)	240(2)	54(8)	118(10)	-6(7)	97(12)	38(10)
C(12)	154(12)	57(7)	169(13)	-61(8)	99(11)	-42(8)
O(13)	89(5)	44(3)	60(4)	-9(3)	36(3)	-15(3)
C(14)	59(5)	38(4)	62(6)	4(4)	17(4)	-16(4)
C(15)	80(7)	56(6)	94(8)	5(6)	4(6)	-27(6)
C(16)	49(6)	95(9)	126(11)	34(8)	10(7)	-36(6)
C(17)	51(6)	95(9)	122(10)	60(8)	36(7)	0(6)
C(18)	67(6)	62(6)	71(6)	23(5)	29(5)	11(5)
C(19)	31(4)	44(4)	61(5)	16(4)	9(4)	0(4)
O(99)	150(2)	89(11)	94(12)	-4(9)	22(10)	-30(11)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 140.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[Sr(benzo\text{-}15\text{-}crown\text{-}5)_2(H_2O)_2](I)_2$ **(XXVI)**

atom	x	y	z	U(eq)
H(2A)	566	-1608	2256	80
H(2B)	-559	-678	2405	80
H(3A)	1850	69	2631	80
H(3B)	618	953	2213	80
H(5A)	3175	-656	1996	80
H(5B)	3512	771	2071	80
H(6A)	4398	-625	1183	80
H(6B)	4143	801	1008	80
H(8A)	3856	-1886	551	80
H(8B)	4176	-1030	-98	80
H(8A)^1	4232	-1199	-239	80
H(8B)^1	2861	-703	-850	80
H(9A)	3025	-2665	-702	80
H(9B)	2747	-1457	-1226	80
H(9A)^1	2765	-2588	114	80
H(9'B)^1	2845	-2818	-767	80
H(11A)	1378	-3569	-181	80
H(11B)	676	-3589	-1099	80
H(12A)	-793	-4076	-261	80
H(12B)	-1443	-3258	-1013	80
H(15A)	-3137	-4052	-207	80
H(16A)	-4598	-4320	630	80
H(17A)	-4296	-3120	1776	80
H(18A)	-2632	-1468	2064	80
H(99A)	5552	-1754	3189	50
H(99B)	4888	-2449	3448	50

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

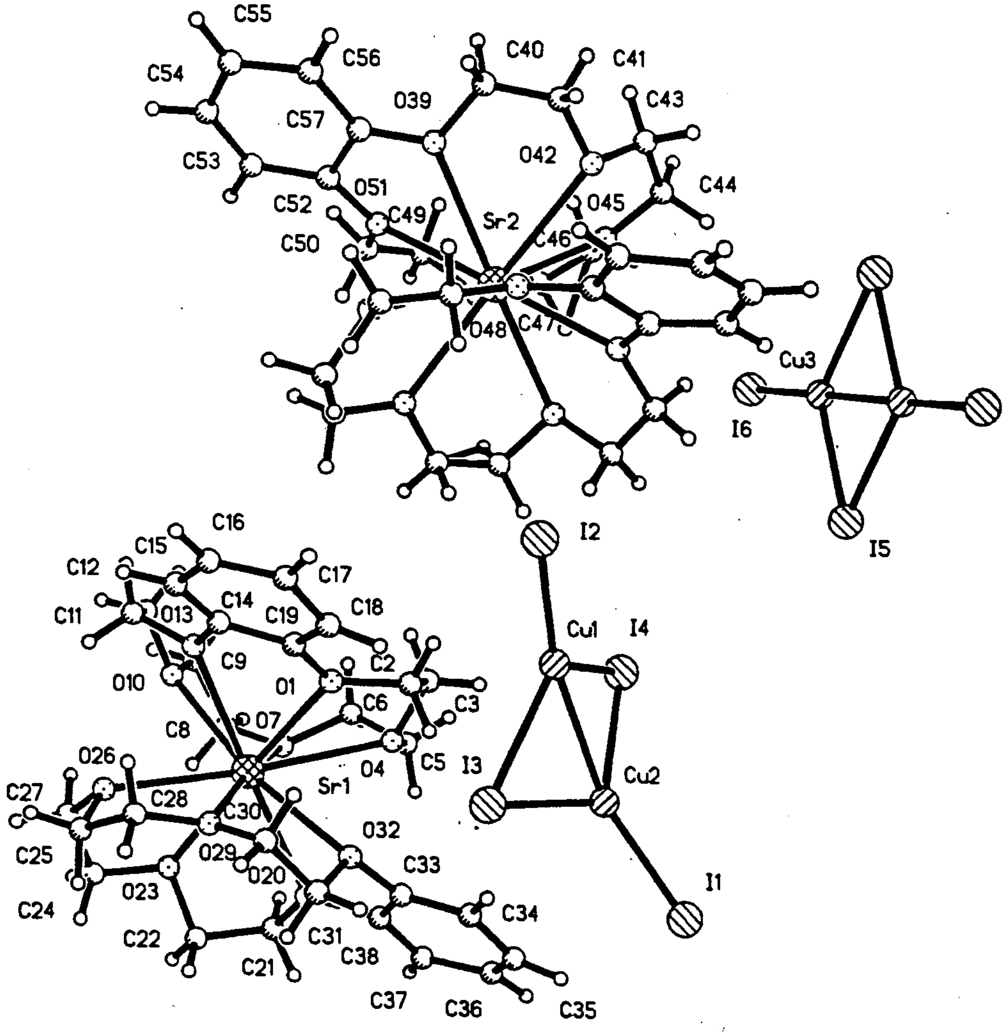


Figure 45. Projection View of $[Sr(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Cu_2I_4)$ **(XXVII)**

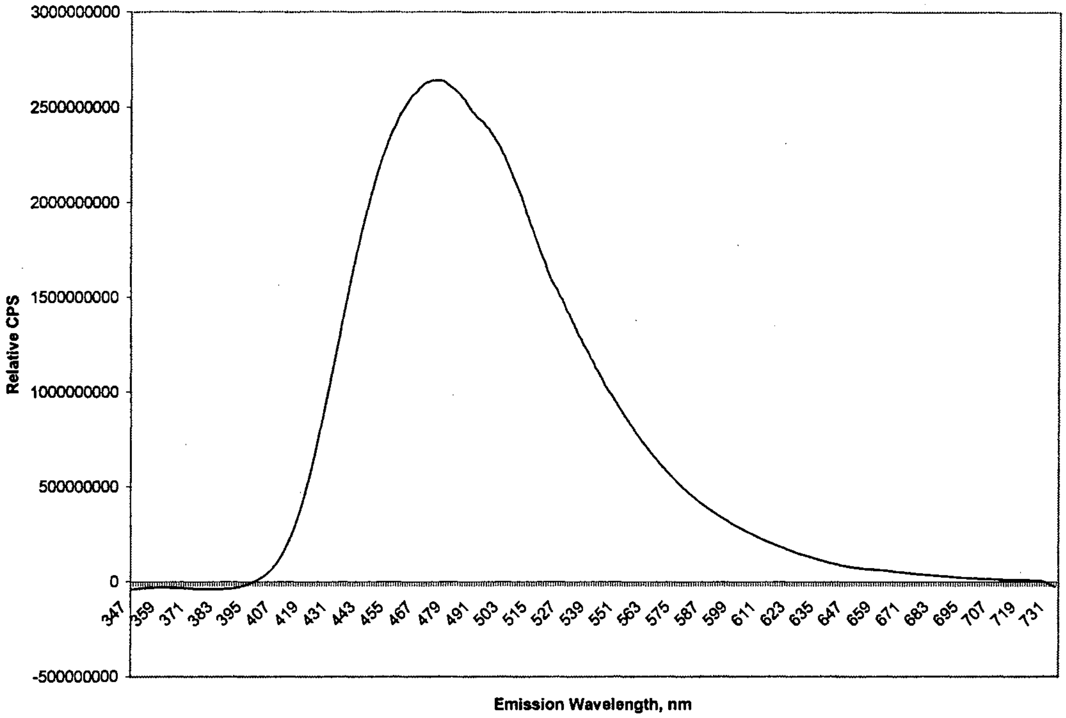


Figure 46. Emission Spectrum of [Sr(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVII)**

Table 141.
Crystal data and structure refinement for $[Sr(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Cu_2I_4)$ **(XXVII)**

Empirical formula	$C_{84}H_{120}Cu_6I_{12}O_{30}Sr_3$
Formula weight	3776.70
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic,C2/c
Unit cell dimensions	a = 33.238(8)Å $\alpha = 90^\circ$
	b = 20.584(5)Å $\beta = 131.49(1)^\circ$
	c = 22.291(4)Å $\gamma = 90^\circ$
Volume	11424(4) $Å^3$
Z, Calculated density	4, 2.196 Mg/m^3
Absorption coefficient	5.793 mm^{-1}
F(000)	7152
Theta range for data collection	1.83 to 30.01 deg.
Index ranges	$-1 \leq h \leq 46$, $-28 \leq k \leq 1$, $-31 \leq l \leq 23$
Reflections collected / unique	18274 / 16593 [R(int) = 0.2358]
Completeness to $2\theta = 30.01^\circ$	48.5%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16593 / 0 / 609
Goodness-of-fit on F^2	0.954
Final R indices $[I>2\sigma(I)]$	R1 = 0.1499, wR2 = 0.1792
R indices (all data)	R1 = 0.4569, wR2 = 0.2801
Largest diff. peak and hole	1.137 and -1.153 e. $Å^{-3}$

Table 142.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Sr(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVII)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
I(1)	1772(1)	3712(1)	5125(1)	57(1)
I(2)	780(1)	879(1)	5907(1)	76(1)
I(3)	551(1)	2119(1)	4021(1)	58(1)
I(4)	1094(1)	3082(1)	6211(1)	57(1)
I(5)	2482(1)	3046(1)	9126(1)	69(1)
I(6)	1520(1)	3718(1)	9709(1)	71(1)
Sr(1)	-1641(1)	3865(1)	2591(1)	29(1)
Sr(2)	0	1164(2)	7500	30(1)
Cu(1)	836(1)	1959(2)	5450(2)	47(1)
Cu(2)	1170(1)	2994(2)	5129(2)	49(1)
Cu(3)	2157(1)	2918(2)	9899(2)	56(1)
O(1)	-970(7)	3002(9)	3771(10)	45(5)
C(2)	-442(12)	3209(11)	4433(15)	46(8)
C(3)	-456(12)	3822(14)	4735(15)	66(10)
O(4)	-744(7)	4291(9)	4074(10)	46(5)
C(5)	-790(12)	4930(14)	4270(2)	57(10)
C(6)	-1292(13)	5025(15)	4050(2)	65(11)
O(7)	-1720(8)	4895(9)	3196(12)	59(6)
C(8)	-2243(11)	5036(15)	2870(2)	70(12)
C(9)	-2480(2)	4470(2)	2960(2)	94(14)
O(10)	-2433(7)	3924(10)	2615(9)	41(5)
C(11)	-2599(11)	3370(2)	2780(2)	61(10)
C(12)	-2487(10)	2756(14)	2560(2)	52(9)
O(13)	-1965(7)	2796(8)	2866(9)	40(5)
C(14)	-1656(10)	2233(12)	3140(2)	33(7)
C(15)	-1842(13)	1622(13)	2980(2)	55(9)
C(16)	-1506(14)	1131(13)	3290(2)	58(9)
C(17)	-950(2)	1180(2)	3790(2)	100(2)
C(18)	-743(13)	1820(2)	3950(2)	57(10)
C(19)	-1108(11)	2372(13)	3638(14)	34(7)
O(20)	-1237(7)	4812(9)	2330(11)	53(6)
C(21)	-1564(11)	5353(13)	1870(2)	46(8)
C(22)	-2074(12)	5110(13)	1120(2)	46(9)
O(23)	-2297(8)	4688(9)	1332(11)	55(6)
C(24)	-2803(14)	4460(2)	600(2)	86(13)
C(25)	-2934(13)	3890(2)	750(2)	96(14)
O(26)	-2546(8)	3381(10)	1199(10)	63(7)

Table 142. (cont.)
Atomic coordinates (x 10^4) and equivalent isotropic
displacement parameters (Å^2 x 10^3) for
[Sr(benzo-15-crown-5)$_2$]$_2$(Cu_2I_4) **(XXVII)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
C(27)	-2518(14)	3040(2)	729(16)	79(13)
C(28)	-2020(12)	2604(15)	1240(2)	59(10)
O(29)	-1576(9)	2997(12)	1831(12)	79(8)
C(30)	-1079(13)	2739(15)	2130(2)	66(10)
C(31)	-768(12)	3299(13)	2290(2)	60(10)
O(32)	-711(6)	3737(9)	2829(9)	37(5)
C(33)	-410(11)	4287(15)	3054(14)	39(8)
C(34)	135(12)	4259(15)	3496(15)	50(9)
C(35)	402(13)	4850(2)	3670(2)	70(11)
C(36)	138(14)	5410(2)	3450(2)	70(12)
C(37)	-422(11)	5496(14)	2980(2)	53(10)
C(38)	-681(11)	4890(14)	2800(15)	36(8)
O(39)	-415(8)	136(8)	7704(11)	47(6)
C(40)	-66(11)	-220(2)	8390(2)	85(13)
C(41)	461(15)	-70(2)	8910(2)	170(3)
O(42)	661(9)	466(11)	8891(13)	66(7)
C(43)	920(2)	780(2)	9620(2)	210(3)
C(44)	980(2)	1420(2)	9600(2)	160(3)
O(45)	592(10)	1739(13)	8911(15)	78(8)
C(46)	390(2)	2310(2)	8960(2)	140(2)
C(47)	-20(19)	2530(2)	8390(2)	190(3)
O(48)	-372(9)	2255(11)	7663(13)	65(7)
C(49)	-850(2)	2210(2)	7500(2)	160(3)
C(50)	-1184(14)	1820(2)	6970(2)	130(2)
O(51)	-969(8)	1189(11)	7017(12)	61(6)
C(52)	-1246(12)	640(2)	6820(2)	74(14)
C(53)	-1792(14)	540(2)	6280(2)	57(10)
C(54)	-2008(14)	-70(2)	6140(2)	71(11)
C(55)	-1755(13)	-595(14)	6500(2)	71(12)
C(56)	-1187(13)	-551(14)	7030(2)	65(10)
C(57)	-941(10)	60(2)	7200(2)	37(8)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 143.
Bond lengths [A] and angles [°] for
[Sr(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVII)**

I(1)-Cu(2)	2.493(4)	C(11)-C(12)	1.48(3)
I(2)-Cu(1)	2.504(4)	C(12)-O(13)	1.39(3)
I(3)-Cu(2)	2.615(4)	C(14)-C(15)	1.34(3)
I(3)-Cu(1)	2.674(4)	C(14)-C(19)	1.39(3)
I(4)-Cu(2)	2.591(4)	C(15)-C(16)	1.31(4)
I(4)-Cu(1)	2.650(4)	C(16)-C(17)	1.40(4)
I(5)-Cu(3)^{1}	2.576(4)	C(17)-C(18)	1.40(5)
I(5)-Cu(3)	2.581(4)	C(18)-C(19)	1.46(4)
I(6)-Cu(3)	2.489(4)	C(21)-C(22)	1.47(3)
Sr(1)-O(29)	2.52(2)	C(22)-O(23)	1.41(3)
Sr(1)-O(7)	2.62(2)	C(24)-C(25)	1.38(4)
Sr(1)-O(20)	2.64(2)	C(25)-O(26)	1.43(4)
Sr(1)-O(10)	2.67(2)	C(27)-C(28)	1.53(4)
Sr(1)-O(13)	2.69(2)	C(28)-O(29)	1.41(3)
Sr(1)-O(26)	2.70(2)	C(3)-O(4)	1.47(3)
Sr(1)-O(1)	2.70(2)	C(30)-C(31)	1.43(3)
Sr(1)-O(23)	2.72(2)	C(31)-O(32)	1.41(2)
Sr(1)-O(4)	2.74 (2)	C(33)-C(34)	1.38(3)
Sr(1)-O(32)	2.782(15)	C(33)-C(38)	1.41(4)
Sr(2)-O(51)^{2}	2.64(2)	C(34)-C(35)	1.39(4)
Sr(2)-O(51)	2.64(2)	C(35)-C(36)	1.34(4)
Sr(2)-O(45)	2.64(2)	C(36)-C(37)	1.42(4)
Sr(2)-O(45)^{2}	2.64(2)	C(37)-C(38)	1.42(4)
Sr(2)-O(48)^{2}	2.70(2)	C(40)-C(41)	1.35(4)
Sr(2)-O(48)	2.70(2)	C(41)-O(42)	1.31(4)
Sr(2)-O(39)^{2}	2.73(2)	C(43)-C(44)	1.34(5)
Sr(2)-O(39)	2.73(2)	C(44)-O(45)	1.36(4)
Sr(2)-O(42)^{2}	2.74(2)	C(46)-C(47)	1.17(5)
Sr(2)-O(42)	2.74(2)	C(47)-O(48)	1.34(4)
Cu(1)-Cu(2)	2.707(5)	C(49)-C(50)	1.24(4)
Cu(3)-I(5)^{1}	2.576(4)	C(5)-C(6)	1.41(3)
Cu(3)-Cu(3)^{1}	2.644(7)	C(50)-O(51)	1.45(3)
O(1)-C(19)	1.34(3)	C(52)-C(53)	1.37(4)
O(1)-C(2)	1.42(3)	C(52)-C(57)	1.43(4)
C(2)-C(3)	1.45(3)	C(53)-C(54)	1.37(4)
O(23)-C(24)	1.44(3)	C(54)-C(55)	1.28(4)
O(26)-C(27)	1.31(3)	C(55)-C(56)	1.42(4)
O(29)-C(30)	1.41(3)	C(56)-C(57)	1.40(4)
O(32)-C(33)	1.37(3)	C(6)-O(7)	1.46(3)
O(39)-C(40)	1.36(3)	C(8)-C(9)	1.49(4)
O(39)-C(57)	1.32(3)	C(9)-O(10)	1.41(3)

Table 143. (cont.)
Bond lengths [A] and angles [°] for
[Sr(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVII)**

O(4)-C(5)	1.43(3)	O(10)-C(11)	1.42(3)
O(42)-C(43)	1.38(4)	O(13)-C(14)	1.39(3)
O(45)-C(46)	1.40(5)	O(20)-C(21)	1.41(3)
O(48)-C(49)	1.38(4)	O(20)-C(38)	1.40(3)
O(51)-C(52)	1.34(4)	O(7)-C(8)	1.40(3)
Cu(2)-I(3)-Cu(1)	61.55(11)	O(51)^2-Sr(2)-O(48)	118.2(7)
Cu(2)-I(4)-Cu(1)	62.17(11)	O(51)-Sr(2)-O(48)	59.6(7)
Cu(3)^1-I(5)-Cu(3)	61.68(14)	O(45)-Sr(2)-O(48)	60.9(8)
O(29)-Sr(1)-O(7)	169.9(7)	O(45)^2-Sr(2)-O(48)	75.0(8)
O(29)-Sr(1)-O(20)	95.2(7)	O(48)^2-Sr(2)-O(48)	67.5(9)
O(7)-Sr(1)-O(20)	75.8(6)	O(51)^2-Sr(2)-O(39^2	57.7(6)
O(29)-Sr(1)-O(10)	124.0(6)	O(51)-Sr(2)-O(39)^2	124.4(7)
O(7)-Sr(1)-O(10)	61.1(6)	O(45)-Sr(2)-O(39)^2	119.2(7)
O(20)-Sr(1)-O(10)	128.5(6)	O(45)^2-Sr(2)-O(39)^2	102.1(7)
O(29)-Sr(1)-O(13)	78.6(6)	O(48)^2-Sr(2)-O(39)^2	107.2(6)
O(7)-Sr(1)-O(13)	110.7(5)	O(48)-Sr(2)-O(39)^2	174.7(6)
O(20)-Sr(1)-O(13)	172.5(6)	O(51)^2-Sr(2)-O(39)	124.4(7)
O(10)-Sr(1)-O(13)	59.0(6)	O(51)-Sr(2)-O(39)	57.7(6)
O(29)-Sr(1)-O(26)	60.2(7)	O(45)-Sr(2)-O(39)	102.1(7)
O(7)-Sr(1)-O(26)	118.4(7)	O(45)^2-Sr(2)-O(39)	119.2(7)
O(20)-Sr(1)-O(26)	111.2(6)	O(48)^2-Sr(2)-O(39)	174.7(6)
O(10)-Sr(1)-O(26)	71.2(6)	O(48)-Sr(2)-O(39)	107.2(6)
O(13)-Sr(1)-O(26)	69.6(5)	O(39)^2-Sr(2)-O(39)	78.1(8)
O(29)-Sr(1)-O(1)	78.9(7)	O(51)^2-Sr(2)-O(42)^2	108.6(6)
O(7)-Sr(1)-O(1)	109.4(6)	O(51)-Sr(2)-O(42)^2	72.6(6)
O(20)-Sr(1)-O(1)	119.2(6)	O(45)-Sr(2)-O(42)^2	172.5(7)
O(10)-Sr(1)-O(1)	101.6(5)	O(45)^2-Sr(2)-O(42)^2	58.7(8)
O(13)-Sr(1)-O(1)	55.8(5)	O(48)^2-Sr(2)-O(42)^2	112.3(6)
O(26)-Sr(1)-O(1)	116.7(6)	O(48)-Sr(2)-O(42)^2	119.6(7)
O(29)-Sr(1)-O(23)	96.5(7)	O(39)^2-Sr(2)-O(42^2	61.2(6)
O(7)-Sr(1)-O(23)	75.0(6)	O(39)-Sr(2)-O(42)^2	70.5(6)
O(20)-Sr(1)-O(23)	59.4(6)	O(51)^2-Sr(2)-O(42)	72.6(6)
O(10)-Sr(1)-O(23)	82.2(6)	O(51)-Sr(2)-O(42)	108.6(6)
O(13)-Sr(1)-O(23)	125.2(6)	O(45)-Sr(2)-O(42)	58.7(8)
O(26)-Sr(1)-O(23)	61.5(6)	O(45)^2-Sr(2)-O(42)	172.5(7)
O(1)-Sr(1)-O(23)	175.2(6)	O(48)^2-Sr(2)-O(42)	119.6(7)
O(29)-Sr(1)-O(4)	121.2(6)	O(48)-Sr(2)-O(42)	112.3(6)
O(7)-Sr(1)-O(4)	61.3(6)	O(39)^2-Sr(2)-O(42)	70.5(6)
O(20)-Sr(1)-O(4)	74.0(6)	O(39)-Sr(2)-O(42)	61.2(6)
O(10)-Sr(1)-O(4)	105.1(5)	O(42)^2-Sr(2)-O(42)	116.6(10)
O(13)-Sr(1)-O(4)	105.4(5)	I(2)-Cu(1)-I(4)	126.40(14)
O(26)-Sr(1)-O(4)	174.8(5)	I(2)-Cu(1)-I(3)	122.05(15)

Table 143. (cont.)
Bond lengths [A] and angles [°] for
[Sr(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVII)**

O(1)-Sr(1)-O(4)	59.9(6)	I(4)-Cu(1)-I(3)	111.36(13)
O(23)-Sr(1)-O(4)	122.2(5)	I(2)-Cu(1)-Cu(2)	163.8(2)
O(29)-Sr(1)-O(32)	59.4(6)	I(4)-Cu(1)-Cu(2)	57.84(11)
O(7)-Sr(1)-O(32)	117.1(6)	I(3)-Cu(1)-Cu(2)	58.16(10)
O(20)-Sr(1)-O(32)	56.5(5)	I(1)-Cu(2)-I(4)	122.35(15)
O(10)-Sr(1)-O(32)	170.5(5)	I(1)-Cu(2)-I(3)	122.37(14)
O(13)-Sr(1)-O(32)	116.1(5)	I(4)-Cu(2)-I(3)	115.26(14)
O(26)-Sr(1)-O(32)	115.8(6)	I(1)-Cu(2)-Cu(1)	159.7(2)
O(1)-Sr(1)-O(32)	69.8(5)	I(4)-Cu(2)-Cu(1)	59.99(11)
O(23)-Sr(1)-O(32)	106.6(6)	I(3)-Cu(2)-Cu(1)	60.29(12)
O(4)-Sr(1)-O(32)	67.5(5)	I(6)-Cu(3)-I(5)#1	121.45(15)
O(51)^{2}-Sr(2)-O(51)	177.8(10)	I(6)-Cu(3)-I(5)	120.2(2)
O(51)^{2}-Sr(2)-O(45)	76.1(7)	I(5)^{1}-Cu(3)-I(5)	118.32(14)
O(51)-Sr(2)-O(45)	102.8(7)	I(6)-Cu(3)-Cu(3)^{1}	179.1(3)
O(51)^{2}-Sr(2)-O(45)^{2}	102.8(7)	I(5)^{1}-Cu(3)-Cu(3)^{1}	59.25(15)
O(51)-Sr(2)-O(45)^{2}	76.1(7)	I(5)-Cu(3)-Cu(3)^{1}	59.07(14)
O(45)-Sr(2)-O(45)^{2}	126.7(13)	C(19)-O(1)-C(2)	122(2)
O(51)^{2}-Sr(2)-O(48)^{2}	59.6(7)	C(19)-O(1)-Sr(1)	119(2)
O(51)-Sr(2)-O(48)^{2}	118.2(7)	C(2)-O(1)-Sr(1)	118.2(15)
O(45)-Sr(2)-O(48)^{2}	75.0(8)	O(1)-C(2)-C(3)	110(3)
O(45)^{2}-Sr(2)-O(48)^{2}	60.9(8)	C(46)-O(45)-Sr(2)	117(2)
C(11)-O(10)-C(9)	108(2)	C(47)-C(46)-O(45)	121(4)
C(11)-O(10)-Sr(1)	122(2)	C(47)-O(48)-C(49)	106(3)
C(12)-O(13)-C(14)	119(2)	C(47)-O(48)-Sr(2)	114(2)
C(12)-O(13)-Sr(1)	119.8(15)	C(49)-C(50)-O(51)	115(3)
C(14)-C(15)-C(16)	120(3)	C(49)-O(48)-Sr(2)	117(2)
C(14)-C(19)-C(18)	117(3)	C(5)-C(6)-O(7)	109(2)
C(14)-O(13)-Sr(1)	119.1(14)	C(5)-O(4)-C(3)	115(2)
C(15)-C(14)-C(19)	122(2)	C(5)-O(4)-Sr(1)	114(2)
C(15)-C(14)-O(13)	126(2)	C(50)-C(49)-O(48)	116(4)
C(15)-C(16)-C(17)	125(3)	C(50)-O(51)-Sr(2)	117(2)
C(16)-C(17)-C(18)	116(3)	C(52)-C(53)-C(54)	122(3)
C(17)-C(18)-C(19)	120(3)	C(52)-O(51)-C(50)	123(3)
C(19)-C(14)-O(13)	112(2)	C(52)-O(51)-Sr(2)	120(2)
C(2)-C(3)-O(4)	108(2)	C(53)-C(52)-C(57)	114(4)
C(21)-O(20)-C(38)	117(2)	C(54)-C(55)-C(56)	115(3)
C(21)-O(20)-Sr(1)	118.8(15)	C(55)-C(54)-C(53)	127(3)
C(22)-O(23)-Sr(1)	119(2)	C(55)-C(56)-C(57)	120(3)
C(24)-C(25)-O(26)	121(3)	C(56)-C(57)-C(52)	122(3)
C(24)-O(23)-C(22)	107(2)	C(57)-O(39)-C(40)	124(2)
C(24)-O(23)-Sr(1)	120(2)	C(57)-O(39)-Sr(2)	119(2)
C(25)-C(24)-O(23)	109(3)	C(6)-O(7)-Sr(1)	119(2)

Table 143. (cont.)
Bond lengths [A] and angles [°] for
$[Sr(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Cu_2I_4)$ **(XXVII)**

C(25)-O(26)-Sr(1)	110(2)	C(8)-O(7)-C(6)	116(2)
C(27)-O(26)-C(25)	110(2)	C(8)-O(7)-Sr(1)	114(2)
C(27)-O(26)-Sr(1)	120(2)	C(9)-O(10)-Sr(1)	120(2)
C(28)-O(29)-C(30)	113(2)	O(1)-C(19)-C(14)	117(3)
C(28)-O(29)-Sr(1)	121(2)	O(1)-C(19)-C(18)	126(3)
C(3)-O(4)-Sr(1)	117.7(15)	O(10)-C(11)-C(12)	112(2)
C(30)-C(31)-O(32)	113(3)	O(10)-C(9)-C(8)	108(2)
C(30)-O(29)-Sr(1)	122(2)	O(13)-C(12)-C(11)	107(2)
C(31)-C(30)-O(29)	104(3)	O(20)-C(21)-C(22)	108(2)
C(31)-O(32)-Sr(1)	113.2(15)	O(23)-C(22)-C(21)	107(2)
C(33)-C(34)-C(35)	117(3)	O(26)-C(27)-C(28)	109(2)
C(33)-C(38)-C(37)	124(3)	O(29)-C(28)-C(27)	108(3)
C(33)-C(38)-O(20)	112(3)	O(32)-C(33)-C(34)	122(3)
C(33)-O(32)-C(31)	120(2)	O(32)-C(33)-C(38)	118(2)
C(33)-O(32)-Sr(1)	116(2)	O(39)-C(57)-C(52)	115(3)
C(34)-C(33)-C(38)	121(3)	O(39)-C(57)-C(56)	123(3)
C(35)-C(36)-C(37)	127(3)	O(4)-C(5)-C(6)	111(3)
C(36)-C(35)-C(34)	120(3)	O(42)-C(41)-C(40)	124(4)
C(37)-C(38)-O(20)	124(2)	O(42)-C(43)-C(44)	114(4)
C(38)-C(37)-C(36)	111(3)	O(45)-C(44)-C(43)	118(4)
C(38)-O(20)-Sr(1)	122.0(15)	O(51)-C(52)-C(53)	129(4)
C(40)-O(39)-Sr(2)	117(2)	O(51)-C(52)-C(57)	117(3)
C(41)-C(40)-O(39)	121(3)	O(7)-C(8)-C(9)	110(2)
C(41)-O(42)-C(43)	106(3)	C(44)-O(45)-Sr(2)	122(3)
C(41)-O(42)-Sr(2)	116(2)	C(46)-C(47)-O(48)	127(4)
C(43)-O(42)-Sr(2)	120(2)	C(46)-O(45)-C(44)	118(3)

Symmetry transformations used to generate equivalent atoms:
1= -x+1/2,-y+1/2,-z+2   2= -x,y,-z+3/2

Table 144.
Anisotropic displacement parameters ($\AA^2 \times 10^3$) for $[Sr(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Cu_2I_4)$ **(XXVII)**

atom	U11	U22	U33	U23	U13	U12
I(1)	57(2)	50(2)	76(2)	-13(1)	49(1)	-11(1)
I(2)	91(2)	59(2)	84(2)	-1(1)	61(2)	-13(1)
I(3)	61(2)	53(2)	59(1)	-2(1)	39(1)	-9(1)
I(4)	57(2)	59(2)	61(1)	2(1)	41(1)	1(1)
I(5)	96(2)	54(2)	81(2)	9(1)	69(2)	16(1)
I(6)	65(2)	76(2)	73(2)	10(1)	47(1)	28(1)
Sr(1)	29(2)	26(2)	31(1)	-1(1)	20(1)	-2(1)
Sr(2)	36(2)	28(2)	34(2)	0	26(2)	0
Cu(1)	42(2)	38(2)	61(2)	14(2)	35(2)	2(2)
Cu(2)	40(2)	47(3)	63(2)	-1(2)	35(2)	-7(2)
Cu(3)	47(3)	53(3)	61(2)	-7(2)	34(2)	10(2)
O(1)	38(13)	31(13)	51(12)	13(11)	23(11)	14(10)
C(2)	100(3)	0(2)	50(2)	-22(14)	60(2)	-30(2)
C(3)	70(2)	30(2)	50(2)	20(2)	20(2)	10(2)
O(4)	66(15)	27(12)	50(12)	-19(10)	41(12)	4(10)
C(5)	120(3)	40(2)	90(2)	-10(2)	110(3)	10(2)
C(6)	110(3)	80(3)	50(2)	-40(2)	70(2)	-40(2)
O(7)	73(17)	43(15)	70(15)	4(12)	52(14)	23(12)
C(8)	50(2)	70(3)	40(2)	-0(2)	10(2)	80(2)
C(9)	170(4)	50(3)	130(3)	40(3)	130(3)	60(3)
O(10)	40(13)	45(15)	34(11)	9(10)	24(10)	3(10)
C(11)	20(2)	70(3)	80(2)	-10(2)	30(2)	10(2)
C(12)	30(2)	60(2)	80(2)	10(2)	40(2)	-23(15)
O(13)	34(12)	29(12)	45(11)	-10(9)	22(10)	-3(9)
C(14)	30(2)	8(15)	80(2)	-4(14)	40(2)	9(12)
C(15)	90(3)	10(2)	70(2)	20(2)	50(2)	20(2)
C(16)	100(3)	0(16)	90(2)	-10(2)	70(2)	-0(2)
C(17)	110(4)	140(5)	110(3)	60(3)	110(3)	80(3)
C(18)	60(2)	70(3)	60(2)	40(2)	50(2)	40(2)
C(19)	60(2)	20(2)	30(2)	-14(13)	32(16)	-22(15)
O(20)	31(13)	39(14)	68(14)	30(11)	25(12)	21(10)
C(21)	60(2)	30(2)	70(2)	-10(2)	60(2)	-10(2)
C(22)	90(3)	20(2)	50(2)	17(15)	50(2)	10(2)
O(23)	49(15)	40(14)	40(12)	-14(11)	15(11)	-22(11)
C(24)	90(3)	60(3)	110(3)	60(2)	60(3)	10(2)
C(25)	90(3)	90(3)	30(2)	-10(2)	10(2)	-0(3)
O(26)	90(2)	50(2)	23(11)	24(11)	23(12)	-3(13)

Table 144. (cont.)
Anisotropic displacement parameters ($Å^2 \times 10^3$) for
$[Sr(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Cu_2I_4)$ **(XXVII)**

atom	U11	U22	U33	U23	U13	U12
C(27)	110(3)	90(3)	30(2)	-30(2)	50(2)	-70(3)
C(28)	60(2)	60(3)	40(2)	-40(2)	20(2)	-10(2)
O(29)	60(2)	110(2)	82(16)	-70(2)	53(14)	-29(15)
C(30)	80(3)	30(2)	90(3)	-30(2)	60(2)	-40(2)
C(31)	90(3)	30(2)	60(2)	-40(2)	50(2)	20(2)
O(32)	13(10)	61(15)	29(10)	-4(10)	11(9)	-8(10)
C(33)	20(2)	70(3)	20(15)	-31(15)	8(14)	-40(2)
C(34)	60(2)	60(2)	40(2)	20(2)	30(2)	-0(2)
C(35)	40(2)	80(3)	80(3)	-30(2)	40(2)	-30(2)
C(36)	100(3)	70(3)	90(3)	-60(2)	80(3)	-60(2)
C(37)	40(2)	40(2)	110(3)	-40(2)	60(2)	-40(2)
C(38)	25(2)	40(2)	30(2)	7(14)	10(15)	26(15)
O(39)	47(15)	32(13)	56(14)	32(11)	31(12)	27(11)
C(40)	10(2)	90(3)	150(4)	20(3)	50(2)	10(2)
C(41)	70(3)	260(7)	100(3)	110(4)	30(3)	-50(4)
O(42)	80(2)	70(2)	80(2)	32(14)	67(15)	15(14)
C(43)	370(9)	170(6)	40(3)	0(3)	120(4)	-10(6)
C(44)	90(3)	220(6)	40(3)	40(3)	-10(2)	-110(4)
O(45)	90(2)	70(2)	60(2)	-41(15)	40(2)	-20(2)
C(46)	150(5)	120(5)	60(3)	-20(3)	30(3)	-90(4)
C(47)	230(6)	120(4)	80(3)	-70(3)	50(4)	100(4)
O(48)	75(18)	80(2)	80(2)	-25(14)	66(16)	-20(14)
C(49)	190(6)	160(5)	100(4)	-130(4)	90(4)	-130(4)
C(50)	120(3)	180(4)	100(3)	20(3)	80(3)	150(3)
O(51)	31(13)	80(2)	90(2)	-8(14)	47(13)	-13(12)
C(52)	0(2)	160(4)	40(2)	10(2)	5(17)	30(2)
C(53)	90(3)	50(3)	50(2)	20(2)	60(2)	20(2)
C(54)	70(3)	90(3)	40(2)	10(2)	30(2)	-20(2)
C(55)	70(3)	20(2)	70(2)	20(2)	30(2)	-50(2)
C(56)	60(3)	20(2)	70(2)	30(2)	30(2)	20(2)
C(57)	4(16)	70(2)	50(2)	-30(2)	20(2)	-20(15)

The anisotropic displacement factor exponent takes the form:
$-2 pi^2 [h^2 a^{2*} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 145.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for [Sr(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVII)**

atom	x	y	z	U(eq)
H(2A)	-241	3283	4270	80
H(2B)	-258	2883	4845	80
H(3A)	-103	3978	5178	80
H(3B)	-651	3755	4910	80
H(5A)	-722	5256	4041	80
H(5B)	-517	4964	4843	80
H(6A)	-1314	5468	4162	80
H(6B)	-1337	4748	4349	80
H(8A)	-2460	5124	2305	80
H(8B)	-2242	5416	3116	80
H(9A)	-2850	4540	2674	80
H(9B)	-2287	4399	3512	80
H(11A)	-2979	3395	2470	80
H(11B)	-2427	3352	3333	80
H(12A)	-2732	2699	1992	80
H(12B)	-2519	2390	2796	80
H(15A)	-2223	1552	2630	80
H(16A)	-1651	699	3163	80
H(17A)	-719	805	4039	80
H(18A)	-372	1889	4215	80
H(21A)	-1388	5632	1759	80
H(21B)	-1638	5598	2154	80
H(22A)	-1999	4876	834	80
H(22B)	-2321	5454	787	80
H(24A)	-2780	4382	200	80
H(24B)	-3071	4789	405	80
H(25A)	-3248	3709	257	80
H(25B)	-3034	4011	1055	80
H(27A)	-2518	3315	379	80
H(27B)	-2827	2765	407	80
H(28A)	-1956	2413	920	80
H(28B)	-2058	2260	1494	80
H(30A)	-1125	2443	1757	80
H(30B)	-902	2518	2629	80
H(31A)	-416	3179	2500	80
H(34A)	317	3848	3683	80
H(35A)	773	4845	3921	80

Table 145. (cont.)
Hydrogen coordinates (x 10^4) and isotropic
displacement parameters ($Å^2$x 10^3) for
[Sr(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVII)**

atom	x	y	z	U(eq)
H(36A)	357	5792	3638	80
H(37A)	-589	5916	2817	80
H(40A)	-88	-661	8236	80
H(40B)	-192	-196	8669	80
H(41A)	648	-417	902	80
H(41B)	579	-80	9441	80
H(43A)	1278	599	9971	80
H(43B)	758	663	9831	80
H(44A)	1321	1527	9761	80
H(44B)	980	1584	10003	80
H(46A)	655	2616	9356	80
H(46B)	208	2147	9134	80
H(47A)	185	2783	8310	80
H(47B)	-205	2837	8457	80
H(49A)	-1010	2629	7358	80
H(49B)	-772	2073	7983	80
H(50A)	-1329	2010	6468	80
H(50B)	-1477	1746	6950	80
H(53A)	-2011	916	5997	80
H(54A)	-2389	-118	5723	80
H(55A)	-1940	-989	6419	80
H(56A)	-989	-947	7282	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

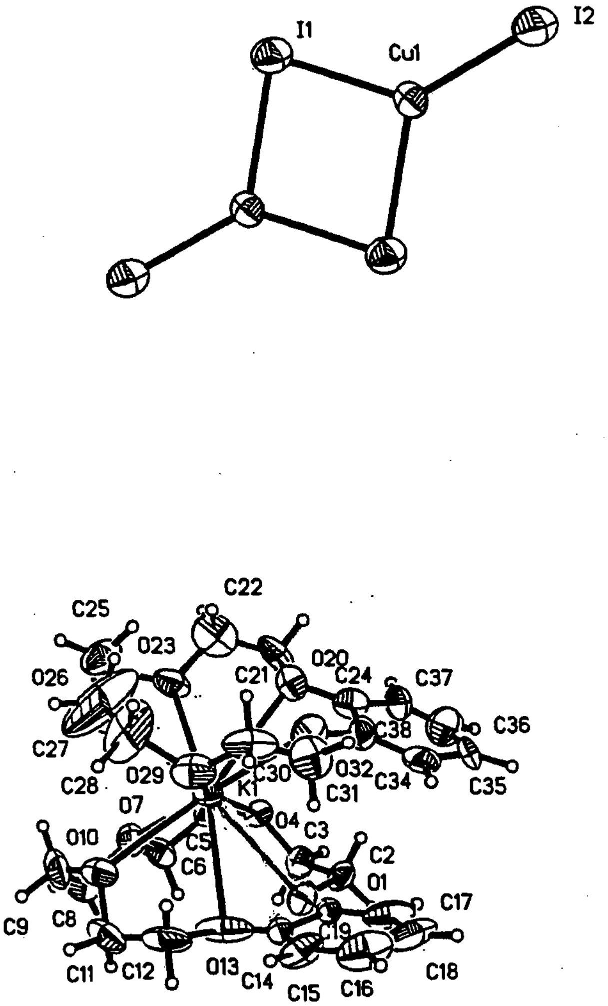


Figure 47. Projection View of [K(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVIII)**

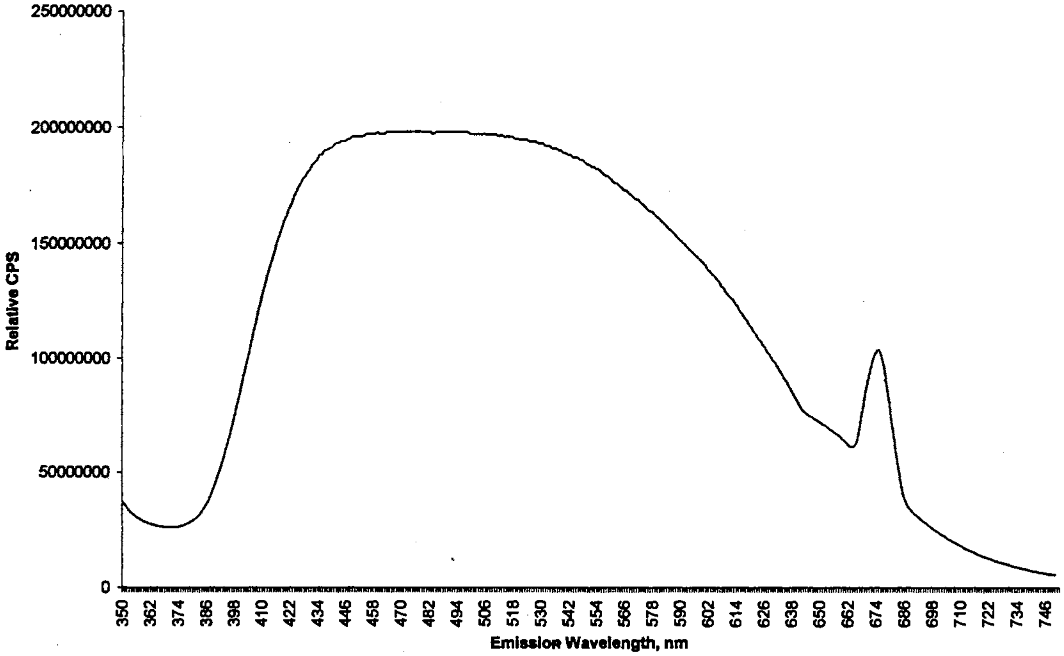


Figure 48. Emission Spectrum of [K(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVIII)**

Table 146.
Crystal data and structure refinement for
[K(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) (**XXVIII**)

Empirical formula	$C_{56} H_{80} Cu_2 I_4 K_2 O_{20}$
Formula weight	1786.08
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\overline{1}$
Unit cell dimensions	a = 12.303(4) Å α = 103.58(4)°
	b = 12.450(5) Å β = 95.23(3)°
	c = 12.663(7) Å γ = 111.19(3)°
Volume	1724.4(13) Å^3
Z, Calculated density	1, 1.720 Mg/m^3
Absorption coefficient	2.592 mm^{-1}
F(000)	884
Theta range for data collection	1.81 to 30.00 deg.
Index ranges	$-1 \leq h \leq 16$, $-16 \leq k \leq 15$, $-17 \leq l \leq 17$
Reflections collected / unique	11066 / 9826 [R(int) = 0.0576]
Completeness to 2θ =30.00°	97.5%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9826 / 0 / 371
Goodness-of-fit on F^2	0.981
Final R indices [I>2σ(I)]	R1 = 0.1116, wR2 = 0.2802
R indices (all data)	R1 = 0.2935, wR2 = 0.3927
Extinction coefficient	0.0000(9)
Largest diff. peak and hole	1.833 and -0.927 e. Å^{-3}

Table 147.
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for ?.
[K(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVIII)**

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
K(1)	17799(2)	11355(3)	7889(2)	57(1)
Cu(1)	4493(1)	4855(2)	-1427(1)	64(1)
I(1)	3949(1)	3185(1)	-280(1)	86(1)
I(2)	3825(2)	4796(1)	-3434(1)	126(1)
O(1)	19768(9)	13630(9)	7793(9)	73(3)
C(2)	20467(13)	13349(13)	7039(14)	71(4)
C(3)	21013(13)	12616(14)	7523(13)	68(4)
O(4)	20110(8)	11511(8)	7537(8)	64(3)
C(5)	20500(2)	10961(14)	8239(14)	78(5)
C(6)	20522(13)	11430(2)	9387(12)	72(4)
O(7)	19362(9)	11247(10)	9579(9)	80(3)
C(8)	19305(15)	11760(2)	10700(14)	90(5)
C(9)	18110(2)	11580(2)	10789(15)	100(6)
O(10)	17590(9)	12150(10)	10151(10)	83(3)
C(11)	17860(2)	13350(2)	10686(15)	108(8)
C(12)	17630(2)	13930(2)	9880(2)	111(8)
O(13)	18405(9)	13936(10)	9121(11)	88(4)
C(14)	18411(14)	14452(15)	8289(14)	74(4)
C(15)	17760(2)	15095(15)	8170(2)	106(7)
C(16)	17750(2)	15560(2)	7330(3)	129(11)
C(17)	18520(3)	15450(2)	6580(3)	157(13)
C(18)	19260(2)	14790(2)	6690(2)	90(5)
C(19)	19144(14)	14307(14)	7573(13)	68(4)
O(20)	17435(9)	9899(11)	5553(9)	79(3)
C(21)	17910(2)	8980(2)	5473(14)	100(6)
C(22)	17320(2)	8260(2)	6110(2)	121(8)
O(23)	17567(12)	8867(10)	7225(10)	92(4)
C(24)	16880(2)	8290(2)	7940(2)	105(7)
C(25)	15700(2)	8400(2)	7800(2)	127(8)
O(26)	15915(11)	9570(12)	8262(12)	98(4)
C(27)	14820(3)	9680(4)	8240(5)	310(4)
C(28)	14720(2)	10500(3)	8120(3)	200(2)
O(29)	15538(10)	11499(11)	7716(12)	98(4)
C(30)	14990(2)	11580(2)	6690(2)	113(8)
C(31)	15850(2)	12040(2)	6050(2)	112(7)
O(32)	16454(12)	11366(11)	5836(11)	89(3)
C(33)	17280(2)	11530(2)	5132(14)	84(5)

Table 147. (cont.)
Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $[K(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Cu_2I_4)$ (**XXVIII**)

atom	x (σ (x))	y (σ(y))	z (σ(z))	U(eq)
C(34)	17550(2)	12450(2)	4610(2)	112(8)
C(35)	18460(3)	12450(3)	3900(2)	158(15)
C(36)	18930(3)	11590(3)	3900(2)	155(13)
C(37)	18630(2)	10800(2)	4291(14)	105(7)
C(38)	17809(15)	10690(2)	4957(14)	74(4)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 148. (cont.)
Bond lengths [A] and angles [^{o}] for
[K(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) (**XXVIII**)

Cu(1)-I(2)	2.573(3)	C(27)-C(28)	1.11(4)
Cu(1)-I(1)	2.733(3)	C(27)-O(26)	1.42(4)
Cu(1)-I(1)’	2.773(3)	C(31)-C(30)	1.41(3)
I(1)-Cu(1)’	2.773(3)	C(34)-C(33)	1.39(3)
K(1)-O(26)	2.736(12)	C(35)-C(34)	1.53(4)
K(1)-O(7)	2.798(11)	C(35)-C(36)	1.38(5)
K(1)-O(29)	2.846(13)	C(37)-C(36)	1.13(4)
K(1)-O(4)	2.857(11)	C(38)-C(33)	1.40(3)
K(1)-O(10)	2.875(12)	C(38)-C(37)	1.37(3)
K(1)-O(23)	2.911(12)	C(6)-C(5)	1.43(2)
K(1)-O(32)	2.958(14)	C(8)-C(9)	1.44(3)
K(1)-O(20)	2.983(12)	O(10)-C(11)	1.38(2)
K(1)-O(1)	3.038(11)	O(10)-C(9)	1.43(2)
K(1)-O(13)	3.037(12)	O(23)-C(22)	1.40(3)
K(1)-C(14)	3.523(11)	O(23)-C(24)	1.46(2)
K(1)-C(5)	3.53(2)	O(26)-C(25)	1.35(3)
O(4)-C(3)	1.43(2)	O(29)-C(28)	1.52(3)
O(4)-C(5)	1.38(2)	O(29)-C(30)	1.46(3)
O(1)-C(2)	1.40(2)	O(32)-C(31)	1.32(3)
O(1)-C(14)	1.72(3)	O(32)-C(33)	1.41(2)
O(20)-C(38)	1.34(2)	O(7)-C(8)	1.44(2)
O(20)-C(21)	1.44(2)	C(14)-C(15)	1.86(4)
O(13)-C(12)	1.45(2)	C(14)-C(18)	1.68(4)
O(13)-C(14)	1.77(3)	C(15)-C(16)	1.33(4)
C(6)-O(7)	1.42(2)	C(17)-C(16)	1.40(4)
C(12)-C(11)	1.47(3)	C(18)-C(17)	1.49(4)
C(21)-C(22)	1.37(3)	C(2)-C(3)	1.52(2)
C(25)-C(24)	1.50(3)	O(10)-K(1)-O(32)	130.0(4)
C(11)-O(10)-C(9)	113(2)	O(13)-C(12)-C(11)	114(2)
C(11)-O(10)-K(1)	122.1(12)	O(13)-C(14)-C(15)	77(2)
C(12)-O(13)-C(14)	150(2)	O(13)-C(14)-C(18)	179(2)
C(12)-O(13)-K(1)	103.5(10)	O(13)-C(14)-K(1)	59.6(5)
C(14)-K(1)-C(5)	101.1(6)	O(13)-C(14)-O(1)	92.0(8)
C(14)-O(1)-K(1)	91.2(8)	O(13)-K(1)-C(14)	30.1(6)
C(14)-O(13)-K(1)	90.3(8)	O(13)-K(1)-C(5)	105.8(4)
C(15)-C(14)-K(1)	113.4(14)	O(20)-C(38)-C(33)	112(2)
C(15)-C(16)-C(17)	119(3)	O(20)-C(38)-C(37)	130(2)
C(16)-C(15)-C(14)	99(2)	O(20)-K(1)-C(14)	106.3(6)
C(16)-C(17)-C(18)	120(3)	O(20)-K(1)-C(5)	84.9(4)
C(17)-C(18)-C(14)	97(2)	O(20)-K(1)-O(1)	98.0(3)
C(18)-C(14)-C(15)	104.1(12)	O(20)-K(1)-O(13)	135.8(5)

Table 148. (cont.)
Bond lengths [A] and angles [°] for
[K(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVIII)**

C(18)-C(14)-K(1)	119.8(14)	O(23)-C(24)-C(25)	108(2)
C(2)-O(1)-C(14)	136.6(15)	O(23)-K(1)-C(14)	156.2(8)
C(2)-O(1)-K(1)	109.8(8)	O(23)-K(1)-C(5)	64.9(4)
C(21)-C(22)-O(23)	115(2)	O(23)-K(1)-O(1)	130.5(4)
C(21)-O(20)-K(1)	112.5(9)	O(23)-K(1)-O(13)	166.6(4)
C(22)-C(21)-O(20)	105(2)	O(23)-K(1)-O(20)	55.4(4)
C(22)-O(23)-C(24)	121(2)	O(23)-K(1)-O(32)	98.8(4)
C(22)-O(23)-K(1)	117.9(11)	O(26)-C(25)-C(24)	106(2)
C(24)-O(23)-K(1)	105.9(10)	O(26)-K(1)-C(14)	142.4(7)
C(25)-O(26)-C(27)	107(2)	O(26)-K(1)-C(5)	113.6(4)
C(25)-O(26)-K(1)	121.4(13)	O(26)-K(1)-O(1)	169.6(4)
C(27)-C(28)-O(29)	131(3)	O(26)-K(1)-O(10)	72.2(4)
C(27)-O(26)-K(1)	119(2)	O(26)-K(1)-O(13)	120.8(4)
C(28)-C(27)-O(26)	119(4)	O(26)-K(1)-O(20)	91.2(4)
C(28)-O(29)-K(1)	107.2(14)	O(26)-K(1)-O(23)	59.3(4)
C(3)-O(4)-C(5)	112.7(12)	O(26)-K(1)-O(29)	61.0(4)
C(3)-O(4)-K(1)	121.6(8)	O(26)-K(1)-O(32)	94.3(4)
C(30)-O(29)-C(28)	113(2)	O(26)-K(1)-O(4)	131.8(4)
C(30)-O(29)-K(1)	119.5(13)	O(26)-K(1)-O(7)	91.2(4)
C(31)-C(30)-O(29)	111(2)	O(29)-K(1)-C(14)	83.8(6)
C(31)-O(32)-C(33)	124(2)	O(29)-K(1)-C(5)	174.4(4)
C(31)-O(32)-K(1)	111.3(13)	O(29)-K(1)-O(1)	112.7(4)
C(33)-C(34)-C(35)	113(2)	O(29)-K(1)-O(10)	76.3(4)
C(33)-O(32)-K(1)	103.7(10)	O(29)-K(1)-O(13)	77.1(3)
C(34)-C(33)-C(38)	122(2)	O(29)-K(1)-O(20)	96.4(4)
C(36)-C(35)-C(34)	115(2)	O(29)-K(1)-O(23)	111.4(4)
C(36)-C(37)-C(38)	124(3)	O(29)-K(1)-O(32)	56.0(4)
C(37)-C(36)-C(35)	128(4)	O(29)-K(1)-O(4)	163.4(4)
C(37)-C(38)-C(33)	117(2)	O(32)-C(31)-C(30)	111(2)
C(38)-O(20)-C(21)	117.8(15)	O(32)-C(33)-C(34)	123(2)
C(38)-O(20)-K(1)	106.6(10)	O(32)-C(33)-C(38)	115(2)
C(5)-O(4)-K(1)	107.6(10)	O(32)-K(1)-C(14)	74.0(4)
C(6)-C(5)-K(1)	83.7(10)	O(32)-K(1)-C(5)	127.8(4)
C(6)-O(7)-K(1)	116.5(8)	O(32)-K(1)-O(1)	87.9(4)
C(8)-O(7)-C(6)	114.3(12)	O(32)-K(1)-O(13)	94.6(4)
C(8)-O(7)-K(1)	117.9(10)	O(32)-K(1)-O(20)	49.9(4)
C(9)-O(10)-K(1)	108.2(9)	O(4)-C(3)-C(2)	110.5(12)
Cu(1)-I(1)-Cu(1)'	81.75(8)	O(4)-C(5)-C(6)	115.9(15)
I(1)-Cu(1)-I(1)'	98.25(8)	O(4)-C(5)-K(1)	50.5(8)
I(2)-Cu(1)-I(1)	133.91(9)	O(4)-K(1)-C(14)	85.4(7)
I(2)-Cu(1)-I(1)'	127.83(9)	O(4)-K(1)-C(5)	21.9(3)

Table 148. (cont.)
Bond lengths [A] and angles [°] for
[K(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) (**XXVIII**)

O(1)-C(14)-C(15)	169(2)	O(4)-K(1)-O(1)	56.3(3)
O(1)-C(14)-C(18)	87(2)	O(4)-K(1)-O(10)	115.9(3)
O(1)-C(14)-K(1)	59.6(5)	O(4)-K(1)-O(13)	99.4(3)
O(1)-C(2)-C(3)	105.3(12)	O(4)-K(1)-O(20)	74.6(3)
O(1)-K(1)-C(14)	29.2(6)	O(4)-K(1)-O(23)	75.4(4)
O(1)-K(1)-C(5)	72.4(3)	O(4)-K(1)-O(32)	108.8(4)
O(1)-K(1)-O(13)	48.8(3)	O(7)-C(6)-C(5)	110.2(13)
O(10)-C(11)-C(12)	108.3(15)	O(7)-C(8)-C(9)	110.0(15)
O(10)-C(9)-C(8)	115(2)	O(7)-K(1)-C(14)	106.8(4)
O(10)-K(1)-C(14)	88.0(7)	O(7)-K(1)-C(5)	41.4(4)
O(10)-K(1)-C(5)	101.0(4)	O(7)-K(1)-O(1)	88.4(3)
O(10)-K(1)-O(1)	98.6(3)	O(7)-K(1)-O(10)	60.7(4)
O(10)-K(1)-O(13)	57.9(4)	O(7)-K(1)-O(13)	90.6(4)
O(10)-K(1)-O(20)	163.4(4)	O(7)-K(1)-O(20)	120.7(4)
O(10)-K(1)-O(23)	112.8(4)	O(7)-K(1)-O(23)	76.1(4)
O(7)-K(1)-O(32)	169.1(4)	O(7)-K(1)-O(29)	134.7(4)
O(7)-K(1)-O(4)	60.8(3)		

Symmetry transformations used to generate equivalent atoms:
‘= -x+1,-y+1,-z

Table 149.
Anisotropic displacement parameters ($Å^2$ x 10^3) for [K(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVIII)**

atom	U11	U22	U33	U23	U13	U12
K(1)	46(2)	52(2)	61(2)	10(1)	3(1)	12(1)
Cu(1)	49(1)	86(1)	58(1)	18(1)	17(1)	27(1)
I(1)	66(1)	84(1)	93(1)	20(1)	8(1)	16(1)
I(2)	115(1)	107(1)	104(1)	16(1)	20(1)	-6(1)
O(1)	66(6)	79(7)	98(8)	43(6)	30(6)	41(6)
C(2)	59(9)	55(9)	93(11)	22(8)	36(8)	12(7)
C(3)	61(9)	78(10)	77(10)	26(8)	28(8)	35(8)
O(4)	61(6)	50(5)	75(6)	15(5)	14(5)	18(5)
C(5)	86(11)	62(10)	88(12)	35(9)	5(9)	26(9)
C(6)	64(9)	90(11)	56(9)	26(8)	-9(7)	25(8)
O(7)	60(6)	95(8)	72(7)	30(6)	7(5)	15(6)
C(8)	69(11)	117(15)	76(12)	30(11)	-9(9)	31(10)
C(9)	97(14)	140(2)	58(10)	33(11)	37(10)	35(13)
O(10)	68(7)	77(7)	81(8)	-7(6)	13(6)	22(6)
C(11)	71(11)	130(2)	63(11)	-28(12)	24(9)	10(11)
C(12)	87(13)	77(12)	120(2)	-40(12)	53(13)	11(10)
O(13)	60(6)	69(7)	115(9)	-6(6)	20(6)	22(5)
C(15)	110(15)	49(10)	180(2)	24(12)	34(14)	58(11)
C(16)	100(2)	80(2)	210(3)	30(2)	-20(2)	51(14)
C(17)	150(2)	55(13)	210(3)	40(2)	-70(2)	-2(15)
C(18)	71(11)	80(12)	107(14)	30(10)	-8(10)	20(9)
O(20)	70(7)	105(9)	74(7)	25(7)	22(6)	45(7)
C(21)	130(2)	120(2)	52(10)	-7(10)	11(10)	74(15)
C(22)	160(2)	120(2)	140(2)	40(2)	30(2)	110(2)
O(23)	129(11)	71(7)	69(7)	0(6)	-4(7)	48(7)
C(24)	150(2)	55(10)	120(2)	33(11)	44(15)	37(12)
C(25)	90(2)	100(2)	150(2)	47(15)	-12(14)	-8(13)
O(26)	72(8)	76(9)	149(12)	49(8)	32(8)	19(7)
C(27)	130(3)	220(4)	620(10)	300(6)	-30(4)	20(3)
C(28)	110(2)	240(4)	320(5)	150(4)	160(3)	80(2)
O(29)	68(7)	96(9)	117(10)	12(7)	12(7)	30(7)
C(30)	75(13)	81(13)	150(2)	-25(13)	-29(14)	43(11)
C(31)	110(2)	130(2)	110(2)	48(15)	-5(13)	70(2)
O(32)	103(9)	81(8)	107(9)	39(7)	20(7)	56(7)

Table 149. (cont.)
Anisotropic displacement parameters (Å^2 x 10^3) for [K(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) (**XXVIII**)

atom	U11	U22	U33	U23	U13	U12
C(33)	81(11)	92(13)	63(10)	39(10)	-5(9)	10(10)
C(34)	120(2)	85(13)	71(12)	7(11)	-47(12)	3(12)
C(35)	260(4)	110(2)	36(10)	29(11)	0(16)	-10(2)
C(36)	160(3)	140(3)	110(2)	30(2)	60(2)	-10(2)
C(37)	130(2)	100(2)	57(11)	22(10)	43(11)	14(13)
C(38)	70(10)	68(10)	81(11)	12(9)	9(9)	33(9)

The anisotropic displacement factor exponent takes the form:
$-2 \pi^2 [h^2 a^{2*} U_{11} + ... + 2 h k a^* b^* U_{12}]$

Table 150.
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [K(benzo-15-crown-5)$_2$]$_2$(Cu$_2$I$_4$) **(XXVIII)**

atom	x	y	z	U(eq)
H(2A)	21060	14060	6952	80
H(2B)	19968	12868	6331	80
H(3A)	21571	12455	7096	80
H(3B)	21433	13078	8264	80
H(5A)	21288	11037	8150	80
H(5B)	19988	10121	8001	80
H(6A)	20868	11067	9835	80
H(6B)	21002	12277	9609	80
H(8A)	19731	12618	10879	80
H(8B)	19678	11468	11199	80
H(9A)	17668	10725	10528	80
H(9B)	18064	11848	11553	80
H(11A)	18693	13738	11014	80
H(11B)	17418	13419	11264	80
H(12A)	16825	13498	9483	80
H(12B)	17749	14745	10234	80
H(15A)	17201	15166	8644	80
H(16A)	17295	16027	7237	80
H(17A)	18558	15799	5977	80
H(18A)	19799	14679	6212	80
H(21A)	18752	9322	5768	80
H(21B)	17774	8533	4709	80
H(22A)	17506	7564	6003	80
H(22B)	16479	7994	5845	80
H(24B)	16747	7452	7737	80
H(24A)	17280	8655	8703	80
H(25A)	15354	8158	7033	80
H(25B)	15160	7903	8166	80
H(27A)	14479	9439	8843	80
H(27B)	14318	9085	7570	80
H(28A)	13922	10297	7750	80
H(28B)	14776	10913	8879	80
H(30A)	14521	12043	6851	80
H(30B)	14477	10786	6232	80

Table 156. (cont.)
Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for $[K(benzo\text{-}15\text{-}crown\text{-}5)_2]_2(Cu_2I_4)$ (**XXVIII**)

atom	x	y	z	U(eq)
H(31A)	15503	12139	5392	80
H(31B)	16411	12812	6514	80
H(34A)	17209	13035	4718	80
H(35A)	18670	12998	3459	80
H(36A)	19568	11688	3497	80
H(37A)	18988	10227	4166	80

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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