CORRELATION OF STRUCTURE AND SOLID STATE EMISSION PROPERTIES OF ANIONIC COPPER(I) HALIDE COMPLEXES

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CHAPTER I

INTRODUCTION AND BACKGROUND

Copper(I) halide complexes have been the subject of numerous investigations because of the wide variety of structural motifs displayed [1-2]. While most motifs involve tetrahedral copper and a build up of Cu_2I_2 rhombohedra, differences in stoichiometry, in overall charge and in structural complexity abound. The basis for such behaviour lies in the structure of Cu atom, which has a $4s^1 3d^{10}$-configuration. The copper(I) ion (d^{10} configuration) normally accepts 4 pairs of electrons to form a tetrahedral copper. However with space filling ligands coordination numbers of copper(I) may be 2 or 3 as well [3-5].

Cuprous halides, and cuprous compounds in general, are less stable than Cu(II) compounds. Although the reaction

$$2Cu_{(g)}^{+} \rightarrow Cu^{2+}_{(g)} + Cu_{(s)}$$

is endothermic (ΔH = +870 kJ mol^{-1}) [6], the relative stability of the two ions in crystalline and dissolved states depends strongly on the interaction of Cu^+ and Cu^{2+} with their surroundings (lattice energy or solvation energy). These values are greater for Cu^{2+} than for Cu^+, thus making the resulting ΔH negative, that is ionic cuprous salts are less stable than cupric. But if the ligand is iodide, the significantly covalent character of the bond leads to a positive ΔH, and consequently, cuprous iodides are quite stable. The stability of copper halides (CuX) increases in the order: F(I) $\ll$ Cl(I) < Br(I) < I(I)

in accordance with the relative base strength of halide-ions. This fact is also in agreement with Pearson's theory of hard and soft acids and bases, according to which Cu^+ and I^- represent a soft acid and a soft base respectively [7].

Copper (I) halide complexes ($Cu_pX_qB_r$, $p \leq q$) in general may be divided in two large groups:

1) Mixed-ligand complexes with neutral Cu_pX_q clusters ($p = q$) and a neutral electron pair donating ligand B. Both halide and B are directly coordinated to copper(I). The ligand B contains a trivalent donor atom (N, P, As, Sb) with a pair of unshared electrons: tertiary amines [8-10], trialkyl- and triarylphosphines, arsines, stybins [11-14]. The structural diversity of the Cu_pX_p fragments only include: $Cu_2X_2L_2$ and $[(CuXL_2)_2]$ rhombohedra, $[(CuXL)_x]$ polymeric pleated sheets, $Cu_4X_4L_4$ and $Cu_4X_4L_6$ chairs and $Cu_4X_4L_4$ cubes. In these compounds copper completes its trigonal planar and tetrahedral coordination by binding to one or more ligand donor atoms as well as to halide.

Among the ligands, observed along with halides in the coordination sphere of copper (I) are unsaturated hydrocarbons (non-conjugated dienes, cycloalkenes) [15-16], which donate π-electrons to the metal ion forming a dative metal – ligand bond. I.e., in tetranuclear complex between copper(I) chloride and 1,4-pentadiene [17], the cubane Cu_4X_4 cores are bridged by 1,4-pentadiene ligands, each ligand thus coordinating to two different copper(I) atoms, forming an infinite ribbon.

2) Ionic species with negatively charged $[Cu_pX_q]^{-(q-p)}$ clusters ($q > p$). These anionic species are crystallized with positively charged species, giving ionic solids. Here the cation is typically bulky organic ligand bearing positive charge: quaternary ammonium [18-21], phosphonium and arsonium ions [22-26].

The complexes of the second type are more stable as solids, probably due to the strength of the ionic interactions in the crystal lattice. For type I complexes, the ligands X and B must be spatially compatible. This ligand compatibility in the inner coordination sphere is the factor which limits the number of ligands able to coexist with halides and narrows the variety of the corresponding complexes.

Besides these two strictly defined classes, there have been synthesized and structurized many compounds of mixed type: they contain either amine, coordinated to copper in anionic part and forming ionic associate with phosphonium and arsonium quaternary cations or anionic species $[Cu_n(PPh_3)_nX_m]^{-(n-m)}$, associated with protonated or quaternary amines [27-30].

A great number of publications have discussed copper-halide structures with electron pair donating sulfur-containing ligands. These S-containing soft ligands are different in nature: thiourea, thiobiuret, thiophene derivatives, alkyldithiocarbamates [31-33]. These ligands usually chelate to the metal via the sulphur atoms in tetrahedral, halide bridged oligonuclear copper structures.

There have been attempts to establish a correlation between coordination number of copper(I) and properties of the cation such as size, shape and distribution of the positive charge [34-36]. Investigation on cuprous halide complexes with symmetrically substituted unipositive quaternary ammonium, phosphonium and arsonium cations indicates a distinct inverse correlation between cation size and the geometry of copper ion [34]: a larger cation corresponds to the lower metal coordination number. The concentration of halide ligand in the crystalline phase was seen to be inversely proportional to the cation size, and favors to the higher coordination number. This

correlation however appears to be valid only for a series of complexes with similar cations (shape and charge distribution).

Further discussion is restricted to anionic species, in which all ligands are iodide ions. The stoichiometry of anionic copper(I) – halides complexes gives no information about their structural motifs. The possibility of different coordination numbers for copper, which can be displayed in the same $[Cu_pX_q]^{-(q-p)}$ fragment plus the possibility of bridging copper atoms with halogens gives rise to an impressive variety of structural motifs, both discrete and polymeric in nature. The discrete anionic complexes are known to vary their copper content from 1 to 9 (Table 1). The largest known discrete anionic

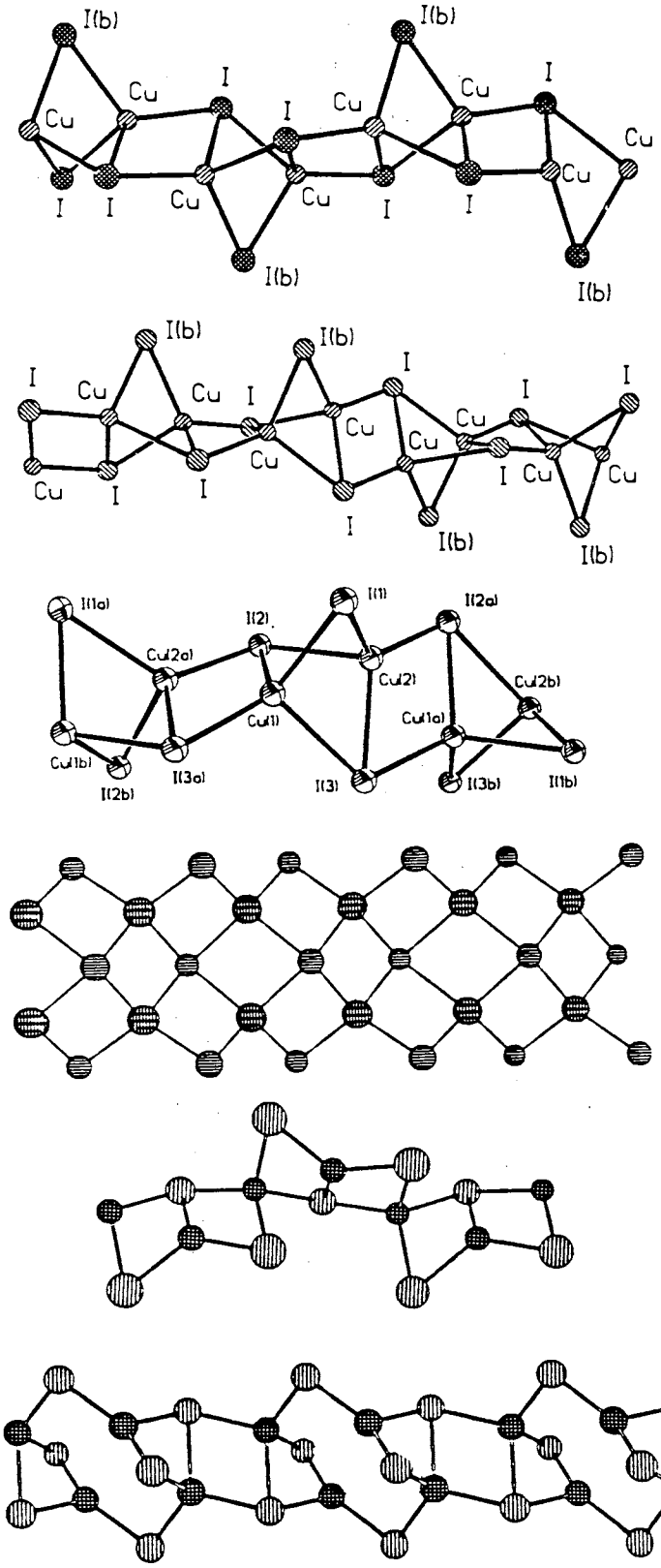
TABLE 1

NUCLEARITY OF DISCRETE ANIONIC HALOCUPRATES(I)

Nucleocity	Anionic species	References
Mononuclear	$[CuX_2]^-$, $[CuX_3]^{2-}$, $[CuX_4]^{3-}$	33, 35, 37-41
Dinuclear	$[Cu_2X_4]^{2-}$, $[Cu_2X_5]^{3-}$, $[Cu_2X_6]^{4-}$	42-46
Trinuclear	$[Cu_3X_6]^{3-}$	47-48
Tetranuclear	$[Cu_4X_6]^{2-}$, $[Cu_4X_8]^{4-}$	48-51
Pentanuclear	$[Cu_5X_7]^{2-}$, $[Cu_5X_{16}]^{11-}$	52-53
Hexanuclear	$[Cu_6X_9]^{3-}$, $[Cu_6X_{11}]^{5-}$	54-55
Heptanuclear	$[Cu_7X_{10}]^{3-}$	56
Octanuclear	$[Cu_8X_{13}]^{5-}$	50
Nanonuclear	$[Cu_9X_{13}]^{4-}$	57
Hexatris-decanuclear	$[Cu_{36}X_{56}]^{20-}$	58

halocuprate(I) $[Cu_{36}I_{56}]^{20-}$ has been identified by H.Hartl and F.Fuchs [58]. Further condensation of halocuprate (I) ions leads to polymeric anionic species, which are also very diverse: $[CuX_2]^-$, $[CuX_3]^{2-}$, $[Cu_2X_3]^-$, $[Cu_3X_5]^{2-}$ [48, 50, 59-62]. Each of these stoichiometries may exist in different motifs. F.i., for $[Cu_2X_3]^-$ there are known six different structural patterns (Fig.1). Three of these complexes may be viewed as a ribbon of Cu_2X_2 rhombs which share opposite edges, with an additional iodine atom bridging the copper atoms of every alternate rhomb [50, 63-65]. The location of the bridging iodides, which may be on either side of the polymeric sheet, determines the difference between these structures. The first one has a sequence of I bridging *up, down, up, down*, the second one – *two up, two down*, and the third one has all bridging iodides on the same side. The latter exists with a helix-like tertiary structure with iodine atoms directed outwards: *up, up, up, up* [65]. The fourth structure [66] may be represented as double chain of Cu_2X_2 rhombs, in which copper exhibits tetrahedral configuration. In the fifth structure, two Cu_2X_2 rhombohedra share Cu – I edges, forming Cu_3X_3 fragments, which compose a polymeric sheet by sharing corners and projecting alternatively upward and downward from the polymeric direction [67]. The sixth structure [36] possesses in addition to Cu_2X_2 rhombohedra an eight membered ring, where copper(I) is 3- and 4-coordinated.

This study is primarily focused on discrete anionic species, exhibiting planar trigonal configuration: tetraiododicuprates (I) Cu_2I_4 and hexaiodotetracuprates(I) Cu_4I_6. $[Cu_2X_4]^2$ exists as a copper-iodide rhomb, in which two trigonal planar copper atoms are bridged by two iodides and in addition, each of Cu atoms is bound to a terminal iodide. Fig.2 shows two possible geometric types observed for $[Cu_2X_4]^{2-}$ anions: 1) a planar,



up, down up, down

up, up, down, down

up, up, up, up

Figure 1. Different motifs displayed by $Cu_2I_3^-$ polymeric species

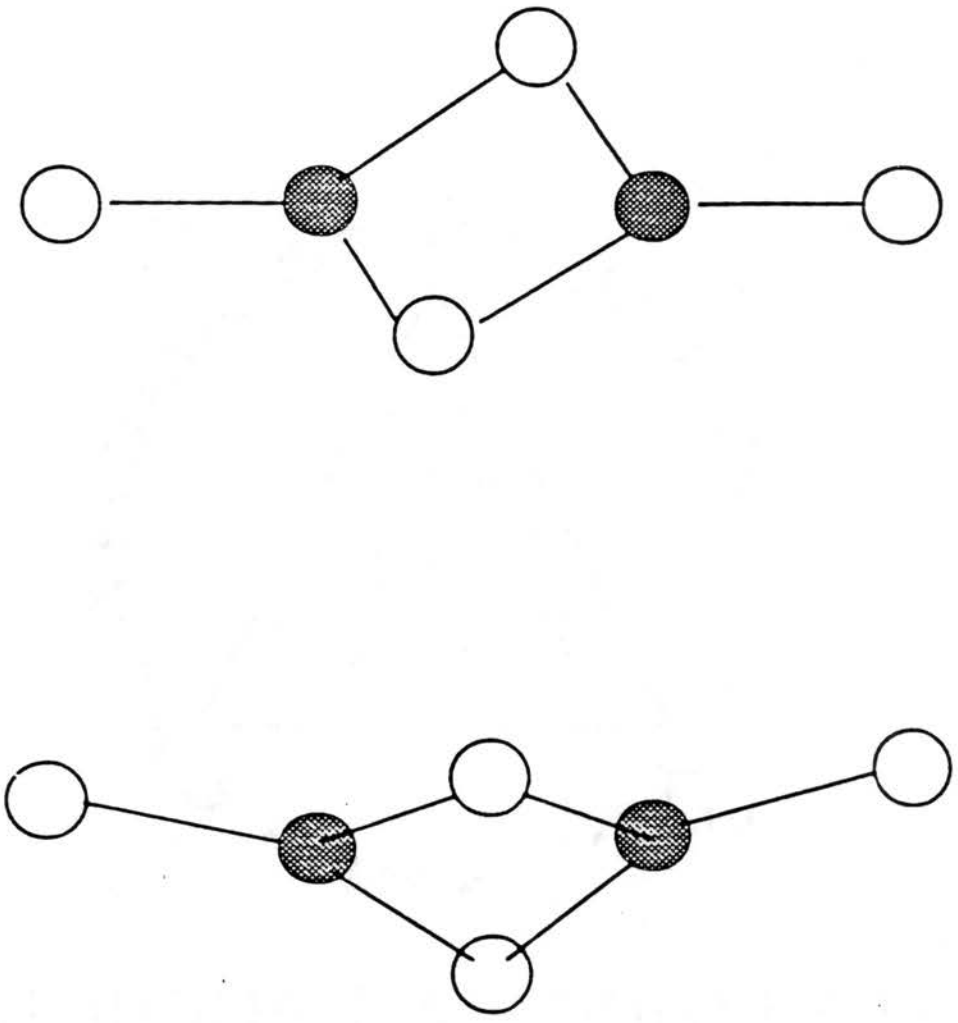


Figure 2. Planar and bent configurations of tetraiododicuprate (I)

possibly centrosymmetric rhomb and 2) asymmetric rhomb, bent about the line connecting the bridging iodides. Structural characteristics of known tetraiododicuprates (I) are given in Table 2. Despite the differences in geometry, the corresponding Cu - $I_{bridging}$, Cu - $I_{terminal}$ and Cu ...Cu distances are very similar.

TABLE 2

STRUCTURAL PARAMETERS OF TETRAIODODICUPRATES (I) Cu_2I_4

Cation	Symmetry elements	Distances, Å			Reference
		Cu - $I_{bridging}$	Cu - $I_{terminal}$	Cu ...Cu	
$[N(C_3H_7)_4]^+$	Center of symmetry	2.571(1) 2.582(1)	2.499(1)	2.698(2)	68
$[N(C_4H_9)_4]^+$	Center of symmetry	2.566(2) 2.592(2)	2.514(2)	2.726(4)	69
$[NaL][NaL.H_2O]^{2+}$ *)	Center of symmetry	2.557(4) 2.587(4)	2.484(3)	2.678(6)	42
$[(MeCN)CuL]^+$ **)	Center of symmetry	2.55(1) 2.56(1)	2.52(1)	2.78(1)	70
$[As(C_6H_5)_4]^+$	Bent	2.578(3) – 2.610(3)	2.490(3) 2.491(3)	2.663(4)	71
$[P(C_6H_5)_4]^+$	Bent	2.562(2) – 2.588(2)	2.471(2) 2.480(2)	2.647(2)	45

*) - L = 15-crown-5

**) L = 2.6-bis[1-phenyl-1-(pyridin-2-yl) ethyl] pyridine

Hexahalotetracuprates (I) have been the object of study in this laboratory [72]. These complexes consist of a tetrahedron of Cu atoms, bridged on all edges by halogen atoms. Theoretically, different members of such a cluster may be related each other by various symmetry elements (Fig. 3):

1) Two fold axis through any opposite pair of iodine atoms, bisecting opposite edges of the copper rhombohedron.
2) Mirror plane through any pair of copper atoms and the iodine atom bridging them as well as iodine on the opposite side of the iodide polyhedron.
3) Three fold axis through any copper atom and the center of the opposite triangular face

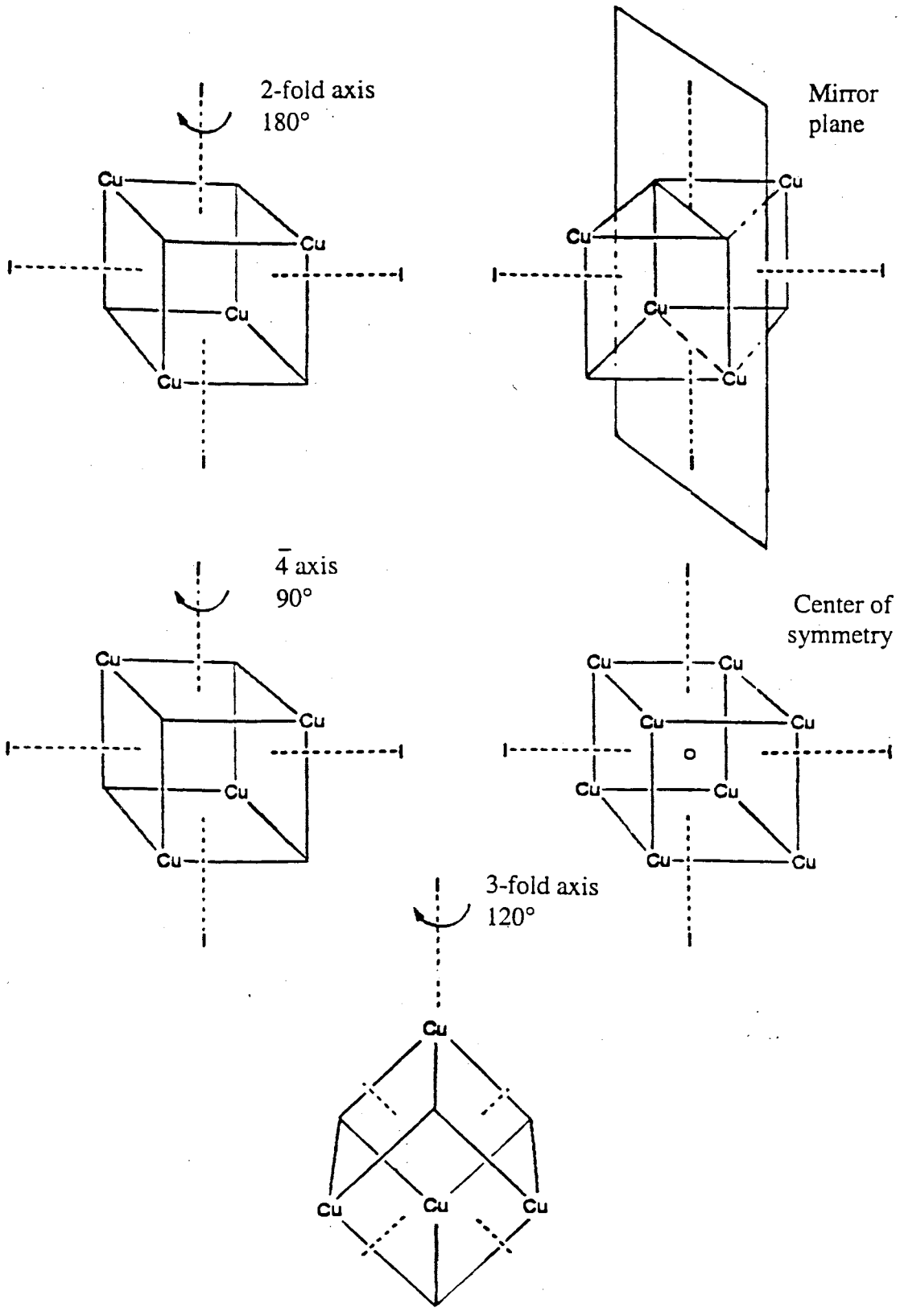


Figure 3. Symmetry elements within $Cu_4I_6^{2-}$ cluster

formed by copper atoms.

4) 4 bar axis through the centers of two opposite edges of copper polyhedron.
5) Center of symmetry, located in the center of tetrahedron. The last case is valid only when the $[Cu_4X_6]^{2-}$ cluster is disordered, since it is not otherwise centrosymmetric in nature. In disordered structures we have two copper tetrahedra, rotated with respect to each other, so that the whole fragment resembles a cube with Cu atoms at the vertexes and six iodide atoms centered above the six faces of the cube.

The increased attention to copper halide complexes is explained by their luminescent properties, first reported by J.T.Randall in 1938 for cuprous chloride [73]. The discovery of solid state emission of copper halides and its sensitivity to temperature caused a series of investigations on the syntheses of different cuprous complexes, performed by Hardt in 1970-1980 [74-78]. He synthesized numerous copper (I) complexes with Lewis bases and reported their luminescence at ambient and low temperature. The term 'fluorescence thermochromism' was introduced to specify the phenomenon of changing wavelength of emission upon lowering temperature. However it later appeared, that this wavelength shift may be either real or caused by the eye's unequal sensitivity to intensity changes with temperature.

Copper halides are of interest both for theoretical investigations and for practical purposes. These materials can be of potential use as fluorescent/phosphorescent sensitizers for photoconductors [79-80]. Because of their structural diversity and different coordination surroundings, they represent a convenient topic for luminescence studies. The variety of structural motifs, exhibited by the same stoichiometric unit, allows elucidation of the mechanism and dynamics of the excitation processes, which depend

upon the structural parameters, and particularly, on symmetry elements present in a given solid state structure. Understanding the influence of these factors may be helpful in further synthesis of the copper halide complexes, possessing desirable luminescent properties.

The ability of copper (I) complexes to emit in the solid state when excited in the ultraviolet, has its origin in the electron configuration of copper atom. Since *d-d* transitions cannot occur in d^{10} complexes, the photochemical processes involve other types of electron excited states. For copper (I) in general there are five possible mechanisms of excitation:

1) Metal-to-Ligand-Charge-Transfer (MLCT). An electron from the $3d^{10}$ orbital of copper (I) is excited to a π^* antibonding orbital of an aromatic ligand, giving $3d^9\pi^{*1}$ excited configuration. Such transitions are prominent in systems containing easily oxidized metal and an aromatic ligand with low energy acceptor orbital. This is valid for many copper (I) – ligand complexes, in which the donor atom is a part of an unsaturated system, such as in pyridine or phenanthroline. Formally, MLCT represents oxidation of copper (I), accompanied by reduction of a ligand.
2) Ligand – Ligand Interaction (LLI). This is a $\pi \rightarrow \pi^*$ transition between orbitals localized on a coordinated aromatic ligand. Because of the small influence of complexation on transition energy, the wavelength of absorption closely matches in energy and intensity, the $\pi \rightarrow \pi^*$ transition of a free ligand. This feature serves as diagnostic tool in band assignment.
3) Single Metal Excitation, involving a single metal described as a $3d^{10} \rightarrow 3d^9 4s^1$ transition and results in a radial redistribution of electron density between orbitals

localized on the metal. This transition is forbidden and is consequently of low intensity. The alternative metal-centered transition $3d^{10} \rightarrow 3d^{9}4p^{1}$ is allowed, but requires higher energy to produce (λ<190 nm).

4) Metal – Metal Interaction (MMI). This mechanism was used to explain the solid state emission of copper (I) halides with short copper-copper distances (less than 2.6 Å). It is depicted as a $3d^{10}3d^{10} \rightarrow 3d^{9}3d^{10}4s^{1}$ transition and has been supported by molecular orbital calculations. When copper atoms approach each other closely, there has been observed a significant contribution of *4s* and *4p* orbitals to the main *3d* orbitals. The result of it was the lowering the binding energy, which is an indicator of attractive forces between two close copper atoms.
5) Donon Acceptor Pair (DAP). This mechanism takes place when a ligand donates an electron to the metal atom. *Ab initio* calculations, performed for $Cu_nX_nL_m$ species showed that the HOMO orbital of such complexes is dominated by iodine *p*-orbitals whereas the LUMO orbitals are dominated by copper based *p*-orbitals. Formally, this transition is equivalent to oxidation of iodide followed by partial reduction of copper.

The correlation of emission properties with structural characteristics of copper (I) halide complexes, supported by *ab initio* calculations, has been of interest in a series of works done in this laboratory [73, 81-83]. The most frequently studied compounds for such investigations were "cubane" $Cu_4X_4L_4$ with a neutral copper-iodide fragment, possessing a tetrahedral configuration. Hu and co-workers [83] investigated linear CuX_2^- species and found that regardless of the symmetry elements present in a given structure, the compounds emit approximately in the same range: 465-515 nm. Because of the absence of copper-copper and ligand - ligand interactions in these compounds, the only

possible excitation mechanisms may involve either copper atom itself, or arise from a donor-acceptor interaction.

Systematic study of $Cu_2X_2B_4$ mixed complexes has been conducted by Bao and co-workers [81]. This investigation involved aliphatic amines as neutral ligands B, and therefore confined emission origin only to metal-metal interaction or single metal excitation of copper atoms. Fields [73] studied hexahalocuprates and tetraiododicuprates anionic clusters combined with alkali and alkaline earth metal complexed amines and quaternary phosphonium and arsonium ions. It was found that the presence of a symmetry element within the Cu_4I_6 cluster or throughout iodine atoms does not influence the wavelength of emission, while a symmetry element, passing through copper atoms, changed emission. The data, obtained for Cu_2I_4 clusters, was not sufficient enough to draw any definite conclusions about the connection between structural and luminescent properties. These works were often complicated by the quenching effects of aromatic components of ligand or cation.

The goal of this work was to prepare examples of two types of discrete complexes $[Cu_2I_4]^{2-}$ and $[Cu_4I_6]^{2-}$ using alkali and alkaline earth metals, complexed with crown ethers, as bulky cations with well screened charge and no quenching ability; identify them by single crystal X-ray analysis; measure the luminescence of these complexes; and seek a correlation between the single crystal motif and the wavelength of emission. *Ab initio* calculations were expected to help in attaining this objective. Furthermore, polymeric anionic Cu – iodide species were synthesized and examined for their structural and luminescence properties. There are no data in the literature concerning luminescence properties of polymeric clusters.

In this study 8 new complexes were synthesized of type $Cu_2I_4^{2-}$ and 3 of type $Cu_4I_6^{2-}$ plus 9 new polymeric species and 4 new materials of other types.

CHAPTER II

X-RAY CRYSTALLOGRAPHY

A crystal is a homogeneous body consisting of a three-dimensional periodic ordering of atoms, ions or molecules. The inherent periodicity of a crystal structure, together with the magnitude of the interatomic distances (~1-2 Å in length), enables a crystal to act as a three-dimensional diffraction grating for an X-ray beam of wavelength comparable to the interatomic distances. X-ray crystallography is crystal structure analysis, performed by recombining, mathematically, the intensities of the diffracted X-rays to synthesize an image of the molecular structure, which produced the diffraction. This structural elucidation method provides us not only structural parameters of the crystal (composition, connectivity, interatomic distances, bond angles, conformation, chirality), but an indication of the distribution of electron density in the areas occupied by the atoms as well [84].

A crystal can belong to 7 possible crystal classes (Table 3), which are defined by the geometry of the unit cell and the smallest repeating unit or motif of the crystal structure. The crystal class is characterized by the length of 3 edges (**a**, **b**, **c**) and the magnitude of the 3 angles between them (α, β, γ). The seven crystal systems represent primitive (P) lattices. In addition, there are seven centered lattices, forming altogether 14 Bravais lattices (Table 3). Every centered lattice has more symmetry than the primitive lattice in the same system: face centered (A, B, C or F) or body centered (I).

The convolution of a crystal lattice with 10 possible point symmetry operations: identity, center of symmetry, rotation and inversion axes, mirror plane (Fig.4, 5), gives rise to 32 crystallographic point groups (Table 3). In order to describe the internal

TABLE 3

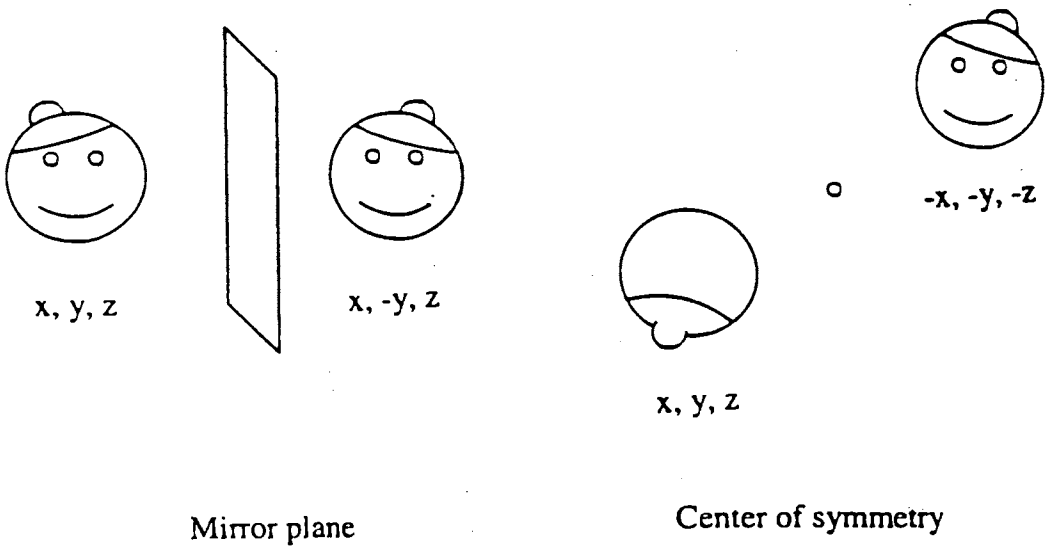
CLASSIFICATION OF CRYSTAL SYSTEMS [85]

Crystal systems (7)	Axial and Angular constraints	Bravais Lattices (14)	Crystallographic Point Groups (32)*
Triclinic	$a\neq b\neq c$ $\alpha\neq\beta\neq\gamma$	P	1, $\underline{1}$ (C_1, C_i)
Monoclinic	$a\neq b\neq c$ $\alpha=\gamma=90°$, $\beta\neq 90°$	P, C	2, m, 2/m (C_2, C_s, C_{2h})
Orthorhombic	$a\neq b\neq c$ $\alpha=\beta=\gamma=90°$	P, C, I, F	222, mm2, mmm (D_2, C_{2v}, D_{2h})
Tetragonal	$a=b\neq c$ $\alpha=\beta=\gamma=90°$	P, I	4, $\underline{4}$, 4/m, 422, 4mm, $\underline{4}$2m, 4/mmm (C_4, S_4, C_{4h}, D_4, C_{4v}, D_{2d}, D_{4h})
Cubic	$a=b=c$ $\alpha=\beta=\gamma=90°$	P, I, F	23, m3, 432, $\underline{4}$3m, m3m (T, T_h, O, T_d, O_h)
Trigonal	$a=b=c$ $\alpha=\beta=\gamma\neq 90°$, $\gamma<120°$	R	3, $\underline{3}$, 32, 3m, $\underline{3}$m (C_3, C_{3i}, D_3, C_{3v}, D_{3d})
Hexagonal	$a=b\neq c$ $\alpha=\beta=90°$, $\gamma=120°$	P	6, $\underline{6}$, 6/m, 622, 6mm, $\underline{6}$m2, 6/mmm (C_6, C_{3h}, C_{6h}, D_6, C_{6v}, D_{3h}, D_{6h})

* - in parentheses are given Schoenflies symbols

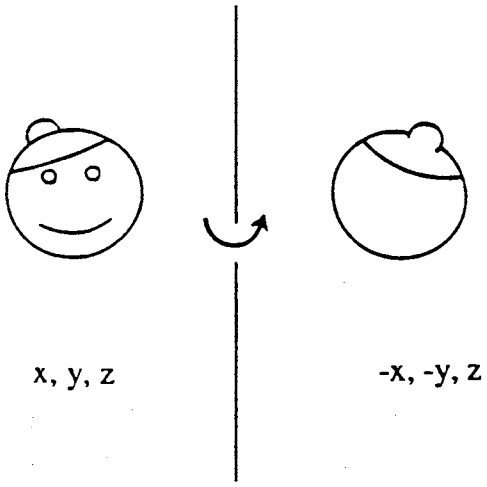
arrangement of crystals, allowance must be made for translational symmetry elements: screw axes and glide planes, relating the internal structural components (atoms, molecules) to each other. The combination of 14 Bravais lattices with possible symmetry elements results in the set of 230 structural arrangements called space groups.

According to the Bragg's law [86], diffraction of X-rays by a crystal is maximal,



Mirror plane

Center of symmetry



2-fold axis

Figure 4. Representation of non-translational symmetry elements

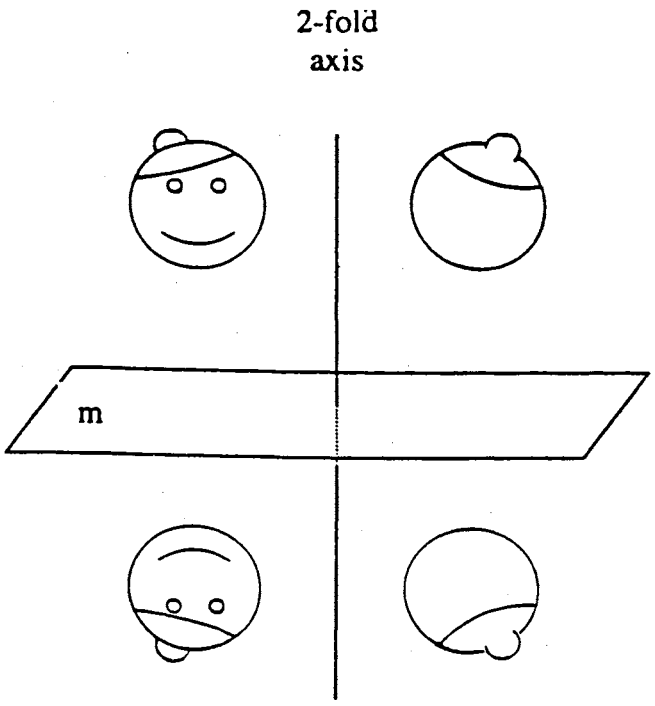


Figure 5. Symmetry elements in 2/m point group: 2-fold axis and a mirror plane perpendicular to it, producing a center of symmetry

when the diffracted beams are in phase and positively enforce each other, i.e. when the following equation is satisfied:

$$\mathbf{n\lambda = 2d \sin \theta} \qquad (1)$$

where λ = the wavelength of the radiation used, **d** is the distance between the lattice planes, θ is the angle of incidence of the X-ray beam and **n** = the diffraction order. Using a monochromatic beam of X-rays (λ constant) and rotating a particular single crystal (**d**-values are constant), one can observe diffraction only for specific (and clearly defined) values of the angle of incidence, giving rise to a specific diffraction pattern. The diffraction pattern, being specific for every crystal structure and governed by Bragg's law, reflects the unit cell and the lattice type of a crystal. However, it differs from the point group symmetry in one important respect: it always has a center of symmetry, even when one is not present in the crystal, since the diffraction effects are inherently centrosymmetric, that is, the reflections **hkl** and $\overline{\mathbf{hkl}}$ are identical (Friedel's law) [87]. The diffraction pattern is therefore that of the crystal point group together with a center of symmetry. In this way the 32 point groups, when applied to diffraction patterns, reduce to 11 centro-symmetric point groups or *Laue* groups.

The ray reflected from a given set of planes, has an inherent intensity, which depends on the number of electrons present on these planes, the latter being influenced by the kinds of atoms present and their relative positions in the unit cell. The raw intensity data are obtained by integration of a continuous photometer trace through a reflection and its adjacent background. If background has been measured on either side of the reflection for one-half the time used in counting peak, then the net intensity equals [84]:

$$\mathbf{I_{int} = (I_{peak} - I_{bgl} - I_{bgr}) \times Scan\ speed} \qquad (2)$$

where $\mathbf{I_{int}}$ = integrated intensity, $\mathbf{I_{peak}}$ = measured intensity, $\mathbf{I_{bg1}}$ and $\mathbf{I_{bg2}}$ are the background intensities on either side of the peak. The intensities represent values, which are normally distributed about the mean (true) value of **N** (number of counts) with a standard deviation equal to $\sqrt{N}$:

$$\sigma(\mathbf{I_{int}}) = \sqrt{\mathbf{I_{peak}} + \mathbf{I_{bgl}} + \mathbf{I_{bgr}}} \times \mathbf{Scan\ speed} \qquad (3)$$

The reflection is defined as observed when its intensity is statistically significant:

$$\mathbf{I_{int}} > 2\sigma(\mathbf{I_{int}}) \qquad (4)$$

where $\sigma(\mathbf{I_{int}})$ – standard deviation of $\mathbf{I_{int}}$. For each Bragg reflection, the raw data normally consist of the Miller indices (**h,k,l**), the integrated intensity $\mathbf{I_{hkl}}$ and its standard deviation $\sigma(\mathbf{I})$. The preliminary manipulation of raw intensities (data reduction) includes corrections for polarization, Lorentz effect, absorption and crystal decomposition [85].

(i) The polarization factor **p** takes into account the partial polarization of the unpolarized primary beam which occurs during the diffraction process.. It arises because of the difference in reflection efficiency of the components of the X ray beam at different values of θ. The usual X-ray beam is unpolarized: its parallel ($\mathbf{I_{para}}$) and perpendicular ($\mathbf{I_{perp}}$) components are equal in intensity:

$$\mathbf{I_{para}} = \mathbf{I_{perp}} = \mathbf{I_o/2} \qquad (5)$$

The parallel component of the beam is diffracted with efficiencies, independent of the reflection angle, while the perpendicular one is diffracted with less efficiency at higher 2θ angles:

$$\mathbf{I_{para}} = \mathbf{KI_o/2}$$

$$\mathbf{I_{perp}} = \mathbf{KI_o}\cos^2 2\theta/2 \qquad (6)$$

The total scattered intensity of an incident X-ray beam (**I**) is obtained:

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

where $\mathbf{I_o}$ is the intensity of the incident X-ray beam and **K** = the reflection factor for the crystal planes. The expression $\mathbf{(1+\cos^2 2\theta)/2}$, known as the polarization factor **p**, is a function of 2θ only and is independent of the method of data collection.

(ii) Lorentz factor **L** takes into account the relative time each reflection is in diffracting position. When crystal is rotated at a constant angular velocity ω, the linear speeds of different lattice points will be different, depending on their perpendicular distance from the axis of rotation, that is on the values of θ: minimal **L** corresponds to $\theta = 45°$ ($2\theta = 90°$). The correction is defined so as to remedy this effect:

$$\mathbf{L = 1 / \sin 2\theta} \qquad (8)$$

Lorentz and polarization factors, when combined together, give a single trigonometric expression called *Lorentz-polarization factor* **Lp**:

$$\mathbf{Lp = (1+\cos^2 2\theta) / 2\sin 2\theta} \qquad (9)$$

(iii) Absorption factor - This factor compensates for the reduction of diffracted intensity due to radiation absorption by the crystal. The extent of the absorption depends on the path length of the beam through the crystal, the atomic contents of the cell and the wavelength of the incident X-ray beam. The absorption factor A is defined as:

$$\mathbf{A = (1/V)\ \exp(\ \mu L)dV} \qquad (10)$$

where μ is the linear absorption coefficient, **L** is the path length of a beam diffracted by volume element **dV** and **V** is the volume of the crystal.

(iii) Decomposition factor – reflects the decrease in intensity during data collection because of crystal decomposition. Assuming the decomposition to be linear in time and

monitoring a set of standard reflections at regular intervals throughout the data collection process allows to express the correction factor as:

$$\mathbf{D = I_{orig} / I_{ave}} \tag{11}$$

where $\mathbf{I_{orig}}$ is the original intensity of a standard reflection and $\mathbf{I_{ave}}$ is the average current intensity of the standard reflection. The overall corrected intensity after all corrections are applied, is equal to:

$$\mathbf{I_{corr} = I_{int} \times (Lp)^{-1} \times A^{-1} \times D} \tag{12}$$

where $\mathbf{I_{int}}$ is the integrated intensity and $\mathbf{I_{corr}}$ is the corrected intensity.

The structure factor, $\mathbf{F_{hkl}}$ is a function, describing the overall scattering, produced by all atoms in the unit cell. It represents a resultant of superposed electromagnetic waves scattered in the direction of the **(h,k,l)** reflection from **N** atoms in the unit structure, each of them having a scattering factor [88]:

$$\mathbf{F_{hkl} = \sum_{j}^{N} f_j \exp 2\pi i\,(hx_j + ky_j + lz_j) = A_{hkl} + iB_{hkl}} \tag{13}$$

where $\mathbf{f_i}$ – individual scattering factors, $\mathbf{x_j}$, $\mathbf{y_j}$, $\mathbf{z_j}$ – the positional parameters of atom **j** in the unit cell and $\mathbf{A_{hkl}}$ and $\mathbf{B_{hkl}}$ are the projections of $\mathbf{F_{hkl}}$ on the **x** and **y** axes, defined as:

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

$$\mathbf{B_{hkl} = \sum_{j}^{N} f_j \sin 2\pi i\,(hx_j + ky_j + lz_j)} \tag{14}$$

From equations (13) and (14) follows :

$$\mathbf{F_{hkl} = |F_{hkl}| \exp i\alpha(h,k,l)} \tag{15}$$

where

$$\mathbf{|F_{hkl}| = (A_{hkl}^2 + B_{hkl}^2)^{1/2}} \tag{16}$$

is the structure amplitude and $\alpha(\mathbf{h,k,l})$ is the phase of the structure factor $\mathbf{F_{hkl}}$, defined as the difference in period or an angle between the wave resulting from a specific set of planes and the wave resulting from scattering at the origin:

$$\alpha(\mathbf{h,k,l}) = \tan^{-1}(\mathbf{B_{hkl}}/\mathbf{A_{hkl}}) \qquad (17)$$

The structure amplitude is the most important quantity, derived from the intensities. It is proportional to the square root of the corrected intensity:

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

where $\mathbf{K_s}$ is a scale factor. Thus, data reduction process actually represents a conversion of observed $\mathbf{I_{hkl}}$ to $\mathbf{F_{hkl}}$ values, which are usually denoted as $\mathbf{F_{obs}}$. The standard deviation of $|\mathbf{F_{hkl}}|$, $\sigma\mathbf{F}$, is calculated as:

$$\sigma\mathbf{F} = \tfrac{1}{2}\,\mathbf{K}/(\mathbf{Lp})^{1/2}[\mathbf{N} + \mathbf{N_{bgr}} + \mathbf{N_{bgl}} + (\mathbf{0.01N_{pk}})^2]/(\mathbf{N} - \mathbf{N_{bgr}} - \mathbf{N_{bgl}})^{1/2} \qquad (19)$$

where $\mathbf{N}$ – the total peak count;

$\mathbf{N_{bg1}}$ and $\mathbf{N_{bg2}}$ are the background counts on either side of the peak;

$\mathbf{N_{pk}} = \mathbf{N} - \mathbf{N_{bgr}} - \mathbf{N_{bgl}}$.

The structure factors used in the calculation of electron density maps may be considered as the sum of the wavelets scattered from all the elements of electron density [89]:

$$\mathbf{F_{hkl}}\,(\mathbf{h,k,l}) = \int \rho(\mathbf{x,y,z})\,\exp 2\pi(\mathbf{hx} + \mathbf{ky} + \mathbf{lz})\,\mathbf{dx\,dy\,dz} \qquad (20)$$

Solution of structure deals with the inverse problem (calculation of electron density maps from structure factors) which may be solved using Fourier transform, if the phase angle is known. The electron density is calculated as the Fourier transform of the structural factors and vice versa:

$$\rho(\mathbf{x,y,z}) = (1/\mathbf{V_c})\sum_{\mathbf{h}}\sum_{\mathbf{k}}\sum_{\mathbf{l}} \mathbf{F_{hkl}}\,\exp[-2\pi\mathbf{i}\,(\mathbf{hx} + \mathbf{ky} + \mathbf{lz})] \qquad (21)$$

where $\rho(x,y,z)$ is the electron density or the number of electrons per unit volume at some point x,y,z and V_c – unit cell volume. The expression for a three dimensional Fourier transform, assuming that Friedel's law holds, is:

$$\rho(x,y,z) = 2/V_c \sum_h \sum_k \sum_l | F_{hkl} | \cos [2\pi (hx + ky + lz) - \alpha(h,k,l)] \qquad (22)$$

From the equation (22) follows that for calculating the electron density map we need $|F_{hkl}|$ (or $|F_{obs}|$ values) and phase angles, that are not directly measurable. This is so called 'phase problem' in crystallography.

There are three ways commonly used to deduce the relative phase angles [84-85]:

1) Direct methods, based on the concept that the electron density map is never negative, and that it consists of isolated, sharp peaks at atomic positions. They make it possible to derive phase angles for a set of structures directly from the values of $|F_{hkl}|$ (experimental data). At present this is the method of choice for organic molecules. The first step is to modify structure factors so that the maximal information on atomic positions can be extracted from them. This is done by converting $|F_{hkl}|$ values into normalized structure factors, $|E_{hkl}|$:

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

where ε is an integer, that is generally equal to 1. This procedure makes X-scattering intensities essentially independent of $\sin\theta/\lambda$. The distribution of the $|E|$ values is independent of the size and content of the unit cell, but it does depend on the presence or absence of a center of a symmetry. The intensities from a noncentrosymmetric crystal are generally nearer the mean that those from a centrosymmetric crystal:

$|\mathbf{E}| = \sqrt{\pi}/2 = 0.886$, for non-centrosymmetric structures,

$|\mathbf{E}| = \sqrt{2\pi} = 0.798$, for centrosymmetric structures.

The general equation (21) for an electron density map in case of a centrosymmetric structure is simplified to:

$$\rho(\mathbf{x,y,z}) = \mathbf{2/V_c} \sum_{\mathbf{h}} \sum_{\mathbf{k}} \sum_{\mathbf{l}} \pm |\mathbf{F_{hkl}}| \cos 2\pi (\mathbf{hx + ky + lz}) \qquad (24)$$

because the phase angle can only be either 0° or 180°, giving $\sin\alpha = 0$ and $\cos\alpha = \pm 1$. Therefore, the problem of phase angles is equivalent to sign determination.

The so-called Harker-Kasper inequality [89] is helpful in phase (sign) determination:

$$\mathbf{U_{hkl}^2 < \tfrac{1}{2} (1 + U_{2h,2k,2l})} \qquad (25)$$

where $\mathbf{U_{hkl}}$, unitary structure factor, is defined as:

$$\mathbf{U_{hkl} = F_{hkl} / F_{000}} \qquad (26)$$

with $\mathbf{F_{000}}$, equal to number of electrons in the unit cell. Here and further for simplicity, bold **h** means **h,k,l**. Using equation (24), from the **U** values one can get a sign of **F**. Suppose, we have two reflections 100 and 200 with their unitary structure amplitudes equal to 0.6. Then (24) is only satisfied if $|\mathbf{U_{2h,2k,2l}}| = +0.6$, so the sign of $\mathbf{F_{2h,2k,2l}}$ must be +. So, if both 200 and 100 reflections are intense, the phase of the 200 must be positive, which is consistent with either choice of phase sign for the 100 reflection.

A more general approach, showing the relationship between signs, is described by the so-called Sayre equation:

$$\mathbf{s(h,k,l) \approx s(h',k',l') \times s(h - h', k - k', l - l')} \qquad (27)$$

where **s** means "sign of", $\mathbf{s(h,k,l)}$, equal to $\mathbf{F_{hkl}} / |\mathbf{F_{hkl}}|$, is either + or – and **(h,k,l)**, $\mathbf{(h',k',l')}$ and $\mathbf{(h-h', k-k', l-l')}$ compose a triplet of strong observed reflections. This equation may

be used to expand the number of known phases. For example, if reflections 112, $3\bar{2}5$ and $4\bar{1}7$ are all intense, and the reflections 112 and $3\bar{2}5$ have phases of $0°$ (signs +), then $4\bar{1}7$ probably also has a phase angle of $0°$. Probability of each triplet is estimated by statistical methods, and if it is high, the triple relationship is accepted as true. The probability that equation (27) holds:

$$\mathbf{P} = \frac{1}{2} + \frac{1}{2}\tanh\left[\left(\frac{\sigma_3}{\sigma_2^{3/2}}\right)\left|\mathbf{E(h,k,l)E(h',k',l')E(h-h',k-k',l-l')}\right|\right] \qquad (28)$$

Here

$$\sigma_k = \sum_j^N n_j^k \qquad (29)$$

where $\mathbf{n_j}$ is the fraction of the scattering power, represented by atom **j**. If all the atoms are alike, $\sigma_3/\sigma_2^{3/2}$ is equal to $\sqrt{N}$ and (27) becomes:

$$\mathbf{P_+(E_{hkl})} = \frac{1}{2} + \frac{1}{2}\tanh\left[N^{-1/2}\left|\mathbf{E(h,k,l)E(h',k',l')E(h-h',k-k',l-l')}\right|\right] \qquad (30)$$

where $P_+(\mathbf{E_{hkl}})$ is the probability that $\mathbf{E_{hkl}}$ is positive.

The determination of phases for non-centrosymmetric structures is more difficult, because their values are not restricted to $0°$ or $180°$. Usually, phases are derived by the tangent formula:

$$\tan[\alpha_H] = \frac{\sum_{h'}\left|E_K E_{H-K}\right|\sin(\alpha_K + \alpha_{H-K})}{\sum_{h'}\left|E_K E_{H-K}\right|\cos(\alpha_K + \alpha_{H-K})} \qquad (31)$$

where $\mathbf{H \equiv h,k,l}$; $\mathbf{K \equiv h',k',l'}$ and $\alpha(\mathbf{hkl})$ – is the phase angle of the structure factor. After a significant number of phases are estimated the trial structure can be determined.

2) The second method of relative phase determination, the Patterson method, is only useful for determining the crystal structure of compounds that contain heavy atoms (e.g., elements following sulphur in the periodic table). The Patterson map, commonly designated **P(uvw)** is a Fourier synthesis that uses only the indices and $|F_{hkl}|^2$ values of each diffracted beam. The Patterson function is defined by [87]:

$$\mathbf{P(u,v,w)} = \mathbf{1/V_c} \sum_{h} \sum_{k} \sum_{l} \mathbf{|F_{hkl}|^2 \cos 2\pi (hu + kv + lw)} \qquad (32)$$

or in terms of electron density,

$$\mathbf{P(u,v,w)} = \mathbf{V} \int\int\int \rho(x,y,z)\, \rho(x+u, y+v, z+w)\, \mathbf{dxdydz} \qquad (33)$$

The useful feature of Patterson function is that it contains squares of the srtucture factors and only cosine terms of them, so that no phases are needed. It represents the convolution of the electron density at points **(x,y,z)** in the unit cell with the electron density at points **(x+u, y+v, z+w)**. A peak at **(u,v,w)** in the Patterson map is really a vector from the origin to the point **(u,v,w)**, which implies the presence of two atoms (x_1,y_1,z_1) and (x_2,y_2,z_2) such that the relative coordinates will be $u=x_2-x_1$, $v=y_2-y_1$, $w=z_2-z_1$. The vectors between heavy atoms are the most visible, because the height of a peak in a Patterson map is proportional to Z_iZ_j, where Z_i and Z_j are the atomic numbers of atoms at the ends of the vector. Specific peaks are associated with the vectors between atoms which are related by symmetry operators (mirrors, rotation axes, screw axes and glide planes). These peaks are located along so-called 'Harker planes' or 'Harker lines'. A Harker plane implies one of the values u,v,w is fixed (for example, at 0 or ½) and a Harker line is formed when two of the values are fixed (e.g., **u**00, 0,1/2,**w**). These are vectors between atoms and their own symmetry equivalents. There are also vectors between independent atoms. Analysis of Patterson vectors results in the positional parameters of the heavy atoms, which give the

initial trial structure (Fig.6).

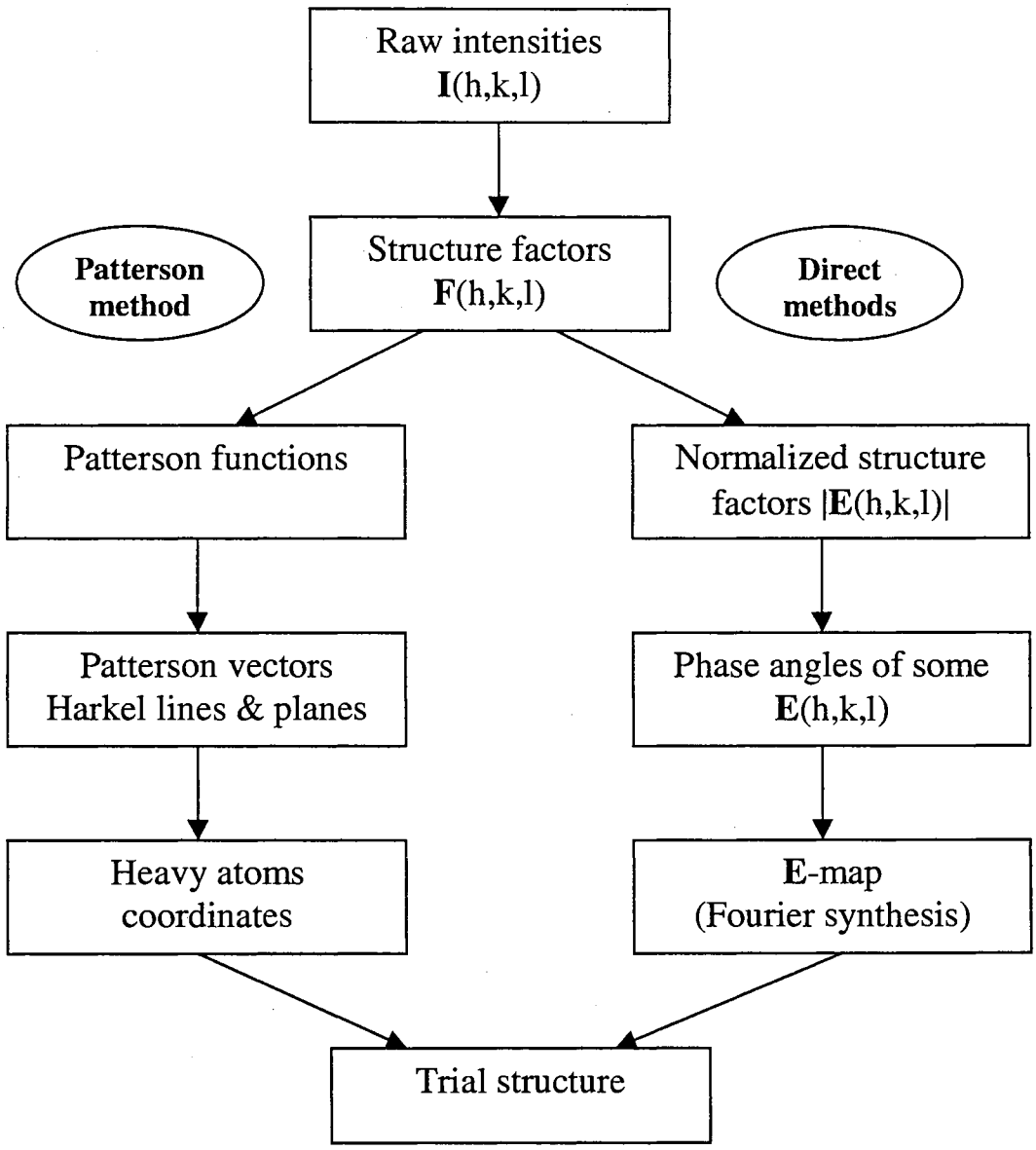


Figure.6. Flow diagram of solving structure by Patterson or direct methods

3) The alternative method of phase estimation is the isomorphous replacement method [85], which is more suitable for macromolecules (proteins and nucleic acids). In this case isomorphism is needed between the crystalline macromolecule and its heavy-atom derivative obtained by soaking a heavy atom (M) into a hole in the structure, i.e.,

displacing solvent. The observed differences in the intensities of reflections, therefore, result only from the presence of M. The contribution to the structure factors made by the rest of the structure, $\mathbf{F_R}$, is the same for both crystal structures. If the structure amplitudes for the initial macromolecule and its heavy-atom derivative are $|\mathbf{F_R}(h,k,l)|$ and $|\mathbf{F_{M+R}}(h,k,l)|$ for corresponding pairs of reflections, the location of the variable atom (heavy atom) can be deduced from difference Patterson map using $||\mathbf{F_{M+R}}| - |\mathbf{F_R}||^2$ as coefficients in equation (32). For a biological macromolecule, which necessarily crystallizes in a noncentrosymmetric space group, at least two different heavy atom derivatives are needed to avoid ambiguity in the determination of the phase angle $\alpha(\mathbf{h,k,l})$ and M and M' must be in the same site.

When the initial structure is defined by one of the methods, the phased structure factors ($\mathbf{F_{calc}}$) are calculated and compared with the measured values ($\mathbf{F_{obs}}$). This is performed by a least squares refinement, which improves the atomic positional parameters of the calculated structure and identifies additional (missing) atoms. The correctness of the model is given by the *residual factor*, $\mathbf{R_f}$:

$$\mathbf{R_f} = \frac{\sum_{hkl} \left| |\mathbf{F_{obs}}| - |\mathbf{F_{calc}}| \right|}{\sum_{hkl} |\mathbf{F_{obs}}|} \tag{34}$$

Least squares refinement is followed by a Fourier synthesis, which is made using the differences $|\mathbf{F_{obs}}| - |\mathbf{F_{calc}}|$. The largest peak on a difference map may indicate the location of missing atoms.

The cycle involving refinement of atomic positions and difference Fourier searching for missing atoms is repeated until all non-hydrogen atoms have been found.

As the model approaches completion, the lessening difference between $\mathbf{F_{obs}}$ and $\mathbf{F_{calc}}$ is reflected in a lower $\mathbf{R_f}$ value.

The atom positions are first refined using isotropic temperature parameters, which describe the thermal oscillation of atoms about their rest positions (assuming the spherical shape of atoms). The effect of thermal motion causes the decrease in the atomic scattering factors with increasing angles 2θ as a consequence of the finite size of the atom regarded as a scattering source. This effect is taken into account by multiplying the scattering factors of atoms by an exponential factor [87]:

$$\mathbf{f_j = f_{jo} \exp\left[-B_{iso}(\sin^2\theta)/\lambda^2\right]} \qquad (35)$$

where $\mathbf{f_{jo}}$ is the scattering factor for a stationary atom and $\mathbf{B_{iso}}$ is the isotropic thermal parameter of atom **j**, which is considered to be related to the mean-square amplitude ($\overline{\mathbf{u}}^2$) of atomic vibration by:

$$\mathbf{B_{iso} = 8\pi^2 \overline{u}^2} \qquad (36)$$

A better approximation is to describe the atomic motion in terms of an ellipsoid with larger amplitudes of vibration in some directions than in others. Six parameters for each of type of atom, the anisotropical displacement parameters, $\mathbf{b_{ij}}$, are introduced into exponential factor

$$\mathbf{\exp[-(b_{11}h^2 + b_{22}h^2 + b_{33}h^2 + b_{12}hk + b_{13}hl + b_{23}kl)]} \qquad (37)$$

They describe an ellipsoidal electron distribution of the electron density. The size of an ellipsoid is determined by the probability of electron location inside it, which is usually viewed at a 50% level.

Hydrogen atom positions are normally calculated using ideal geometry unless

they can be found from a difference Fourier map. When all atoms have been located, an approximate weight scheme, taking into account systematic errors, can be applied. The weght of every measurement is defined by the reciprocal of the square of its standard deviation, thus increasing the reliability of those values measured more precisely:

$$w(h,k,l) = \frac{1}{\sigma^2[F_{obs}(h,k,l)]} \tag{38}$$

where $w(h,k,l)$ - weighting function. A useful equation, given by least square refinement, is the so-called *goodness of fit*, **GOF**:

$$GOF = \left[\frac{\sum w(|F_{obs}| - |F_{calc}|)^2}{n-m}\right]^{1/2} \tag{39}$$

where **n** – number of parameters (variables) and **m** – number of observations. If the model properly represents the structure that gives rise to the data, the value of the **GOF** is expected to be close to 1. In reality, crystals are not perfect, they are composed of mosaic blocks about 10^{-5} cm in diameter, slightly misoriented with respect to each other. Besides, X-ray beams are never truly monochromatic. As a result, one can observe additional attenuation of the X-ray beam, called *extinction* [90]. Extinction corrections, if necessary, are generally made after refinement. The structural refinement is considered complete when the R_f factor reaches a value 3-6% and all atom bond lengths and angles are reasonable.

Crystal solution and refinement, involving enormous calculations, made significant progress with the development of new sophisticated software packages. XSCANS data collection package [91,92] provides in automatic mode geometrical data collection routines (reflection search and indexing, determination of unit cell parameters

and Laue symmetry) and intensity data collection, including data reduction, space group determination and generation of files for SHELXTL. SHELXTL is an integrated hardware/software package for the determination of crystal structure. It consists of four major programs (Fig.2): XPREP (preparation of data for solving structure), XS (structure solution), XP (molecular graphics program) and XLS (least squares refinement program). In addition, this package provides programs for absorption correction (XEMP), preparation and printing of output data tables (XPUBL and XTEXT).

The alternative package SHELX-98, written by G.M.Sheldrick [93], includes more powerful direct and Patterson methods (SHELXS) and new refinement program, suitable for macromolecules as well.

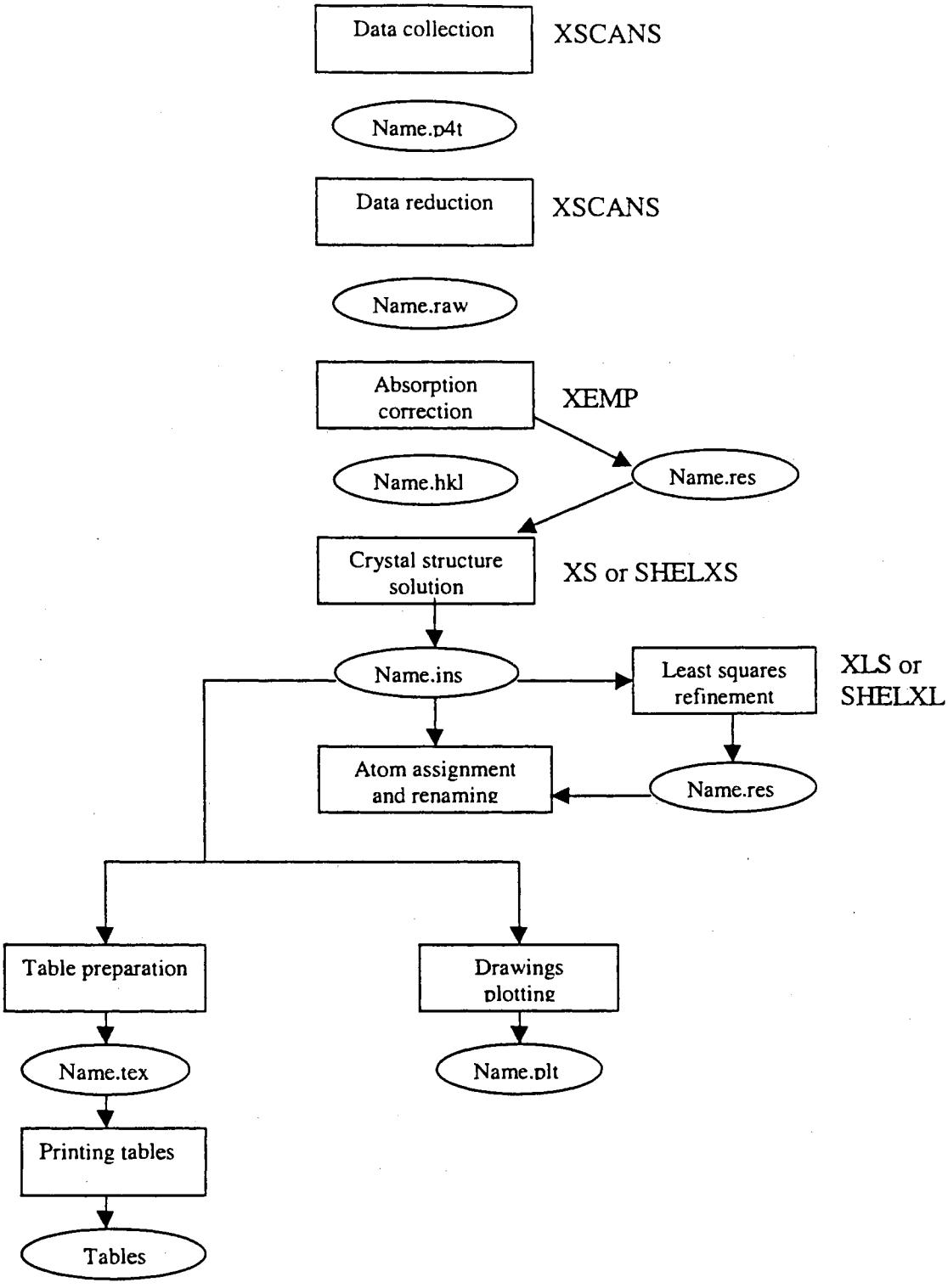


Figure 7. Organization of files and programs, involving in crystal structure determination

CHAPTER III

LUMINESCENCE

Luminescence is the emission of photons from electronically excited states. This implies that a molecule, ion or atom prior to emission has reached the excited state by absorbing energy. Based on the method of excitation, one can distinguish different types of luminescence [94, 95]: *photoluminescence*, resulting from absorption of photons; *chemiluminescence*, which is due to excitation by chemical reaction; *cathodoluminescence*, caused by electron bombardment; *electroluminescence*, produced by electrical energy; *bioluminescence*, as the result of biological process and *radioluminescence*, which is caused by the impact of radioactive particles. In this thesis the term "luminescence" will imply photoluminescence.

Luminescence, as well as any other type of molecular spectroscopy, involves the transitions between the quantized energetic levels of the molecule. According to their multiplicity, S_n denotes *singlet* states: n=0 for the ground state and n>1 for excited states; T_n corresponds to *triplet* states. The term *multiplicity* is the number of possible orientations of the total spin (**S**) and is defined as $\mathbf{2S + 1 = 2\Sigma s + 1}$, where **s** is the individual spin. A molecular electronic state, in which all electrons are paired (have opposite spin orientation in pairs), is referred to as a singlet state (S_n). The total spin of the ground state is zero, making multiplicity of one. Such molecules exhibit no splitting of energy level when being placed in a magnetic field. When one of a pair of electrons is

excited to a higher energy level, a singlet or triplet state is permitted, depending on a change in the spin. If the spin is not changed (S_1), the resulting excited state retains multiplicity of one (singlet). If the spin is changed in the transition (T_1), the excited state contains two unpaired electrons with parallel spins, giving **2S + 1 = 3** possible orientations, that is a multiplicity of 3. Therefore, such an excited state is called a triplet state.

The intensity of a band in a spectrum is proportional to the square of the *transition moment integral* [96]: $\left|\int_{-\infty}^{+\infty} \psi_{el} \hat{M} \psi_{el}^{ex} dv\right|$, where ψ_{el} and ψ_{el}^{ex} are electronic wave functions for the ground and excited states respectively, $\hat{M}$ is the *electric dipole moment operator* and the entire integral is called the transition moment integral. The latter roughly represents charge migration or displacement during the transition. If this integral is equal 0, the band intensity is zero, and the transition is forbidden. In general, in order to estimate, whether the particular transition is allowed or not, we should have good wave functions for the ground and excited states, substitute into this equation and calculate the intensity. However, symmetry considerations may facilitate the procedure, giving some selection rules for electron transitions. An integral can be zero, if the direct product of the integrand belongs to symmetry type A_1, which means, that integrand remains unchanged for any of the symmetry elements belonging to the symmetry of a molecule. Such transitions are considered allowed. From this approach follow some important selection rules for electronic transitions [97]:

1) For a centrosymmetrical molecule all wave functions are either *gerade* (*g*) or *ungerade* (*u*), meaning even and odd respectively. The *d* and *s* orbitals are *g* and *p*

orbitals are *u*. In the centrosymmetric rhombohedral copper (I) iodide cluster ($Cu_2I_4^{-2}$) the ground state (HOMO) is occupied by two electrons with A_g symmetry (Fig.8), therefore molecular orbital has also A_g symmetry (A_g x A_g = A_g). Because the symmetry of operator $\hat{\mathbf{M}}$ in a point group containing an inversion center, is necessarily *ungerade*, it requires the excited state to be ungerade, A_u, so that the integrand retains the initial, A_g symmetry:

$$g \times u \times u = g$$

This leads to the selection rule that transitions $g \rightarrow u$ and $u \rightarrow g$ are allowed, but $g \rightarrow g$ and $u \rightarrow u$ are forbidden.

2) Transitions between states of different multiplicity are forbidden because of the orthogonality of spin functions α and β (spins +1/2 and –1/2).

3) Transitions in molecules without a center of symmetry depend upon the symmetry of initial and final states. In most cases the transitions from HOMO to LUMO are allowed.

The excited molecule can dissipate its excess energy and return to the electron configuration of the ground state. The two general modes of deactivation involve nonradiative and radiative processes. In nonradiative deactivation, the excess electronic energy is converted to translational, rotational or vibrational energy with no emission of radiation. In contrast, the radiative dissipation process involves emission of a photon. A Jablonsky energy-level [98] diagram shows various activation and deactivation processes (Fig.9). Absorption or excitation (very rapid, 10^{-15} s) corresponds to the transitions from the ground singlet state (S_o) to different vibrational levels in the first and higher excited electronic states (S_1, S_2, ...). Molecules in excited vibrational states rapidly dissipate their

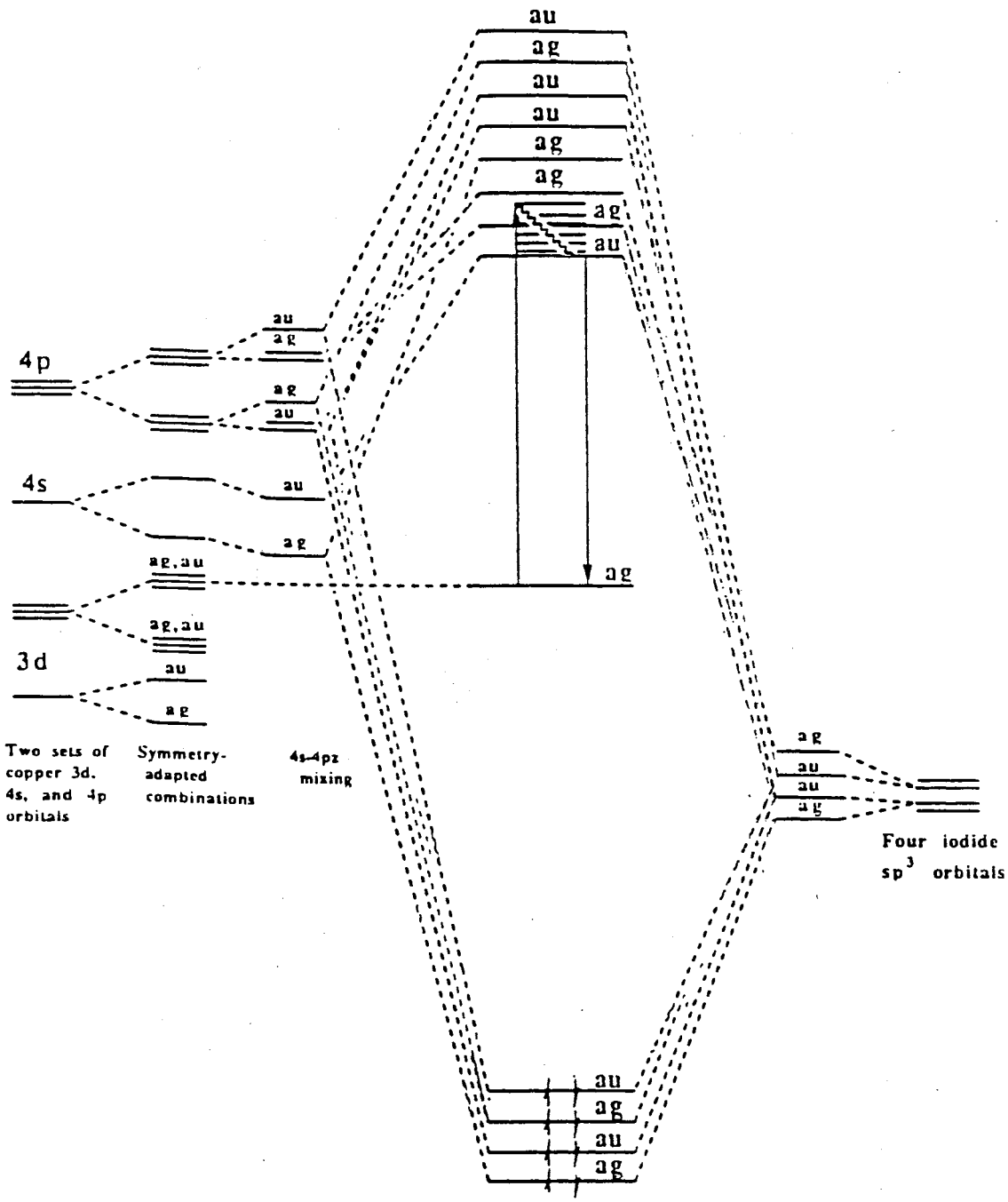


Figure 8. Diagram of molecular orbitals in centrosymmetric Cu(I) – iodide cluster

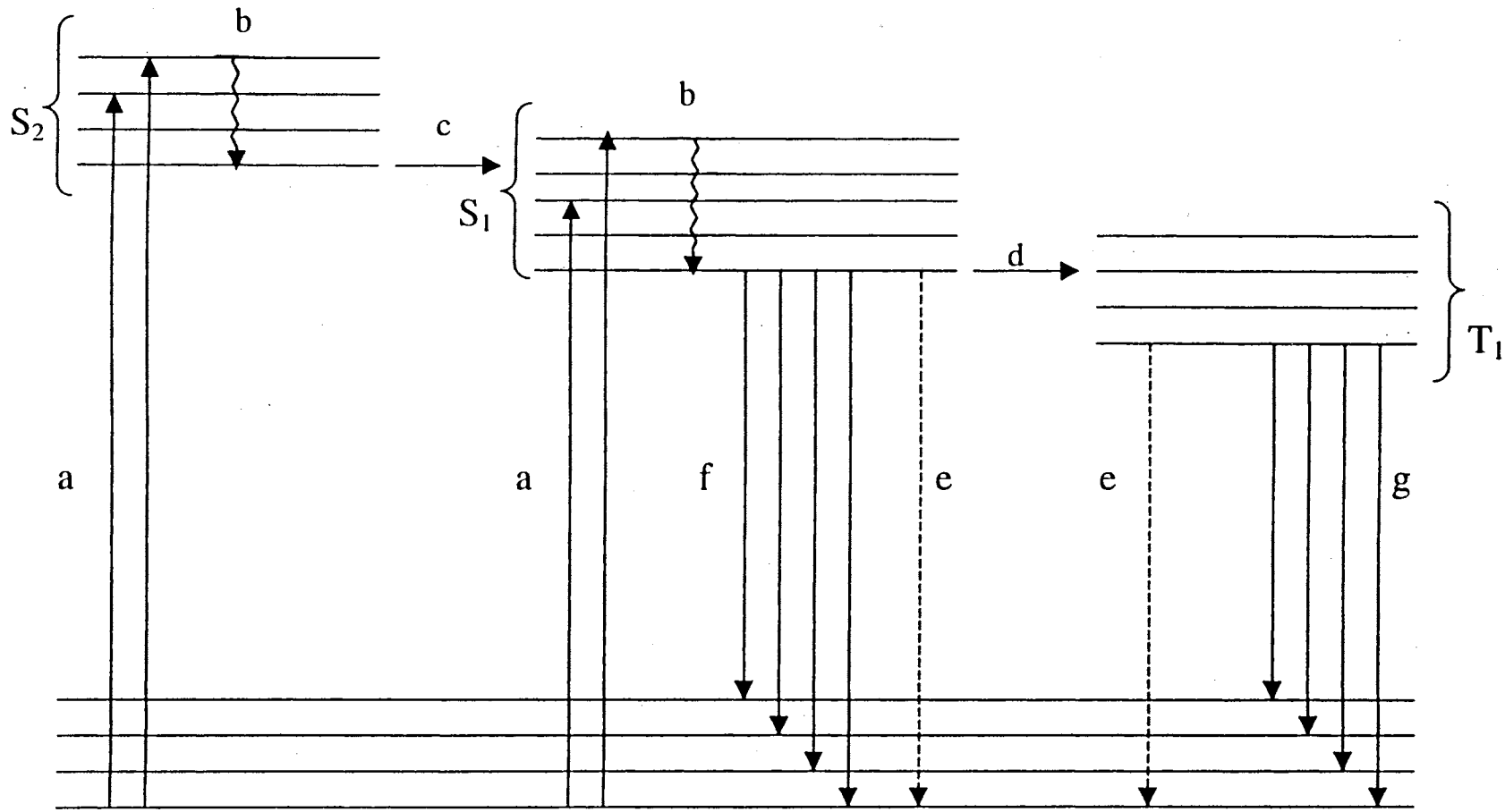


Figure.9. Jablonski diagram: a – absorption; b – vibrational relaxation; c – internal conversion; d – intersystem crossing; e – external conversion; f – fluorescence; g – phosphorescence

excess vibrational energy through thermal motion (intermolecular collisions) and relax to the ground vibrational level in a given electronic state. This nonradiational process is called *vibrational relaxation.*

The crossover between two states of the same multiplicity is a nonradioactive electron state transition called *internal conversion.* It occurs when the lower vibrational states of the higher electronic state are close in energy to higher vibrational levels of the lower electronic state, and results in the conversion of excess electronic energy to excess vibrational energy. Internal conversion occurs more frequently between excited states (e.g., $S_2 \rightarrow S_1$), than between the first excited state and the ground electronic state ($S_o \rightarrow S_1$), the latter being less efficient because of no overlap of the potential energy levels. After internal conversion, the excess vibrational energy is rapidly dissipated through vibrational relaxation to the ground vibrational level of the lower electronic state.

The term external conversion refers to another type of nonradiative transition from excited states to the ground electronic state, in which excess energy is transferred from a given molecule to other species (e.g., solvent or solute molecules). One of the mechanisms of external conversion is dynamic quenching, in which energy transfer occurs during collisions. Therefore, the rate of this process may be sensitive to any temperature changes.

Luminescence, as a radiative deactivation process, is divided into two types, depending on the nature of the ground and excited states. *Fluorescence* is a radiational transition between electronic states of the same multiplicity, e.g., a singlet-singlet transition $S_1 \rightarrow S_o + h\nu$. Usually, only one fluorescence band is observed even if absorption leads to different excited states, because internal inversion and vibrational

relaxation, being faster than fluorescence, lead to the same lowest vibrational state of a given S_n state, so that fluorescence usually involves the same transitions $S_1 \rightarrow S_o$ transitions.

The electron transitions to triplet state ($S_o \rightarrow T_n$), according to the selection rule, are forbidden ($\Delta S=0$), because they require a change in multiplicity, which implies spin change. The triplet state can be populated from excited singlet states by a process called *intersystem crossing*, which represents a crossover between electronic states of different multiplicity ($S_1 \rightarrow T_1$). As with internal conversion, the probability of this transition is enhanced if the vibrational levels overlap. The triplet states usually deactivates by external conversion or intersystem crossing to the ground state ($T_1 \rightarrow S_o$). It can also deactivate by light emission. This radiational deactivation process between electronic states of different multiplicity is called *phosphorescence* ($T_1 \rightarrow S_o + h\nu$). Because this triplet-triplet transition is spin-forbidden, the probability of this process is small, and as a consequence, phosphorescence is much slower than fluorescence.

Two quantitative parameters, frequently measured in fluorescence, are *quantum yield* and *fluorescence lifetime*. Quantum yield, or luminescence quantum efficiency, ϕ_l, indicates the ratio of the number of photons emitted to the number of photons absorbed:

$$\phi_l = \frac{\text{\# of photons emitted}}{\text{\# of photons absorbed}} = \frac{\text{luminescence radiant power}}{\text{absorption radiant power}} \qquad (1)$$

Apparently, quantum yield depends on the relative competition between radiative and nonradiative routes of deactivation. Both routes depopulate the excited states. The fraction of molecules, which follow radiative route, and hence, quantum yield of

fluorescence, ϕ_f, is determined by the rate constants of the corresponding processes and can be given by [94]:

$$\phi_f = \frac{\mathbf{k_f}}{\mathbf{k_f} + \mathbf{k_{ic}} + \mathbf{k_{isc}} + \mathbf{k_{ec}}} \qquad (2)$$

where $\mathbf{k_i}$ are rate constants for the processes, by which the lowest excited singlet state is deactivated: fluorescence ($\mathbf{k_f}$), internal conversion ($\mathbf{k_{ic}}$), intersystem crossing ($\mathbf{k_{isc}}$), external conversion ($\mathbf{k_{ec}}$). This equation is valid under conditions of constant illumination, when a steady-state population of S_1 is achieved. It is also assumed that dissociation processes as well as photochemical reactions are negligible. Equation (2) may be simplified to:

$$\phi_f = \frac{\mathbf{k_f}}{\mathbf{k_f} + \mathbf{k_{nr}}} \qquad (3)$$

where $\mathbf{k_{nr}}$ is the overall total rate constant of nonradiative decay. From (3) follows, that if the rate of nonradiative decay is much smaller, than the rate of fluorescence, $\mathbf{k_{nr}} << \mathbf{k_f}$, the quantum yield approaches to unity. In case $\mathbf{k_{nr}} >> \mathbf{k_f}$, S_1 is deactivated by nonradiative processes before the mol;ecule has a chance to fluorescence. As a result, quantum efficiency ϕ_f is small, and detection of fluorescence is difficult.

Quantum efficiency of phosphorescence, ϕ_p, depends on the rate that the triplet state (T_1) is populated by intersystem crossing and the rate of deactivation. If a steady-state population of T_1 is achieved, ϕ_p is expressed as:

$$\phi_p = \left(\frac{\mathbf{k_{isc}}}{\mathbf{k_f} + \mathbf{k_{nr}}}\right)\left(\frac{\mathbf{k_p}}{\mathbf{k_p} + \mathbf{k'_{nr}}}\right) \qquad (4)$$

where $\mathbf{k_p}$ and $\mathbf{k'_{nr}}$ are the first order rate constants for phosphorescence and nonradiative

deactivation of T_1. Two factors in equation (4) represent respectively the fraction of the absorbed protons that produce triplet states and the fraction of the triplet molecules that undergo phosphorescence. Thus, phosphorescence is favored for molecules and environmental conditions, in which intersystem crossing is favorable ($k_{isc}>k_f$). The temperature is a more important factor for phosphorescence than fluorescence. Cooling can enhance ϕ_p because the quantum efficiency of triplet formation (the first factor in the above equation) is increased by reducing dynamic quenching of S_1. Dynamic quenching may also be reduced by immobilizing the molecules on a solid support or trapping them in cavities or miscelles.

The lifetime of the excited state is defined by the average time the molecule spends in the excited state prior to return to the ground state:

$$\tau = \frac{1}{k_f + k} \qquad (5)$$

The lifetime of the molecule in the absence of nonradiative processes is called the intrinsic lifetime, and is given by:

$$\tau_o = 1/k_f \qquad (6)$$

Lifetime of fluorescence is near 10 ns. Combining (4), (5) and (6) leads to the relationship between the quantum yield and the lifetime:

$$\phi_f = \tau / \tau_o \qquad (7)$$

Thus, quantum yield and lifetime are determined by any factors which effect either of rate constants. The observed low quantum efficiency of phosphorescence at room temperature has its origin in the low rate of emission (k_f). For phosphorescence, the rates of emission are about 10^{-3} s^{-1} and **k** values are near 10^{-9} s^{-1}, giving phosphorescence yield

of 10^{-6}. The lifetime of phosphorescence is usually between 10^{-5} to 10 s. Suppression of nonradiative processes, that may be performed by lowering temperature, decreases relative value of **k**, and therefore, increases quantum yield.

The luminescence efficiency of a given species depends on its structure and on the environment. The nature of the lowest-lying excited singlet state (S_1) is important in determining the luminescence behaviour of a molecule, because fluorescence and intersystem crossing usually occur from this state. For most fluorescent compounds, radiation is produced by either $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow$ **n** transitions, depending on which of those is less energetic. The most efficient fluorescence usually involves (π,π^*) states, due to their higher probability. For (**n**,π^*) states the fluorescence is less favorable, because of the low degree of overlap between **n** and π^* orbitals, but phosphorescence is more efficient, since the rate constant of intersystem crossing, populating triplet state, is much faster between states of different electronic origin: e.g., $S_1(\pi,\pi^*) \rightarrow T_1(\mathbf{n},\pi^*)$.

The luminescence of a fluorophore is studied using standard *spectrofluorometer* with double-beam optics in order to compensate for fluctuations of the source and for inhomogeneities of a sample. A block scheme of a typical instrument, which employs two grating monochromators, is shown in Fig.10. The modern spectrofluorometer is usually equipped by two radiation sources: high pressure *xenon arc lamp* and *a mercury lamp*, which both are bright and powerful sources of UV radiation. The mercury lamp is more efficient and powerful in the ultraviolet, but its emission spectrum is not as continuous as that of a xenon arc lamp. Radiation sources are cooled by a fan to protect from overheating.

Two grating monochromators are used to select excitation and emission

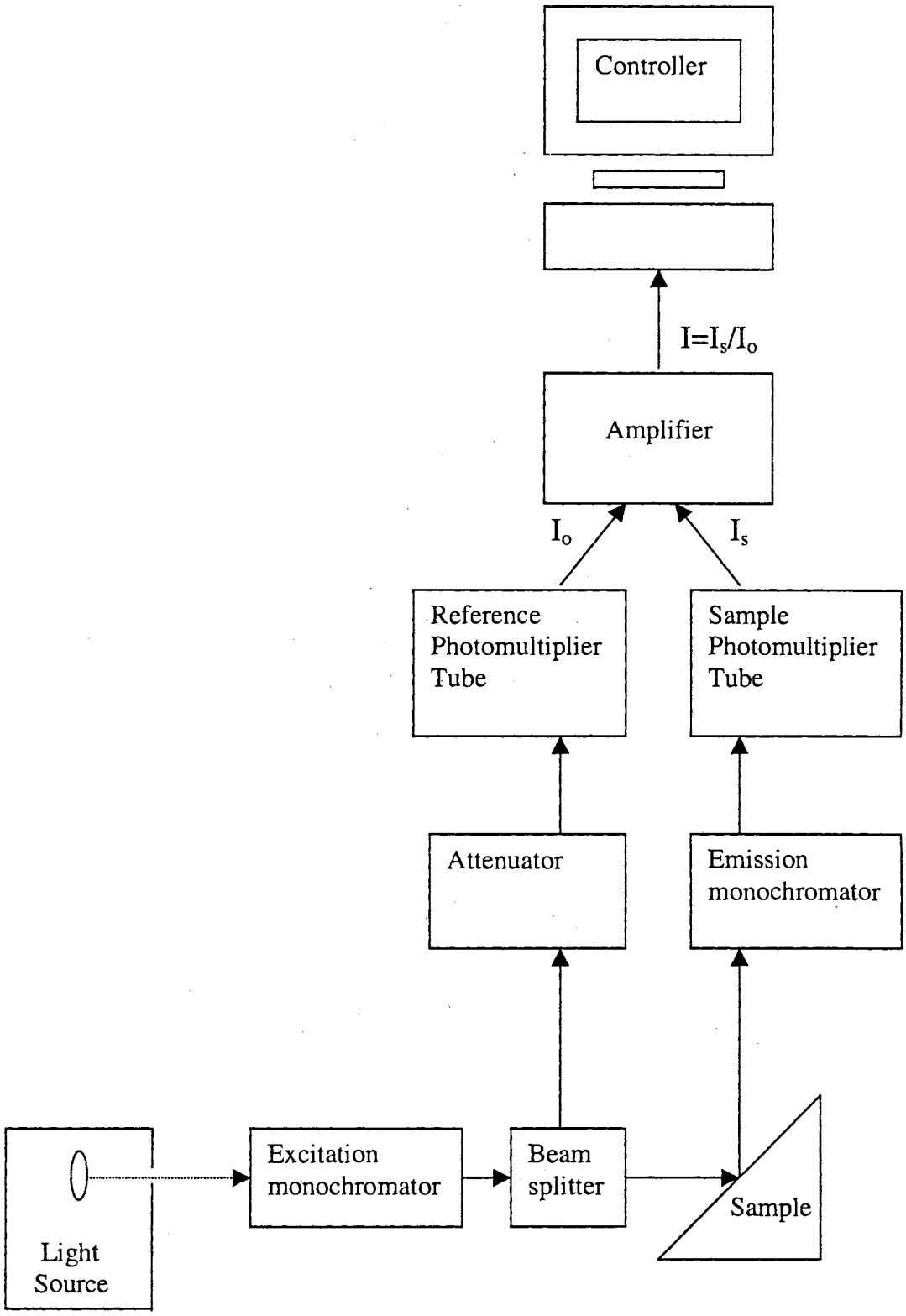


Figure.10. Block-scheme of a typical spectrofluorometer

wavelength. The source beam passes through the *excitation monochromator* and then is split into a reference beam and a sample beam. The reference beam is attenuated so that its intensity becomes comparable with the fluorescence intensity and is detected by reference photomultiplier. The sample beam is focused on the sample, causing the emission of radiation. The emitted radiation passes through *emission monochromator*, which is placed perpendicularly to the excitation beam, thus decreasing scattering effects. Finally the beam passes into a detector (*sample photomultiplier tube*). The signals from the reference and sample photomultiplier tubes (I_o and I_s) are then fed into a *difference amplifier*. The ratio I_s/I_o, serving as the analytical parameter, is computed and displayed on the *controller*. The output results depend not only upon the intensity of fluorescence, but also upon the characteristics of radiation source, detector and monochromator. All of these instrumental parameters are functions of wavelength, differing from instrument to instrument. The modern commercial instruments provide directly corrected spectra, free from instrumental errors.

CHAPTER IV

EXPERIMENTAL

Materials. All chemicals were reagent-grade commercial products, used without further purification. The solvents used were acetone, acetonitrile, ethyl alcohol and water. It was noticed that the solubility of copper(I) iodide complexes in these solvents, in general, increases in order: alcohol < acetone < acetonitrile. Different molar ratios were used to produce favorable conditions for crystal growth. Alkali and alkaline metal iodides were used as their solutions in minimum possible amounts of water, because excess of water favors Cu(I) → Cu(II) oxidation and decreases solubility of CuI. An excess of iodide ions increases solubility of CuI due to the formation of copper(I) iodide complex species. Ascorbic acid was added to prevent oxidation of copper(I) in the molar ratio CuI : ascorbic acid = 2:1.

$[Ba(15\text{-Crown-}5)_2]Cu_2I_4$ (I)

CuI (2 mmol, 0.382 g) was added to 15 mL acetone, in which 2 mmol of 15-crown-5 (0.440 g) was dissolved. This solution was mixed with 3 mL of an aqueous solution of $BaI_2.2H_2O$ (1 mmol, 0.382 g) and heated under reflux for 18 hours to give a colorless solution. After filtering, the resulting solution was allowed to stand. In several hours small colorless rhomb-like crystals of **(I)** were formed.

$[K(Benzo\text{-}15\text{-crown-}5)_2]_2Cu_2I_4$ (II)

$[K(Benzo\text{-}15\text{-crown-}5)_2]I_3$ (XXII)

Benzo-15-crown-5 (2 mmol, 0.536 g) was dissolved in 40 mL acetone, to which was added CuI (2 mmol, 0.382 g) dissolved in 5 mL of saturated KI water solution. The mixture of these two solutions was heated under reflux for 3 hours forming a transparent colorless solution, cooled to room temperature and filtered. Large colorless prism-like crystals of (**II**) were found to form in the filtrate within 2 days and after evaporation of most of the solvent. The mixture was covered and allowed to stand for a month, whereupon dark red-brown prismoid rods of (**XXII**) appeared.

[Rb(Benzo-15-crown-5)$_2$]$_2$Cu$_2$I$_4$ (III)

CuI (1 mmol, 0.191 g) was dissolved in 10 mL of saturated solution of RbI to give a suspension of yellow color, which cleared after adding ascorbic acid. The suspension was added to 20 mL of an acetone solution of benzo-15-crown-5 (3 mmol, 0.784 g) and the resulting mixture was allowed to react under reflux for 18 hours. After the solution had been filtered to remove unreacted solid phase material and cooled to room temperature, prismoid crystals of (**III**) were formed.

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

CuI (1 mmol, 0.191 g) was suspended in 40 mL of an acetone – alcohol solution (volume ratio 1:1) of dicyclohexano-18-crown-6 (1 mmol, 0.400 g). CsI (1 mmol, 0.260 g), dissolved in 3 mL of water, was added to the resulting suspension. The mixture was heated under reflux for 20 hours to dissolution, filtered while hot and allowed to stand at room temperature. Fine snowflake-like crystalline material appeared after cooling to ambient temperature. These were filtered from the mother liquor and recrystallized from an acetone - alcohol mixture. After 2 weeks of slow evaporation (solution covered) large thick hexagonal plates of (**IV**) were formed.

$[Cs_2(Benzo\text{-}18\text{-}crown\text{-}6)_3]Cu_2I_4$ (V)

$[Cs_4(Benzo\text{-}18\text{-}crown\text{-}6)_5]Cu_6I_{10}$ (XVII)

$[Cs_2(Benzo\text{-}18\text{-}crown\text{-}6)_3]I_2.3H_2O$ (XXIII)

CuI (1 mmol, 0.191 g) and benzo-18-crown-6 (2 mmol, 0.626 g) were mixed in 30 mL acetone in the presence of ascorbic acid. An aqueous solution of CsI (10 mL, 5 mmol, 1.300 g) was added to this suspension, followed by heating under reflux for 2 hours. The resulting light yellow solution was cooled to room temperature and filtered. In 3 days clusters of fine colorless non-emitting needles of (**XVII**) were observed to form on the bottom of the beaker. Several days later, after further solvent evaporation colorless needle-like crystals of (**V**), displaying red emission, formed on the sides of the beaker. After filtration to remove crystalline materials the resulting filtrate was allowed to evaporate further. In a week when almost all the solvent has gone, large colorless rhombs of (**XXIII**) appeared at the bottom of the beaker. These three compounds contain the same cationic moiety $[Cs_2(benzo\text{-}18\text{-}crown\text{-}6)_3]^{2+}$, in which two cesium ions are complexed by three crown ether molecules, in *club-sandwich* fashion. Compound (**V**) is the only one emitting from them (red color).

$[Cs_2(18\text{-}Crown\text{-}6)_3]Cu_2I_4$ (VI)

Copper powder (8 mmol, 0.512 g) and crystalline I_2 (2 mmol, 0.508 g) were mixed with 40 mL of an acetone solution of 18-crown-6 (4 mmol, 1.056 g). An aqueous solution of CsI (3 mL, 2 mmol, 0.520 g) was added to this suspension, followed by heating under reflux for 18 hours. Undissolved solid material was removed by filtration and the resulting yellow solution was exposed to evaporation. In 24 hours, there formed on the sides of the beaker large flat plates of (**VI**), which exhibited blue emission.

$[Ba(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ (VII)

$BaI_2.2H_2O$ (1 mmol, 0.427 g), dissolved in 5 mL of water, and 1 mmol of CuI (0.191 g) were added to 40 mL of an acetone solution of benzo-15-crown-5 (2 mmol, 0.536 g). The resulting suspension was heated under reflux for 5 hours. Colorless rhomb-like crystals of (**VII**), showing blue emission, were being formed upon cooling of the solution.

$[Sr(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ (VIII)

SrI_2 (2 mmol, 0.680 g) and benzo-15-crown-5 (1.5 mmol, 0.400 g) were dissolved in 5 mL of water and 30 mL of acetone respectively. These two solutions were mixed and CuI (1 mmol, 0.191 g) was added. The resulting suspension was heated under reflux for 13 hours. An insoluble crystalline mass was precipitated during the reaction. It consisted of rhomb like crystals of (**VIII**), which showed blue emission.

$[Li(H_2O)(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_4I_6$ (IX)

A saturated solution of LiI in water (5 mL) was added to a mixture of 2 mmol (0.382 g) of CuI and 1.5 mmol (0.402 g) of benzo-15-crown-5 in 40 mL of acetone. The resulting suspension was heated under reflux until all solids were completely dissolved (4 hours). The solution was allowed to cool slowly and yellow plates of (**IX**) were observed to form after two days. The color of their emission is yellow.

$[Na_2(H_2O)_3(18\text{-}Crown\text{-}6)_2]Cu_4I_6$ (X)

A mixture of 2 mmol of CuI (0.382 g), 2 mmol of 18-crown-6 (0.528 g) and 3 mL water solution of NaI (3 mmol, 0.450 g) were mixed with 40 mL of acetone and heated under reflux for 6 hours until complete dissolution of the CuI. The resulting yellow solution was filtered and allowed to stand for three days whereupon yellow-green rods of

(**X**) appeared. These crystals possess yellow emission.

[Cs(Benzo-15-crown-5)$_2$]$_2$Cu$_4$I$_6$ (XI)

A saturated solution of CsI in water (10 mL) was added to 2 mmol (0.382 g) of CuI and 2 mmol (0.536 g) of benzo-15-crown-5 in 40 mL of acetone. The resulting mixture was heated under reflux until a clear solution resulted (2 hours). After cooling, the solution was allowed to evaporate slowly. After two days, long colorless needles of the known compound $CsCu_2I_3$ [66] were observed to form, however after another 24 hours yellow prisms of (**XI**) were found. The crystals showed yellow emission.

[K(15-Crown-5)]Cu$_2$I$_3$ (XII)

CuI (2 mmol, 0.382 g), KI (3 mmol, 0.498 g), dissolved in 3 mL water, and 15-crown-5 (2 mmol, 0.400 g) were mixed with 15 mL of acetone. The mixture was heated under reflux for 8 hours. The resulting yellow solution was filtered immediately. Upon standing for 2 days, large colorless polyhedra of (**XII**) crystallized.

[Rb(15-Crown-5)]Cu$_2$I$_3$ (XIII)

A mixture of CuI (2 mmol, 0.382 g), 15-crown-5 (2 mmol, 0.440 g) and RbI (3 mmol, 0.636 g), dissolved in 3 mL water, was heated under reflux in 15 mL acetone in the presence of ascorbic acid. After 24 hours of heating, the resulting yellow solution was filtered and allowed to stand for one month, whereupon yellow plates and colorless rod-like crystals of (**XIII**) appeared.

[Cs(15-Crown-5)]Cu$_2$I$_3$ (XIV)

CuI (2 mmol, 0.382 g), 15-crown-5 (2 mmol, 0.440 g) and CsI (3 mmol, 0.780 g), dissolved in 3 mL water, were mixed with 15 mL acetone. The mixture was heated under reflux for 22 hours. The resulting hot yellow solution was filtered. Upon standing for

two days, large colorless polyhedra of (**XIV**) formed in the filtrate.

$[C_8H_{20}N]Cu_2I_3$ (XV)

A mixture of $[(C_2H_5)_4N]I$ (5 mmol, 1.26 g), copper powder (20 mmol, 1.27 g) and crystalline I_2 (5 mmol, 1.28 g) in 100 mL acetone was heated under reflux until the solution turned yellow. On cooling and following filtration, colorless needle-like crystals of (**XV**) appeared.

[K(18-Crown-6)]Cu_2I_3 (XVI)

A mixture of CuI (2 mmol, 0.382 g), 18-crown-6 (2 mmol, 0.528 g) and KI (3 mmol, 0.498 g), dissolved in 3 mL water, was heated under reflux in 15 mL acetone for 11 hours. The resulting hot yellow solution was filtered. On cooling and standing for 3 days, colorless rod-like crystals of (**XVI**) appeared.

[Sr(15-Crown-5)$_2$]Cu_4I_6 (XVIII)

A saturated solution of SrI_2 (5 mL) was added to 2 mmol (0.382 g) CuI and 2 mmol (0.440 g) of 15-crown-5 in 30 mL acetone. The resulting mixture was heated under reflux until complete dissolution of CuI. After filtration and cooling to room temperature, the solution was allowed to evaporate slowly for 2 days whereupon colorless flat needles of (**XVIII**) appeared.

[Ca(18-Crown-6)]$Cu_5I_7 .3H_2O$ (XIX)

Reactants 18-crown-6 (2 mmol, 0.528 g) and CuI (1.5 mmol, 0.286 g) were mixed in 40 mL acetone. CaI_2 (4 mmol, 0.668 g) was added to the resulting suspension, followed by heating under reflux (3 hours) to dissolution. After cooling to room temperature and filtration to remove small amounts of solid, the yellow solution was covered and allowed to stand at room temperature. Small, colorless prisms of (**XIX**) were

observed to form after three days.

[Zn(18-Crown-6)]$Cu_5I_7 .3H_2O$ (XX)

Metallic zink (2 mmol, 0.130 g), 4 mmol of copper powder (0.256 g), 2 mmol 18-crown-6 (0.528 g) and 1.5 mmol of crystalline I_2 (0.381 g) in 40 ml acetone were heated under the reflux for 24 hours. The resulting yellow solution was cooled, filtered to remove undissolved solid phase residue and allowed to stand. After evaporation of the most liquid large square crystalls were formed. They were dissolved in an acetone-acetonitrile mixture and left to evaporate slowly. After a couple of weeks colorless polyhedra of (**XX**) were formed.

[Sr(18-Crown-6)]$Cu_5I_7 .3H_2O$ (XXI)

SrI_2 (2 mmol, 0.668 g) was dissolved in 5 mL water and mixed with 2 mmol of 18-crown-6 (0.528 g) in 30 mL acetone. After adding 1 mmol of CuI (0.191 g), this mixture was heated under reflux for 4.5 hours to give a clear colorless solution. The resulting solution was cooled to room temperature and filtered to remove any remaining undissolved solid and allowed to stand. After 24 hours, clusters of fine needles were observed. These were collected by filtration and dissolved in acetone. Large colorless prisms of (**XXI**) were formed after several weeks.

[K(Benzo-18-crown-6)]I (XXIV)

A saturated solution of KI in water (10 mL) was added to a mixture of 1 mmol of CuI (0.191 g) and 2 mmol of benzo-18-crown-6 (0.626 g) in 30 mL acetone. The mixture was heated under reflux until a clear solution resulted (2 hours). The solution was cooled and allowed to evaporate slowly. After a week fragile flat needles appeared (red emission, unstable in the X-ray beam). These were separated by filtration and the

filtrate was covered. After a month, large, colorless cubes of (**XXIV**) were found.

Crystallography. Crystals of a suitable size (≤0.5 mm in all three dimensions) of each complex were chosen for X-ray diffraction. A single crystal of good quality was mounted on a Siemens automated four-circle diffractometer equipped with a PC-486DX computer and monochromated molybdenum radiation (λ= 0.71073 Å). Unit cell dimensions were determined using the centered angles for up to fifty independent strong reflections which were refined with least-squares methods by the automated procedure in XSCANS [91]. The intensity data were collected at room temperature using a variable scan rate, a 2θ scan mode with maximal θ, equal to 30.7°. 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 reflections were remeasured after every 97 collected reflections. The raw intensity data were corrected for Lorentz, polarization, decomposition, centering and background effects. Observed reflections ($I > 4\sigma$) were used for solution of the non-hydrogen atom positions by direct methods [84]. Refinement of the scale factor, positional and anisotropic thermal parameters for all atoms was carried out by either XLS[92] or SHELXL [93] to convergence. Scattering factors were taken from the International Tables for Crystallography [99]. Hydrogen atom positions were calculated by using idealized geometry. Furthermore, an empirical absorption correction based on psi scans was applied in the final stages to remove errors due to heavy atom absorption. A weighting scheme and extinction correction were applied in the last stages of refinement.

Fluorescence. Emission spectra of all compounds were measured using an Oriel modular spectrofluorometer and Fluorolog-3. The sample was prepared as a finely

ground powder spread on double-sided tape attached to a 0.5 x 1.5 inch piece of non-emitting black cardboard. A Xe lamp was used as the light source. Measurements were made at room temeperature in the range of 350-700 nm at 1 nm intervals with integration time 0.1 s. The slits of excitation and emission monochromators were 1 nm. A blank sample showed no signals in the area of interest. Some of the spectra were measured at both room and low temperature (10-15K).

The excitation spectra were measured to determine the optimal wavelength of emission by fixing of wavelength of emission and varying the wavelength of excitation. The value of excitation wavelength, producing maximal emission, was chosen for further emission measurements. This excitation wavelength was between 330 and 350 nm. Emission spectrum was received by irradiating the sample at this wavelength and observing the emitted fluorescence with a scanning monochromator which gives a plot of intensity versus wavelength in relative units.

CHAPTER V

RESULTS AND DISCUSSION

In this study 24 previously unknown anionic copper(I) halide complexes were synthesized and structurally characterized by single crystal X-ray analysis. They belong to 4 different groups: 1) tetraiododicuprates (I) $Cu_2I_4^{2-}$, 2) hexaiodotetracuprates (I) $Cu_4I_6^{2-}$, 3) polymeric $Cu_pI_q^{-(q-p)}$ species and 4) simple iodides. Complete crystallographic data and results for all complexes are given in Tables 11-106. Among these four groups of compounds the first two groups exhibit emission properties at room temperature when excited in the ultraviolet. Their emission spectra are presented in Figures 13, 15, 17, 19, 21, 23, 25, 27, 29, 31, 33.

Tetraiododicuprates(I)

Eight complexes, prepared in this study, contain an anionic cluster $Cu_2I_4^{2-}$, in which a pair of copper atoms is bridged by two halide atoms and, in addition, each three coordinate copper atom is bonded to one terminal iodide. Structural variables are: Cu...Cu distance, overall bent or flat conformation, the presence (or absence) and the type of symmetry elements present within the cluster. Structural parameters for these tetraiododicuprates (I) indicate their belonging to four different groups (Table 4). 1) Four complexes contain a *planar* $Cu_2I_4^{2-}$ cluster, centered about an *inversion center.* These complexes **I-IV**, $[Ba(15C5)_2]Cu_2I_4$ (15C5=15-crown-5), $[K(B15C5)_2]Cu_2I_4$ (B15C5 = benzo-15-crown-5), $[Rb(B15C5)_2]Cu_2I_4$ and $[Cs(DC18C6)_2]Cu_2I_4$

TABLE 4

STRUCTURAL AND EMISSION DATA FOR TETRAIODODICUPRATES(I)

Complex	Space group	Distances, Å			λ_{max}, nm
		$Cu\text{-}I_{bridging}$	$Cu\text{-}I_{terminal}$	Cu...Cu	
Type I: center of symmetry					
(I) $[Ba(15C5)_2]Cu_2I_4$	$P2_1/c$	2.578(2) 2.603(2)	2.497(3)	2.810(5)	452
(II) $[K(B15C5)_2]_2Cu_2I_4$	P1bar	2.570(6) 2.577(6)	2.482(6)	3.040(8)	453
(III) $[Rb(B15C5)_2]_2Cu_2I_4$	P1bar	2.59(2) 2.65(2)	2.50(2)	3.117(5)	452
(IV) $[Cs(DC18C6)]_2Cu_2I_4$	$P2_1/c$	2.583(2) 2.588(2)	2.536(2)	2.790(3)	422
Type II: bent					
(V) $[Cs_2(B18C6)_3]Cu_2I_4$	$P2_1/c$	2.572(4) 2.604(4)	2.489(4) 2.500(4)	2.695(5)	675 640(sh)
Type III: mirror + 2-fold axis (2/m)					
(VI) $[Cs_2(18C6)_3]Cu_2I_4$	C2/m	2.556(2) 2.559(2)	2.484(2)	3.138(6)	479
Mixed (I+II) type:					
(VII) $[Ba(B15C5)_2]_3(Cu_2I_4)_3$	C2/c	**I)** center of symmetry			
		2.609(7) 2.609(7)	2.502(5)	2.658(8)	474
		II) bent			
		2.603(4) 2.645(6)	2.508(5) 2.513(6)	2.666(6)	
(VIII) $[Sr(B15C5)_2]_3(Cu_2I_4)_3$	C2/c	**I)** center of symmetry			
		2.593(4) 2.595(5)	2.497(4)	2.666(7)	478
		II) bent			
		2.602(3) 2.637(4)	2.502(4) 2.509(5)	2.667(5)	

(DC18C6 = dicyclohexano-18-crown-6) contain three coordinate copper atoms with Cu...Cu distances which vary from 2.790(3) to 3.117(5) Å and may be considered as non-interactive. $Cu\text{-}I_{terminal}$ distances 2.482(6) - 2.536(2) Å are shorter than $Cu\text{-}I_{bridging}$: 2.570(6) - 2.65(2) Å. 2) A *bent* conformation with no internal crystallographic

symmetry elements is identified in $[Cs_2(B18C6)_3]Cu_2I_4$ (**V**), where B18C6 = benzo-18-crown-6, with copper-copper distance equal to 2.695(5) Å.

In addition to these two types, reported in the literature, but with other cations [42, 45, 68-71], three other $Cu_2I_4^{2-}$ clusters prepared in this work, are previously unseen. 3) $[Cs_2(18C6)_3]Cu_2I_4$ (**VI**), where 18C6 = 18-crown-6, crystallizes with all the atoms of the $Cu_2I_4^{2-}$ rhomb lying on a mirror plane, and with a twofold axis perpendicular to this plane, passing through the center of the cluster (2/m). The copper-copper distance is 3.138(6). 4) Two isostructural compounds (**VII** and **VIII**) of the formula $[M(B15C5)_2]_3(Cu_2I_4)_3$ (where M = Ba, Sr) contain both a flat (type 1) and a bent (type 2) $Cu_2I_4^{2-}$ fragment in the asymmetric unit. Copper-copper distances are short and close for two different rhombs: 2.658(8), 2.666(6) Å for Ba and 2.666(7), 2.667(5) Å for Sr.

All eight complexes show emission at ambient temperature when excited in the ultraviolet region (330 nm). Type 1 compounds show blue emission at 452-453 nm except for $[Cs(DC18C6)_2]Cu_2I_4$, which emits at higher energy – 422 nm (blue-violet color). However, this compound differs in the structure of the cationic part. The first three complexes possess a *sandwich* type of cation with stoichiometry M : crown ether = 1:2 and thus a well-screened cationic charge, while in complex (**IV**) the Cs atom lies in the plane of the crown ether ring and has an additional ionic interaction with a terminal iodide of the $Cu_2I_4^{2-}$ cluster, showing Cs...I distance of 3.861(6) Å, which is close to the sum of their ionic radii: 2.06 Å for iodide and 1.67 Å for cesium [100], giving in total 3.73 Å. The distances metal – iodide in the first three complexes are 6.809(5)-7.872(9) Å. This fact obviously decreases the electron density on the terminal iodides in structure (**IV**) and may change the contribution of their atomic orbitals

to the HOMO and LUMO orbitals of the complex anion.

The bent $Cu_2I_4^{2-}$ cluster is red-emitting: wavelength of maximal emission is 675 Å with a shoulder at 640 Å. The intensity of emission is much lower in comparison with that of the blue emitting complexes. Complex (**VI**) with 2/m symmetry (type 3), showed blue-greenish emission at 478 nm. The emission spectra of mixed type complexes (**VII** and **VIII**) have maximum emission at 474-478 nm and a long wavelength tail (shoulder). Their emission may therefore be considered as a composite of the emission seen for a flat rhomb with a center of symmetry (type 1) and that of a bent one with no symmetry element (type 2). Emission spectra obtained at low temperature (15K) for $[Ba(15C5)_2]Cu_2I_4$, revealed no difference in wavelength of maximum emission.

Ab initio calculations for tetraiododicuprates(I) were performed using the *Gaussian 94* software package [101]. The basis set LANL1DZ, representing core orbitals (non-valent) for heavy atoms from Na to Bi in the form of primitive Gaussian type orbitals (GTO), was chosen. Because a description of molecular orbitals for the structures, as determined by X-ray single crystal analysis was sought, the *Hartree Fock single point* method of calculations [102] was used. A Z-matrix was used as Gaussian input. It was constructed using either Cartesian coordinates (transformed from crystallographic values by the XP program) or using direct bond lengths, bond and dihedral angles from crystallographic results. Both methods were applicable for bent structures with no symmetry elements involved. However, in symmetrical structures the use of Cartesian coordinates, calculated with an error of 10^{-4} Å, lead to nonrecognition of the symmetry by the Gaussian Program, which expects greater precision. For symmetrical structures the original symmetry group was preserved by creating a

dummy atom at the center of symmetry and describing a sequence of atoms by specifying symmetrical distances and angles. Valence electrons for Cu and I of Cu_2I_4 were included in the calculations, thus, 10 x 2 electrons for copper and 8 x 4 electrons for iodides) with inner core electrons represented by pseudopotentials. A total of 52 electrons were considered for the Cu_2I_4 and orbital number 26 is HOMO. The results of calculations are given in Table 5. In centrosymmetric Cu_2I_4 complexes orbitals 26 (HOMO), 27 (LUMO) as well as orbital 28 (LUMO+1) have *u (ungerade)* symmetry. Therefore, orbitals 29 and 31, which are of *g (gerade)* symmetry, are considered as possible excited states because only transitions $A_u \leftrightarrow A_g$ are allowed for centrosymmetric molecules [96]. Taking this into consideration the electronic transition, responsible for excitation of centrosymmetric cluster $Cu_2I_4^{2-}$ will be: – HOMO(26) → LUMO+2(29) or LUMO+4(31) with the following deactivation of this excited state (emission at 452-453 nm). The distribution of electron density between different atomic orbitals in Gaussian outputs is similar for the four centrosymmetric structures. This is consistent with the values of wavelength of emission which are very close to each other. For the bent type of cluster exhibiting emission at longer wavelength (>600 nm), the corresponding electron transition will be HOMO (26) → LUMO (27) for excitation and HOMO (26) ← LUMO (27) for emission. The energy gap between these neighboring orbitals is less than that for the first type complexes, which explains the relative position of bands in luminescence spectra. The mixed type of complexes, containing both types of $Cu_2I_4^{2-}$ units, possess an asymmetrical emission band at 478 nm with a long wavelength tail. Their spectra comprised thus of both bands, but because of a significant difference in intensity (the centrosymmetric complexes emit more intensively) the less

TABLE 5

Contribution of atomic orbitals into HOMO and LUMO molecular orbitals in $Cu_2I_4^{2-}$ emitting complexes

Complex		Molecular orbitals					
Type I: center of symmetry							
(I) $[Ba(15C5)_2]Cu_2I_4$	Atom	HOMO 26	A_u	LUMO+2 29	A_g	LUMO+4 31	A_g
	Cu1	0.19580	5D0	-0.14085	$3p_y$	-0.15829	2s
						-0.22940	$3p_x$
						1.71965	$4p_x$
						-0.30245	$4p_z$
	Cu2	-0.19580	5D0	1.58717	$4p_y$	-0.15829	2s
						0.22940	$3p_x$
						-1.71965	$4p_x$
						0.30245	$4p_z$
	I1 (terminal)	0.23990	$3p_z$	-0.29520	$4p_y$	-0.28102	$4p_x$
		0.24672	$4p_z$				
	I2 (bridging)	0.25267	$3p_z$	-		-0.21734	$4p_z$
		0.26587	$4p_z$				
	I3 (bridging)	0.25267	$3p_z$	-		0.21734	$4p_z$
		0.26587	$4p_z$				
	I4 (terminal)	0.23990	$3p_z$	-0.29520	$4p_y$	0.28102	$4p_x$
		0.24672	$4p_z$				
(II) $[K(B15C5)_2]_2Cu_2I_4$	Atom	HOMO 26	A_u	LUMO+2 29	A_g	LUMO+4 31	A_g
	Cu1	-0.13630	5D0	-0.13658	$3p_y$	-0.23801	$3p_x$
		-0.18438	5D+1	1.48678	$4p_y$	1.63364	$4p_x$
						-0.12062	$4p_z$

TABLE 5 (Continued)

	Cu2	0.13630	5D0	-0.13658	$3p_y$	0.23801	$3p_x$
		0.18438	5D+1	1.48678	$4p_y$	-1.63364	$4p_x$
						0.12062	$4p_z$
	I1 (terminal)	0.15516	$3p_x$	-0.28734	$4p_y$	-0.27635	$4p_x$
		-0.17569	$3p_z$				
		0.17680	$4p_x$				
		-0.17837	$4p_z$				
	I2 (bridging)	0.20836	$3p_x$	-		-0.20161	$4p_z$
		-0.17262	$3p_z$				
		0.21235	$4p_x$				
		-0.17671	$4p_z$				
	I3 (bridging)	0.20836	$3p_x$	-		0.20161	$4p_z$
		-0.17262	$3p_z$				
		0.21235	$4p_x$				
		-0.17671	$4p_z$				
	I4 (terminal)	0.15516	$3p_x$	0.28734	$4p_y$	0.27635	$4p_x$
		-0.17569	$3p_z$				
		0.17680	$4p_x$				
		-0.17837	$4p_z$				
(III) $[Rb(B15C5)_2]_2Cu_2I_4$	Atom	HOMO 26 A_u		LUMO+2 29 A_g		LUMO+4 31 A_g	
	Cu1	0.11785	5D0	-0.13362	$3p_y$	0.12037	2s
		-0.19162	5D+1	1.45309	$4p_y$	-0.23584	$3p_x$
						1.58763	$4p_x$
						0.20929	$4p_z$
	Cu2	-0.11785	5D0	0.13362	$3p_y$	0.12037	2s
		0.19162	5D+1	-1.45309	$4p_y$	0.23584	$3p_x$
						-1.58763	$4p_x$
						-0.20929	$4p_z$

TABLE 5 (Continued)

	I1 (terminal)	0.15516	$3p_x$	-0.28298	$4p_y$	-0.26868	$4p_x$
		-0.17569	$3p_z$				
		0.17680	$4p_x$				
		-0.17837	$4p_z$				
	I2 (bridging)	0.20836	$3p_x$	-		-0.20260	$4p_z$
		-0.17262	$3p_z$				
		0.21235	$4p_x$				
		-0.17671	$4p_z$				
	I3 (bridging)	0.20836	$3p_x$	-		0.20260	$4p_z$
		-0.17262	$3p_z$				
		0.21235	$4p_x$				
		-0.17671	$4p_z$				
	I4 (terminal)	0.15516	$3p_x$	0.28298	$4p_y$	0.26868	$4p_x$
		-0.17569	$3p_z$				
		0.17680	$4p_x$				
		-0.17837	$4p_z$				
(IV) $[Cs(DC18C6)]_2Cu_2I_4$	Atom	HOMO 26 A_u		LUMO+2 29 A_g		LUMO+4 31 A_g	
	Cu1	0.20625	5D0	-0.13906	$3p_y$	-0.24063	$3p_x$
		-0.11332	5D+2	1.59864	$4p_y$	1.77358	$4p_x$
						-0.10359	$4p_z$
	Cu2	-0.20625	5D0	-0.13906	$3p_y$	0.24063	$3p_x$
		0.11332	5D+2	1.59864	$4p_y$	-1.77358	$4p_x$
						0.10359	$4p_z$
	I1 (terminal)	0.24862	$3p_z$	-0.29447	$4p_y$	-0.28460	$4p_x$
		0.25642	$4p_z$				
	I2 (bridging)	0.25952	$3p_z$	-		-0.21971	$4p_z$
		0.27226	$4p_z$				

TABLE 5 (Continued)

	I3 (bridging)	0.25952	$3p_z$	-		0.21972	$4p_z$
		0.27226	$4p_z$				
	I4 (terminal)	0.24862	$3p_z$	0.29447	$4p_y$	0.28460	$4p_x$
		0.25642	$4p_z$				
(VII) $[Ba(B15C5)_2]_3(Cu_2I_4)_3$ **(a)**	Atom	HOMO 26 A_u		LUMO+2 29 A_g		LUMO+4 31 A_g	
	Cu1	0.21173	5D0	-0.14570	$3p_y$	-0.23941	$3p_x$
		-0.11170	5D+2	1.67286	$4p_y$	1.86469	$4p_x$
	Cu2	-0.21173	5D0	0.14570	$3p_y$	0.23941	$3p_x$
		0.11170	5D+2	-1.67286	$4p_y$	-1.86469	$4p_x$
	I1 (terminal)	0.24147	$3p_z$	-0.30107	$4p_y$	-0.29223	$4p_x$
		0.24932	$4p_z$				
	I2 (bridging)	0.26903	$3p_z$	-		-0.23313	$4p_z$
		0.28666	$4p_z$				
	I3 (bridging)	0.26903	$3p_z$	-		0.23313	$4p_z$
		0.28666	$4p_z$				
	I4 (terminal)	0.24147	$3p_z$	0.30107	$4p_y$	0.29223	$4p_x$
		0.24932	$4p_z$				
(VIII) $[Sr(B15C5)_2]_3(Cu_2I_4)_3$ **(a)**	Atom	HOMO 26 A_u		LUMO+2 29 A_g		LUMO+4 31 A_g	
	Cu1	0.21271	5D0	-0.14574	$3p_y$	-0.23901	$3p_x$
		-0.11279	5D+2	1.66907	$4p_y$	1.85742	$4p_x$
	Cu2	-0.21271	5D0	0.14574	$3p_y$	0.23901	$3p_x$
		0.11279	5D+2	-1.66907	$4p_y$	-1.85742	$4p_x$
	I1 (terminal)	0.24195	$3p_z$	-0.30101	$4p_y$	-0.29176	$4p_x$
		0.24974	$4p_z$				
	I2 (bridging)	0.26860	$3p_z$	-		-0.23102	$4p_z$
		0.28611	$4p_z$				

Table 5 (Continued)

	I3 (bridging)	0.26860	$3p_z$	-		0.23102	$4p_z$
		0.28611	$4p_z$				
	I4 (terminal)	0.24195	$3p_z$	-0.30101	$4p_y$	0.29176	$4p_x$
		0.24974	$4p_z$				

Type II: bent

(V) $[Cs_2(B18C6)_3]Cu_2I_4$	Atom	HOMO 26		LUMO 27	
	Cu1	0.21971	5D+2	-1.09920	2s
				-0.15321	$3p_x$
				1.15671	$4p_x$
				-0.16748	$4p_y$
				-0.84169	$4p_z$
	Cu2	-0.22313	5D+2	1.16131	2s
				-0.16688	$3p_x$
				1.04234	$4p_x$
				-0.20219	$4p_y$
				0.14675	$4p_z$
	I1 (terminal)	0.20008	$3p_x$	-0.17675	2s
		-0.07421	$3p_y$	-0.23420	$4p_x$
		0.20576	$4p_x$	0.16205	$4p_z$
		-0.08362	$4p_y$		
	I2 (bridging)	0.20686	$3p_x$	0.11673	$4p_z$
		-0.12038	$3p_y$		
		0.21956	$4p_x$		
		-0.12517	$4p_y$		

TABLE 5 (Continued)

	I3 (bridging)	0.25077	$3p_x$	0.12067	$4p_z$
		-0.12845	$3p_y$		
		0.26476	$4p_x$		
		-0.13226	$4p_y$		
	I4 (terminal)	0.22011	$3p_x$	0.18277	2s
		-0.12680	$3p_y$	-0.21990	$4p_x$
		0.22736	$4p_x$		
		-0.14459	$4p_y$		
(VII) $[Ba(B15C5)_2]_3(Cu_2I_4)_3$ **(b)**	Atom	HOMO 26		LUMO 27	
	Cu1	-0.21849	5D+2	1.24370	2s
				-0.16625	$3p_x$
				1.19907	$4p_x$
				0.55074	$4p_z$
	Cu2	0.23135	5D+2	-1.22521	2s
				-0.15335	$3p_x$
				1.21846	$4p_x$
				-0.77286	$4p_z$
	I1 (terminal)	0.20183	$3p_x$	0.19511	2s
		-0.11890	$3p_z$	-0.24081	$4p_x$
		0.20479	$4p_x$		
		-0.12665	$4p_z$		
	I2 (bridging)	0.28769	$3p_x$	-	$4p_z$
		0.30144	$4p_x$		
	I3 (bridging)	0.23455	$3p_x$	-	$4p_z$
		0.24615	$4p_x$		

TABLE 5 (Continued)

	I4 (terminal)	0.22165	$3p_x$	-0.18358	2s
		0.12791	$3p_z$	-0.24246	$4p_x$
		0.22502	$4p_x$	0.12588	$4p_z$
		0.13537	$4p_z$		
(VIII) $[Sr(B15C5)_2]_3(Cu_2I_4)_3$ **(b)**	Atom	HOMO 26		LUMO 27	
	Cu1	-0.21512	5D+2	1.24158	2s
				-0.16070	$3p_x$
				1.20957	$4p_x$
				0.61455	$4p_z$
	Cu2	0.23070	5D+2	-1.23306	2s
				-0.14837	$3p_x$
				1.205069	$4p_x$
					$4p_z$
	I1 (terminal)	0.18745	$3p_x$	0.18730	2s
		0.37407	$3p_z$	-0.24405	$4p_x$
		0.19830	$4p_x$	-0.08645	$4p_z$
		0.40808	$4p_z$		
	I2 (bridging)	0.27244	$3p_x$	-	$4p_z$
		0.28471	$4p_x$		
	I3 (bridging)	0.24657	$3p_x$	-	$4p_z$
		0.25789	$4p_x$		
	I4 (terminal)	0.12408	$3p_x$	-0.17593	2s
		-0.23304	$3p_z$	-0.24124	$4p_x$
		0.13365	$4p_x$	0.11435	$4p_z$
		-0.24928	$4p_z$		

Type III: mirror + 2-fold axis (2/m)

Table 5 (Continued)

(VI) $[Cs_2(18C6)_3]Cu_2I_4$	Atom	HOMO 26 B_u		LUMO+2 29 B_g		LUMO+4 31 A_g	
	Cu1	-0.24709	5D-2	-0.13424	$3p_z$	-0.24083	$3p_x$
				1.44625	$4p_z$	1.59120	$4p_x$
	Cu2	0.24709	5D-2	0.13424	$3p_z$	0.24083	$3p_x$
				-1.44625	$4p_z$	-1.59120	$4p_x$
	I1 (terminal)	0.19382	$3p_x$	-0.28362	$4p_z$	-0.26922	$4p_x$
		0.22055	$4p_x$				
	I2 (bridging)	0.29968	$3p_x$	-		-0.19153	$4p_y$
		0.30749	$4p_x$				
	I3 (bridging)	0.29968	$3p_x$	-		0.19153	$4p_y$
		0.30749	$4p_x$				
	I4 (terminal)	0.19382	$3p_x$	0.28362	$4p_z$	0.26922	$4p_x$
		0.22055	$4p_x$				

a - centrosymmetric cluster in complexes (**VII**) and (**VIII**)

b - bent fragment in complexes (**VII**) and (**VIII**)

intensive and less energetic band is revealed as a shoulder, causing a small bathochromic shift (~20 nm) of the more energetic band.

Hexaiodotetracuprates(I)

Three of the synthesized copper(I) halide complexes crystallize with the Cu_4I_6 motif, possessing a crystallographic center of symmetry in the center of the disordered cluster. This type of symmetry has been observed in literature for Cu_4I_6 with a number of cations [50-51, 72]. Disorder leads to an apparent cube of copper atoms with an iodide atom centered above each face. Thus, the copper atoms form two tetrahedra each one present 50% of the time. The copper tetrahedron has six edges, each bridged by an iodide atom. Copper is three coordinate with Cu-I average distances 2.561(2) - 2.614(3) Å. Non-bonded copper - copper distances are similar for these three complexes: 2.752(5) - 2.819 (5) Å. These data (Table 6) are consistent with those reported

TABLE 6

STRUCTURAL AND EMISSION DATA FOR $Cu_4I_6^{2-}$ COMPLEXES

Complex	Space group	Distances (Å) and bond angles (°)			λ_{max}, nm
		Cu-I	Cu...Cu	Cu-I-Cu	
(IX) $[Li(H_2O)(B15C5)_2]_2Cu_4I_6$	$P2_1/c$	2.612(3)	2.819(5)	65.6(1)	519
(X) $[Na_2(H_2O)_3(18C6)_2]Cu_4I_6$	$P2_1/c$	2.561(2)	2.752(5)	65.0(1)	525
(XI) $[Cs(B15C5)_2]_2Cu_4I_6$	$P2_1/c$	2.614(3)	2.810(4)	65.5(2)	524

for other known $Cu_4I_6^{2-}$ clusters {cations triphenylmethylphosphonium, $[M(amine)_3]^+$ and $[K(12\text{-crown-}4)_2]^+$ cations [50-51, 72]}.

The three solid materials display intensive yellow emission in the visible at 519-

525 nm when excited in the ultraviolet at 330 nm. This is consistent with the expectation that clusters of similar crystallographic symmetry should display similar emission. Calculation of the contribution of the atomic orbitals to frontier orbitals showed the HOMO level to be dominated by p_y and p_z orbitals associated with four of the iodide atoms whereas the LUMO level is principally copper based (s, p_x, p_y and p_z) and involves all four copper atoms (Table 7). While the disorder results in centrosymmetric species, the emitting tetrahedron Cu_4I_6 is not centrosymmetric and there are no forbidden transitions for this motif.

Polymeric $Cu_pI_q^{-(q-p)}$ complexes

The wide variety of Cu_pI_q motifs seen as polymeric or infinite structures indicates a tendency for the Cu(I) centers to cluster together. Molecular orbital calculations on polynuclear Cu_n^{n+} model species, performed by Hoffmann [103], showed that short Cu...Cu distances (from 2.7 to 2.38 Å), arise as the result of overlap of the empty *4s* and *4p* orbitals with filled *d*-orbitals. With decreasing Cu...Cu distance, the binding energy was observed to be negative which indicates a slight attraction between Cu and Cu in Cu(I) clusters. Cu...Cu separation less than that of the metal bond in copper metal (2.54 Å), by itself is not a sign of M - M bonding, especially, when bridging atoms are present, as they are in all Cu(I) polynuclear strustures. The study of M_2X_6 transition metal systems showed that M...M interaction, depending on the given ligand set, i.e., the identity of the bridging atoms, also displays a weak interaction [104]. In this study short Cu...Cu distances were observed in both discrete and polymeric species. Five of polymeric compounds prepared appeared to have the same stoichiometry, $Cu_2I_3^-$. Each of them may be considered as a chain of Cu_2I_2

TABLE 7

Contribution of atomic orbitals into HOMO and LUMO molecular orbitals in $Cu_4I_6^{2-}$ emitting complex

(X) $[Na_2(H_2O)_3(18\text{-crown-}6)_2]Cu_4I_6$	Atom	HOMO 44		LUMO 45	
	Cu1	0.08190	5D-1	0.53740	2s
				0.51815	$4p_x$
				-0.23459	$4p_y$
				0.87250	$4p_z$
	Cu2	-0.10670	5D+2	0.71106	2s
				-0.50938	$4p_x$
				-0.68062	$4p_y$
				-0.23132	$4p_z$
	Cu3	0.07630	5D-1	0.63856	2s
				0.60140	$4p_x$
				0.19741	$4p_y$
				-0.71123	$4p_z$
	Cu4	-0.06427	5D+2	0.53875	2s
				-0.55960	$4p_x$
				0.83244	$4p_y$
				0.19987	$4p_z$
	I1	0.10115	$3p_y$	-0.08695	2s
		0.26948	$3p_z$		
		0.11069	$4p_y$		
		0.27808	$4p_z$		
	I2	0.19245	$3p_y$	-0.09429	2s
		-0.09947	$3p_z$		
		0.20203	$4p_y$		
		-0.10522	$4p_z$		
	I3	-		0.09262	2s
	I4	-0.13688	$3p_y$	-0.09050	2s
		-0.19950	$3p_z$		
		-0.14108	$4p_y$		
		-0.21182	$4p_z$		
	I5	-0.25239	$3p_y$	-0.08180	2s
		0.17475	$3p_z$		
		-0.26476	$4p_y$		
		0.17929	$4p_z$		
	I6	-		-0.09770	2s

rhombs, sharing opposite edges with an additional bridging iodide on every other rhomb. The first three complexes are isostructural (**XII-XIV**) and display *up, up, down, down* projections of the bridging iodides relative to the polymeric chain, while the other two contain alternating *up, down, up, down* directed iodides (**XV-XVI**). Structural data for these complexes are given in Table 8. Compound (**XVII**) has anionic centrosymmetric cluster $Cu_6I_{10}^{-4}$, which contains a pair of $Cu_2I_3^-$ monomers of **up, down, up, down** type, the ends of them being completed by CuI_2^- fragments.

TABLE 8

STRUCTURAL DATA FOR POLYNUCLEAR $Cu_pI_q^{-(q-p)}$ COMPLEXES

Complex		Space group	Average distances, Å			
			Cu-I bridged	Cu-I non-bridged	Cu…Cu bridged	Cu...Cu non-bridged
	up, up, down, down					
(XII)	$[K(15C5)]Cu_2I_3$	C2/c	2.624(4)	2.689(4)	2.448(7)	2.668(5)
(XIII)	$[Rb(15C5)]Cu_2I_3$	C2/c	2.641(4)	2.725(5)	2.480(7)	2.667(6)
(XIV)	$[Cs(15C5)]Cu_2I_3$	C2/c	2.598(5)	2.703(6)	2.430(9)	2.634(9)
	up, down, up, down					
(XV)	$[C_8H_{20}N]Cu_2I_3$	$Pna2_1$	2.592(4)	2.686(4)	2.470(5)	2.639(5)
(XVI)	$[K(18C6)]Cu_2I_3$	$P2_1/c$	2.649(3)	2.711(3)	2.467(3)	2.661(4)
Moiety of **up, down, up, down**						
(XVII)	$[Cs_4(B18C6)_5]$ $[CuI_2(Cu_2I_3)_2CuI_2]$ *)	P1bar	2.625(3)	2.689(4)	2.448(5)	2.786(7)

*) – discrete $Cu_6I_{10}^{-4}$ species, containing **up, down** fragment

All of these compounds show close Cu…Cu contacts across bridged rhombs (2.430(9) - 2.480(7) Å) and greater separations in the non-bridged rhombs (2.634(9) -

2.668(5) Å). These values are in agreement with the distances reported for the *up, up, up, up* variant (Fig.1), realized in [2,4,6-triphenylthiopyrylium]Cu_2I_3 [65]: 2.479 and 2.634 Å respectively. The Cu-I distances, involving the bridging iodides, are in the range 2.592(4) –2.641(4) Å in all five complexes, similar to those of 2.642-2.651 Å for the *all-up* variant. Cu-I distances along the edges of the polymeric sheet as expected, are shorter for the edges of unbridged rhombohedra. The obtained values are very close to the results published by Batsanov [65]. Thus, it can be concluded that the crystallographic parameters are similar and independent of the tertiary structure of the polymer. None of the polymeric species is emitting at both ambient and at low temperature. Our results show that the determining factor in formation of a particular type of a tertiary structure is the nature of a cation and presence (or absence) of interactions between cation and copper-iodide chain. The first three complexes, formed by 15-crown-5, have *umbrella-type* interaction with the alkali metal displaced from crown ether plane. Thus the alkali metal is easily accessible to ionic interaction with three iodides (two of them bridging) of the polymeric chain, so the result of it – *up, up, down, down* structure. Potassium in [K(18-crown-6)] is completely in the plane and therefore less accessible to multiple metal - iodide interactions. As the result, K is involved with only one iodide producing a tertiary *up, down, up, down* structure. Cation $[(C_2H_5)_4N]$ in complex (**XVI**), possessing a well screened charge, is symmetric and small in size so that it is accomodated in the holes between two bridging iodides, leading to an *up, down up, down* pattern. When the cation is very large and no interaction with the chain is possible, as seen in the case of triphenylthiopyrillium [65], the tertiary structure becomes *up, up, up, up*.

Polymeric $Cu_4I_6^{-2}$ and $Cu_5I_7^{-2}$ species

Among the other polymeric complexes synthesized in this work are several compounds having 5 and 6-membered rings consisting of alternating Cu-I bonds (Table 9). The centrosymmetric $Cu_4I_6^{-2}$ chain ((**XVIII**)) contains a 6 membered ring, in which one of the iodides is located out of the plane of the other 5 atoms. This iodide, in addition, may be viewed as a vertex of two Cu_2I_2 rhombs, sharing one edge. These six-membered rings are connected with each other by bridging iodides. One of the copper atoms is disordered (50% occupancy), however the motif is the same with each possible position.

TABLE 9

STRUCTURAL DATA FOR POLYMERIC $Cu_4I_6^{-2}$ AND $Cu_5I_7^{-2}$ COMPLEXES

Complex	Space group	Average distances, Å			
		Cu-I bridged	Cu-I Ring	Cu-I rhombo-hedra	Cu...Cu
(XVIII) $[Sr(15C5)_2]Cu_4I_6$	Pnma	2.610(4)	2.638(5)	2.781(5)	2.603(6)
(XIX) $[Ca(18C6)]Cu_5I_7.3H_2O$	Pbcm	2.574(3)		2.660(4)	2.838(7) 2.415(9)*)
(XX) $[Zn(18C6)]Cu_5I_7.3H_2O$	Pbcm	2.622(4)		2.699(7)	2.921(10) 2.474(9)*)
(XXI) $[Sr(18C6)]Cu_5I_7.3H_2O$	Pbcm	2.598(5)		2.689(6)	2.895(13) 2.476(9)*)

*) – these distances involve disordered copper atoms

The anionic part of three isostructural $[M(18\text{-crown-6}).3H_2O]Cu_5I_7$ complexes (**XIX-XXI**) contains a 5-membered ring, in which two copper atoms (Cu...Cu distance is 3.103 Å) are bridged by two iodides. These iodides form further Cu_2I_2 rhombs in a complex manner, forming an infinite *snake-like* chain, the number of rhombs depending on the position of two copper atoms, which are disordered. The coordination number of

copper in all four polymeric chains is 3 or 4. The distances, involving disordered copper atoms are extremely short: 2.415(9) - 2.476(11) Å.

None of the polymeric species emits at either ambient or low temperature. Crystal structures of these compounds show short Cu...Cu distances. Thus, the copper – copper interaction is presumed to produce an influence in one of two possible ways: 1) raises the energy level of LUMO or changes orbital contribution to HOMO and/or LUMO such that emission not seen in visible; 2) increases the energy level of HOMO so that energy of ultraviolet radiation is not large enough to produce the necessary excitation.

Simple iodides

Some of the attempts to synthesize copper(I) iodide complexes with metal complexed crown ethers lead to simple iodide, usually crystallized after the species of interest had been isolated and the remaining mother solution was allowed to concentrate. The copper(I) concentration in this solution becomes much less than the concentration of crown ether and iodide, favoring the formation of a simple iodide. $[Cs_2(Benzo\text{-}18\text{-}crown\text{-}6)_3]I_2.3H_2O$ (**XXIII**) and [K(Benzo-18-crown-6)]I (**XXIV**) were characterized by single crystal X-ray analysis (Fig.46, 47). Two iodide atoms in the first structure are connected by hydrogen bonds with one water molecule, lying inbetween them, and each of iodides in addition is coordinated to one more water molecule, giving a trihydrate. The second iodide contains two parallel $[K(18\text{-}crown\text{-}6)]^+$ rings, shifted relative to each other thus giving the K ion the possibility to interact with an oxygen atom of the other ring with K...O distances 3.107(4) Å, longer than K...O distances within the same crown ether ring (2.838(3) Å.

It was observed that after 2-3 months of standing in a covered beaker a reaction mixture in many cases formed red –brown fragile irregular needles. One of those species was isolated and characterized: it is $[K(Benzo\text{-}15\text{-}crown\text{-}5)_2]I_3$ (**XXII**), which formed as the result of an oxidation process: $3I^- - 2e \rightarrow I_3^-$. The linear I_3^- fragment has almost equal I.-I distances of 2.949(1) and 2.956(1) Å, which are in agreement with those reported in the literature for $[Cs(18\text{-}crown\text{-}6)]I_3$, $[K(18\text{-}crown\text{-}6)]I_3$ and [K(benzo-18-crown-6)]I_3 [105-107]: 2.945(1)-2.879(1); 2.916(1)-2.926(1) and 2.874(1)-2.984(1) Å respectively. These three iodides are seen with alkali metal (Cs and K) complexed by an 18C6 ring which interacts with the terminal iodide of the I_3^- chain. The complex synthesized contains sandwich-like $[K(benzo\text{-}15\text{-}crown\text{-}5)_2]^+$ complex with no K...I interaction.

Metal complexed crown ethers as cations of Cu – I complexes

In this study we used *host – guest* type complexes as cations, formed by alkali and alkaline earth metals (or zinc) with crown ethers. As both are hard acid and hard base species, they produce stable chelates involving electrostatic interactions and conformation changes of the crown ether [108]. Analysis of the data obtained for metal – crown ether cations shows a variety of stoichiometry and coordination numbers, depending on the nature of crown ether *(host)* and the bound metal *(guest)*. The crown ethers used in this study can be divided into two groups based on the size of cavity: 15C5 type with 5 oxygen donor atoms in the ring (15-crown-5, benzo-15-crown-5) and 18C6 type with 6 oxygen atoms (18-crown-6, benzo-18-crown-6 and dicyclohexano-18-crown-6). Table 10 shows the average distances M...O and M...I (for the cases where additional coordination of M to iodide is observed) for the complexes studied. It is well

TABLE 10

STRUCTURAL PARAMETERS OF

METAL COMPLEXED CROWN ETHER CATIONS

M	Ionic radius, Å [100]	Crown ether type		M: crown ratio	Coord. number	M ...O, Å	M ...I, Å	Compound
		15C5	18C6					
Li	0.76	B15C5		1:2 flat	6	2.31(2) 1.94(2)*)		**IX**
Na	1.02		B18C6	1:1 flat	8	2.747(10) 2.300(6)*)		**X**
K	1.38	15C5		1:1 umbrella	8	2.764(7)	3.624(4)	**XII**
		B15C5		1:2 sandwich	10	2.908(12)		**II**
		B15C5		1:2 sandwich	10	2.983(7)		**XXII**
			18C6	1:1 flat	7	2.80(3)	3.414(3)	**XVI**
			B18C6	1:1 flat	8	2.838(3) 3.107(4)	3.589(2)	**XXIV**
Rb	1.52	15C5		1:1 umbrella	8	2.92(2)	3.725(3)	**XIII**
		B15C5		1:2 sandwich	10	3.023		**III**
Cs	1.67	15C5		1:1 umbrella	8	3.085(9)	3.809(6)	
		B15C5		1:2 sandwich	10	3.229(9)		**XI**
			18C6	2:3 club-sandwich		3.407(9)		**VI**
			B18C6	2:3 club-sandwich		3.33(2)		**V**
			B18C6	2:3 club-sandwich		3.311(13)		**XVII**
				1:1 umbrella	9	3.155(14)		
			B18C6	2:3 club-sandwich		3.35(2)		**XXIII**
			DC18C6	1:1 (?) umbrella	7	3.148(7)	3.861(6)	**IV**
Ca	1.00		18C6	1:1 flat	9	2.614(12) 2.413(14)*)		**XIX**

TABLE 10 (Continued)

Sr	1.18	B15C5		1:2 sandwich	10	2.71(2)	**VIII**
			18C6	1:1 flat	9	2.73(2)	**XXI**
Ba	1.35	15C5		1:2 sandwich	10	2.859(10) 2.58(2)*)	**I**
		B15C5		1:2 sandwich		2.82(2)	**VII**
Zn	0.74		18C6	1:1 flat	6	2.67(2) 2.44(2)*)	**XX**

*) – Me...O (water) distance

known that the stability of crown ether complexes with metals is determined by the size of a cavity: the lower the difference between the size of a cavity and ionic radius of a metal, the more stable the complexes produced [109]. It should be mentioned, however, that ability to crystallize in a solid phase is not directly connected with stability. Among other factors, which determine the type of species, isolated in the solid phase, are the solubility of the compound in the particular solvent and the nature of the anionic moiety. The latter factor influences in two ways. First, the charge of the anionic $Cu_pI_q^{-(q-p)}$ cluster should be low, so that (q-p) may be either 1 or 2. The second factor is the possibility of additional coordination of the metal complexed by crown ether to bridging iodides of the Cu_pI_q fragment. This was observed in several complexes of alkali metals, which try to achieve high coordination numbers (7-9). As a result, in addition to crown ether's oxygen atoms, occupying 5 or 6 places in the inner coordination sphere, there are 1 to 3 iodide – metal interactions (**XII**, **XIII**, **XIV**, **XVI** and **V**).

All metal - crown ether complexes synthesized display different stoichiometry, normally 1:1 for alkali metals and 1:2 for divalent alkaline earth metals. In addition, 2:3 stoichiometry was observed for cesium chelates with 18-crown-6 and benzo-18-crown-

6 (**VI**, **V** and **XVII**). Complexes of this stoichiometry (*club-sandwich* type) were prepared by Pedersen [110], but not characterized by X-ray structural analysis. The $[Cs_2(18C6)_3]^+$ species has 3 crown ether rings stacked one above the other and each separated from the next by a cesium atom (Fig.20, 22, 39). The stoichiometry 1:1 was seen in two patterns: *flat*, with the metal ion lying in the plane of the ring and *umbrella-type*, in which the metal atom is seen above the plane of the ring because the ligand cavity is too small to accommodate the cation. Flat complexes were observed for potassium, complexed by 18-crown-6 (**XVI**) and benzo-18-crown-6 (**XXIV**) with M...O interactions of 2.80(3) - 2.838(3) Å. This was expected, because the stability of alkali metals with 6-membered ring crown ethers increases in order Li < Na < Cs < Rb < K [111] with potassium ion, displaying only a minimal difference between cavity size (1.34-1.43 Å) and ionic radius (1.38 Å). The complexation of Na with 18-crown-6 is less expected: its ionic radius is too small (1.02 Å) to be fully involved with all 6 oxygen atoms of benzo-18-crown-6 ring and therefore sodium usually does not produce stable complexes with 18C6 compounds. However in this structure (**X**) water molecules coordinate to sodium from both axial positions and fixing its position, enhance the stability of this complex.

Alkaline earth metals (strontium, barium) with ionic radii of 1.18 Å and 1.35 Å, less than the size of 15C5 cavity, form complexes of 1:2 stoichiometry with these crown ethers (**I, VII, VIII**). However, in compounds (**XIX**, **XX**, **XXI**) 18-crown-6 was seen to accommodate three divalent cations of different radius: calcium, strontium and zinc (1.00, 1.18 and 0.74 Å respectively) due to additional coordination of three water molecules from opposite sides of a ring. The corresponding complexes of these

metals $[M(18\text{-crown-6}).3H_2O]Cu_5I_7$ appeared to be isostructural.

An example of an interesting type of complexation behaviour, is provided by $[Li(H_2O)(\text{benzo-15-crown-5})_2]_2Cu_4I_6$ (**IX**). The X-ray crystallographic structure of this compound shows that metal is in the macrocycle cavity, but half of the cavities are empty, since one crown ether has no lithium guest. Lithium, lying in the plane of a ring, is coordinated to water molecules, and these water molecules are connected to the second crown ether by hydrogen bonds. Thus, the complex is 1:1, while the solid state stoichiometry is 1:2.

Among alkali and alkaline earth metals the most productive metal appeared to be Cs, giving 7 different complexes with both 15C5 and 18C6 crown ethers. Cesium atom, having a large ionic radius, is not seen lying in the plane of the ring for any of these complexes. The distances Cs...O varied widely, depending on the type of crown ether, stoichiometry and overall motif. In *umbrella-type* compounds (1:1) metal-oxygen distances are shorter (3.085(9) - 3.155(14) Å), than in *sandwich type* compounds (3.229 (9) Å). Minimal Cs...O interactions are observed in 2:3 *club sandwich* complexes, because one of the crown ether rings is coordinated to two cesium atoms (3.311(13)-3.407(9) Å).

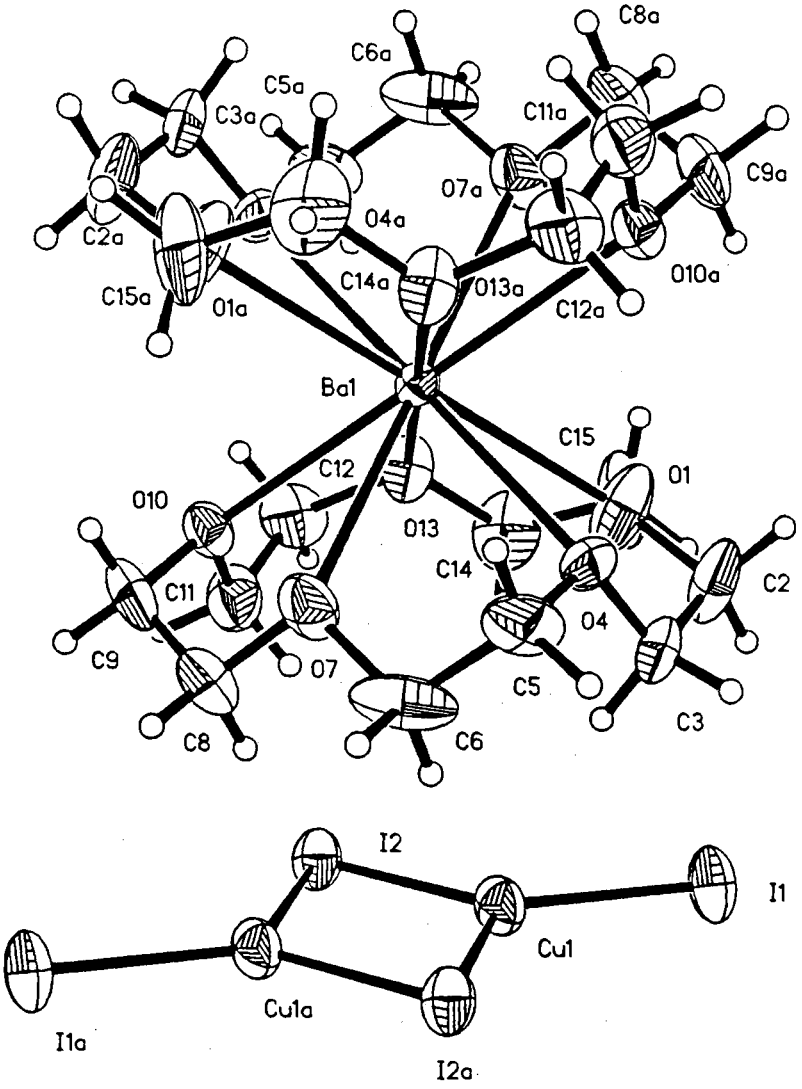


Figure 11. Projection View of $[Ba(15\text{-Crown-}5)_2]Cu_2I_4$ (I)

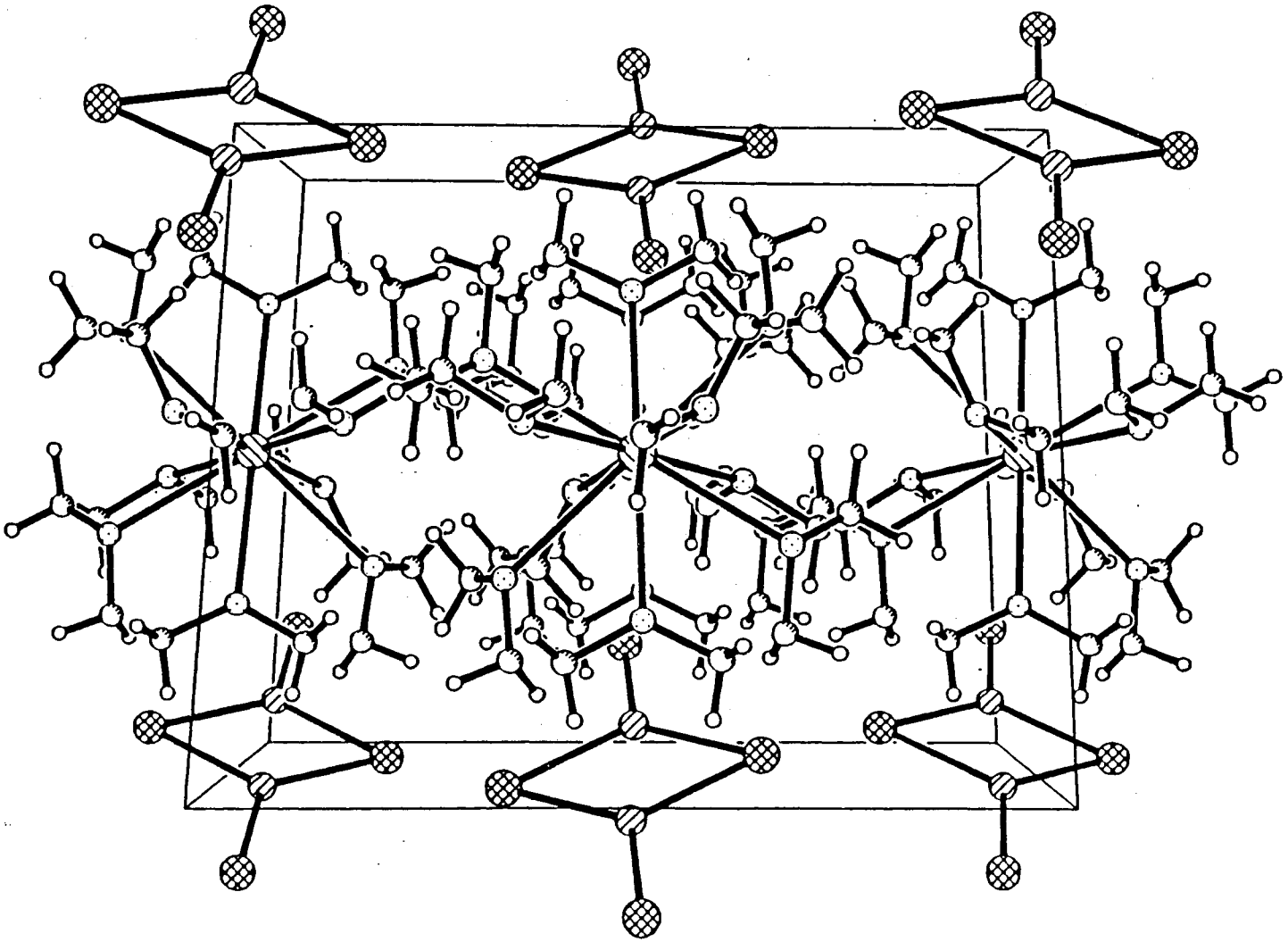


Figure 12. Packing Diagram for of $[Ba(15\text{-Crown-}5)_2]Cu_2I_4$ (**I**)

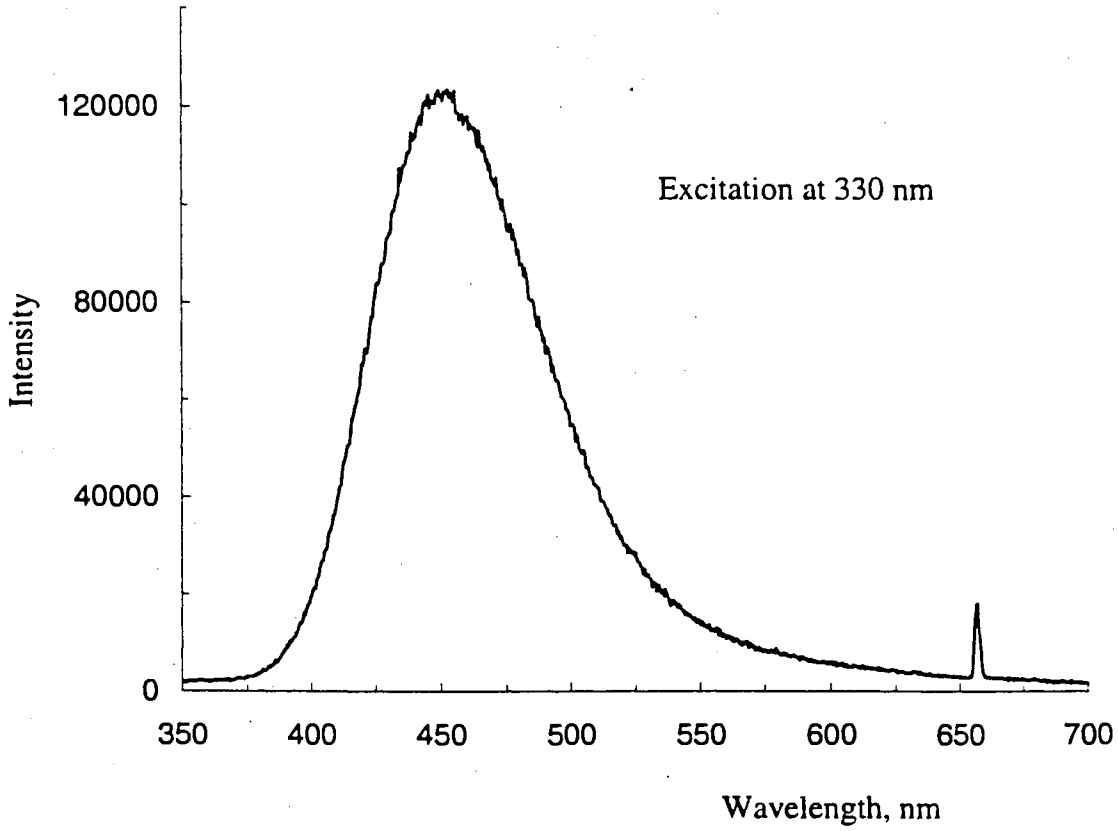


Figure 13. Emission spectrum of $[Ba(15\text{-Crown-}5)_2]Cu_2I_4$ (**I**)

TABLE 11

CRYSTAL DATA FOR

$[Ba(15\text{-Crown-}5)_2]Cu_2I_4$ (**I**)

Formula	$C_{20}H_{40}BaCu_2I_4O_{10}$
Space group	$P2_1/c$
A	12.012(3) Å
B	13.400(3) Å
C	12.305(3) Å
β	117.150(10)°
V	1761.8(7) $Å^3$
Z	2
Mw	1212.5 g $mole^{-1}$
Density (calc.)	2.286 Mg m^{-3}
$\mu(MoK_\alpha)$	5.847 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	1132
Collected Reflections	5013
Independent Reflections	4050
Observed Reflections ($F > 4.0\sigma$)	2065
Number of parameters	170
Final R indices	R=5.42%, R_w=6.21%
R indices (all data)	R=9.99%, R_w= 7.33%
GOF	1.06

TABLE 12

POSITIONAL PARAMETERS FOR

$[Ba(15\text{-Crown-}5)_2]Cu_2I_4$ (**I**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
Ba(1)	0.5	0.5	0.0
I(1)	1.1851(1)	0.5132(1)	0.3099(1)
I(2)	1.0270(1)	0.3395(1)	0.5249(1)
Cu(1)	1.0641(2)	0.4990(2)	0.4289(2)
O(1)	0.7397(10)	0.5092(8)	0.0106(14)
C(2)	0.796(2)	0.6009(11)	0.013(2)
H(2A)	0.7719	0.6232	-0.0693
H(2B)	0.8854	0.5922	0.0523
C(3)	0.7618(14)	0.6759(15)	0.079(2)
H(3A)	0.8029	0.6615	0.1649
H(3B)	0.7906	0.7398	0.0669
O(4)	0.6314(9)	0.6827(7)	0.0367(8)
C(5)	0.587(2)	0.7553(11)	0.0956(14)
H(5A)	0.4985	0.7643	0.0457
H(5B)	0.6272	0.8182	0.1006
C(6)	0.611(2)	0.7225(12)	0.215(2)
H(6A)	0.6991	0.7135	0.2659
H(6B)	0.5807	0.7718	0.2512
O(7)	0.5422(10)	0.6303(7)	0.2016(9)
C(8)	0.579(2)	0.5898(12)	0.3190(14)
H(8A)	0.5513	0.6333	0.3642
H(8B	0.6679	0.5836	0.3630
C(9)	0.523(2)	0.4921(13)	0.307(2)
H(9A)	0.5456	0.4637	0.3861
H(9B)	0.4338	0.4996	0.2658
O(10)	0.5593(9)	0.4237(7)	0.2377(8)
C(11)	0.6746(14)	0.3783(13)	0.3014(15)
H(11A)	0.6803	0.3485	0.3747
H(11B)	0.7403	0.4267	0.3234
C(12)	0.6888(15)	0.3006(11)	0.2201(15)
H(12A)	0.6219	0.2532	0.1976
H(12B)	0.7667	0.2656	0.2626
O(13)	0.6845(8)	0.3445(7)	0.1107(9)
C(14)	0.8059(14)	0.3548(14)	0.117(2)
H(14A)	0.8388	0.2900	0.1149
H(14C)	0.8612	0.3858	0.1934

TABLE 12 (Continued)

C(15)	0.803(2)	0.4199(14)	0.022(2)
H(15C)	0.8859	0.4331	0.0337
H(15A)	0.7590	0.3837	-0.0529

TABLE 13

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[Ba(15\text{-Crown-}5)_2]Cu_2I_4$ (**I**)

Ba(1)-O(1)	2.825 (14)	O(1)-C(2)	1.40 (2)
Ba(1)-O(4)	2.835 (10)	O(1)-C(15)	1.39 (2)
Ba(1)-O(7)	2.883 (11)	C(2)-C(3)	1.47 (3)
Ba(1)-O(10)	2.864 (10)	C(3)-O(4)	1.41 (2)
Ba(1)-O(13)	2.890 (9)	O(4)-C(5)	1.45 (2)
Ba(1)-O(1^i)	2.825 (14)	C(5)-C(6)	1.43 (3)
Ba(1)-O(4^i)	2.835 (10)	C(6)-O(7)	1.46 (2)
Ba(1)-O(7^i)	2.883 (11)	O(7)-C(8)	1.41 (2)
Ba(1)-O(10^i)	2.864 (10)	C(8)-C(9)	1.45 (2)
Ba(1)-O(13^i)	2.890 (9)	C(9)-O(10)	1.45 (2)
I(2)-Cu(1)	2.578 (2)	O(10)-C(11)	1.38 (2)
I(2)-Cu(1^{ii})	2.603 (2)	C(11)-C(12)	1.51 (3)
I(1)-Cu(1)	2.497 (3)	C(12)-O(13)	1.45 (2)
Cu(1)-I(2^{ii})	2.603 (2)	O(13)-C(14)	1.43 (2)
Cu(1)-Cu(1^{ii})	2.810 (5)	C(14)-C(15)	1.45 (3)
O(1)-Ba(1)-O(4)	58.2(3)	O(13)-Ba(1)-O(10^i)	121.2(3)
O(1)-Ba(1)-O(7)	99.1(4)	O(1')-Ba(1)-O(10^i)	101.3(4)
O(4)-Ba(1)-O(7)	58.2(3)	O(4')-Ba(1)-O(10^i)	106.5(3)
O(1)-Ba(1)-O(10)	101.3(4)	O(7')-Ba(1)-O(10^i)	58.2(3)
O(4)-Ba(1)-O(10)	106.5(3)	O(1)-Ba(1)-O(13^i)	122.5(3)
O(7)-Ba(1)-O(10)	58.2(3)	O(4)-Ba(1)-O(13^i)	72.8(3)
O(1)-Ba(1)-O(13)	57.5(3)	O(7)-Ba(1)-O(13^i)	76.4(3)
O(4)-Ba(1)-O(13)	107.2(3)	O(10)-Ba(1)-O(13^i)	121.2(3)
O(7)-Ba(1)-O(13)	103.6(3)	O(13)-Ba(1)-O(13^i)	180.0(1)
O(10)-Ba(1)-O(13)	58.8(3)	O(1')-Ba(1)-O(13^i)	57.5(3)
O(1)-Ba(1)-O(1^i)	180.0(1)	O(4')-Ba(1)-O(13^i)	107.2(3)
O(4)-Ba(1)-O(1^i)	121.8(3)	O(7')-Ba(1)-O(13^i)	103.6(3)
O(7)-Ba(1)-O(1^i)	80.9(4)	O(10')-Ba(1)-O(13^i)	58.8(3)
O(10)-Ba(1)-O(1^i)	78.7(4)	Cu(1)-I(2)-Cu(1^{ii})	65.7(1)
O(13)-Ba(1)-O(1^i)	122.5(3)	I(2)-Cu(1)-I(1)	126.9(1)
O(1)-Ba(1)-O(4^i)	121.8(3)	I(2)-Cu(1)-I(2^{ii})	114.3(1)
O(4)-Ba(1)-O(4^i)	180.0(1)	I(1)-Cu(1)-I(2^{ii})	118.7(1)
O(7)-Ba(1)-O(4^i)	121.8(3)	C(2)-O(1)-C(15)	121.2(15)
O(10)-Ba(1)-O(4^i)	73.5(3)	O(1)-C(2)-C(3)	111(2)
O(13)-Ba(1)-O(4^i)	72.8(3)	C(2)-C(3)-O(4)	112.8(13)
O(1')-Ba(1)-O(4^i)	58.2(3)	C(3)-O(4)-C(5)	117.4(12)
O(1)-Ba(1)-O(7^i)	80.9(4)	O(4)-C(5)-C(6)	110.9(12)
O(4)-Ba(1)-O(7^i)	121.8(3)	C(5)-C(6)-O(7)	107.9(12)

TABLE 13 (Continued)

O(7)-Ba(1)-O(7^{i})	180.0(1)	C(6)-O(7)-C(8)	108.5(11)
O(10)-Ba(1)-O(7^{i})	121.8(3)	O(7)-C(8)-C(9)	109.3(12)
O(13)-Ba(1)-O(7^{i})	76.4(3)	C(8)-C(9)-O(10)	112(2)
O(1')-Ba(1)-O(7^{i})	99.1(4)	C(9)-O(10)-C(11)	115.8(11)
O(4')-Ba(1)-O(7^{i})	58.2(3)	O(10)-C(11)-C(12)	108.3(11)
O(1)-Ba(1)-O(10^{i})	78.7(4)	C(12)-O(13)-C(14)	112.5(11)
O(4)-Ba(1)-O(10^{i})	73.5(3)	O(13)-C(14)-C(15)	111.2(13)
O(7)-Ba(1)-O(10^{i})	121.8(3)	O(1)-C(15)-C(14)	114(2)
O(10)-Ba(1)-O(10^{i})	180.0(1)		

Symmetry operations:

^{i} = 1-x, 1-y, -z

^{ii} = 2-x, 1-y, 1-z

TABLE 14

ANISOTROPIC THERMAL PARAMETERS FOR

$[Ba(15\text{-Crown-}5)_2]Cu_2I_4$ (**I**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	33(1)	37(1)	43(1)	-2(1)	18(1)	-3(1)
I(2)	54(1)	75(1)	82(1)	13(1)	40(1)	9(1)
I(1)	94(1)	92(1)	101(1)	19(1)	73(1)	18(1)
Cu(1)	56(1)	94(1)	67(1)	4(1)	35(1)	0(1)
O(1)	58(6)	80(7)	165(12)	17(6)	65(7)	42(8)
C(2)	111(14)	75(11)	140(17)	-24(10)	98(14)	-7(12)
C(3)	85(11)	138(17)	98(13)	-60(12)	60(11)	-13(13)
O(4)	72(6)	70(7)	70(6)	-32(5)	36(5)	-20(5)
C(5)	113(13)	47(9)	75(11)	-7(9)	35(10)	-24(9)
C(6)	93(12)	68(11)	89(13)	23(10)	5(10)	-51(10)
O(7)	103(8)	62(6)	70(7)	-5(6)	55(6)	-15(6)
C(8)	96(12)	94(13)	55(10)	2(11)	43(9)	-12(10)
C(9)	119(15)	135(18)	64(10)	-10(13)	67(11)	-11(12)
O(10)	73(6)	53(5)	52(5)	-1(5)	31(5)	4(5)
C(11)	63(9)	105(13)	77(11)	13(9)	35(9)	21(10)
C(12)	87(11)	58(10)	81(11)	17(9)	22(9)	35(9)
O(13)	64(5)	63(6)	93(7)	17(5)	46(5)	25(6)
C(14)	62(9)	102(14)	129(15)	42(10)	50(10)	35(13)
C(15)	114(14)	118(15)	135(16)	52(13)	104(14)	35(14)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

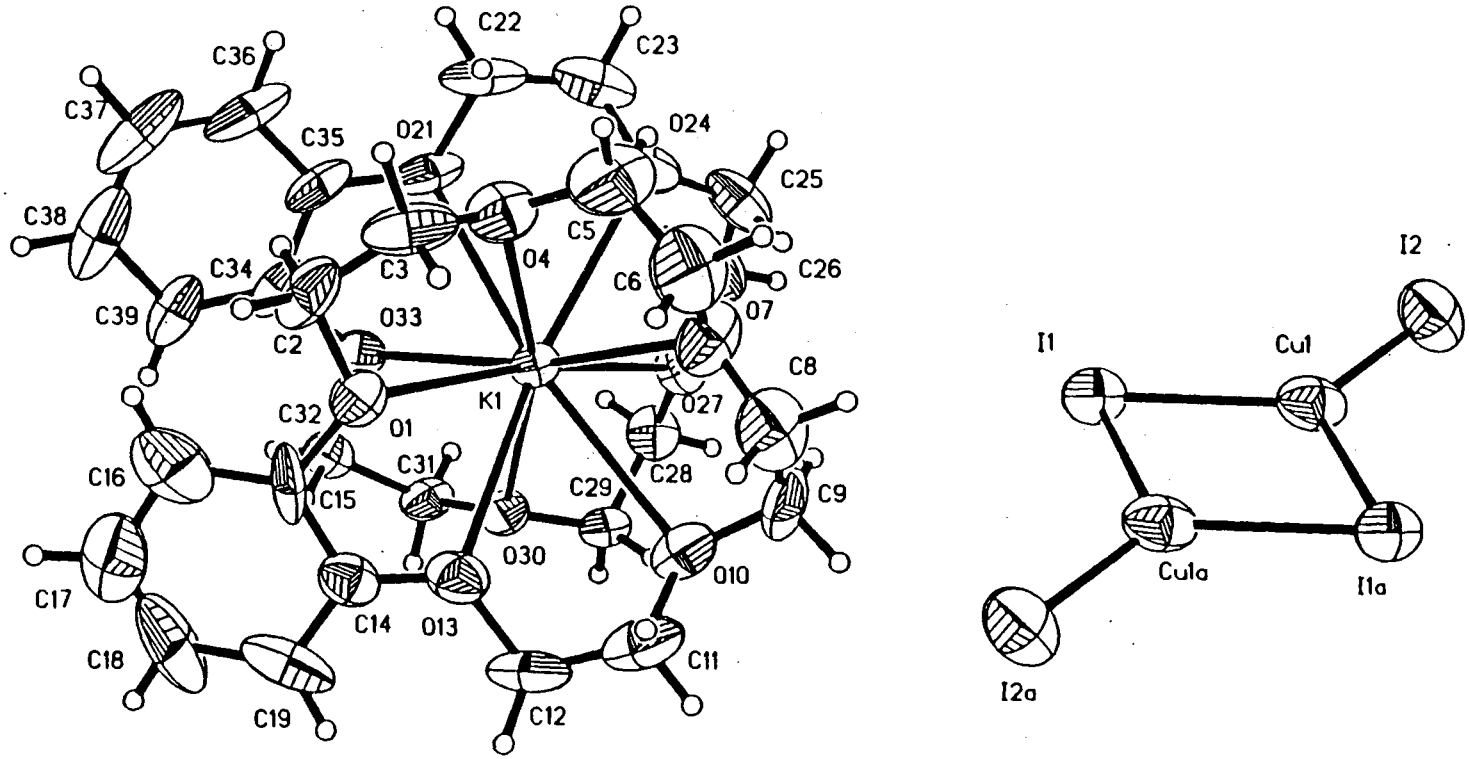


Figure 14. Projection View of $[K(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_4$ **(II)**

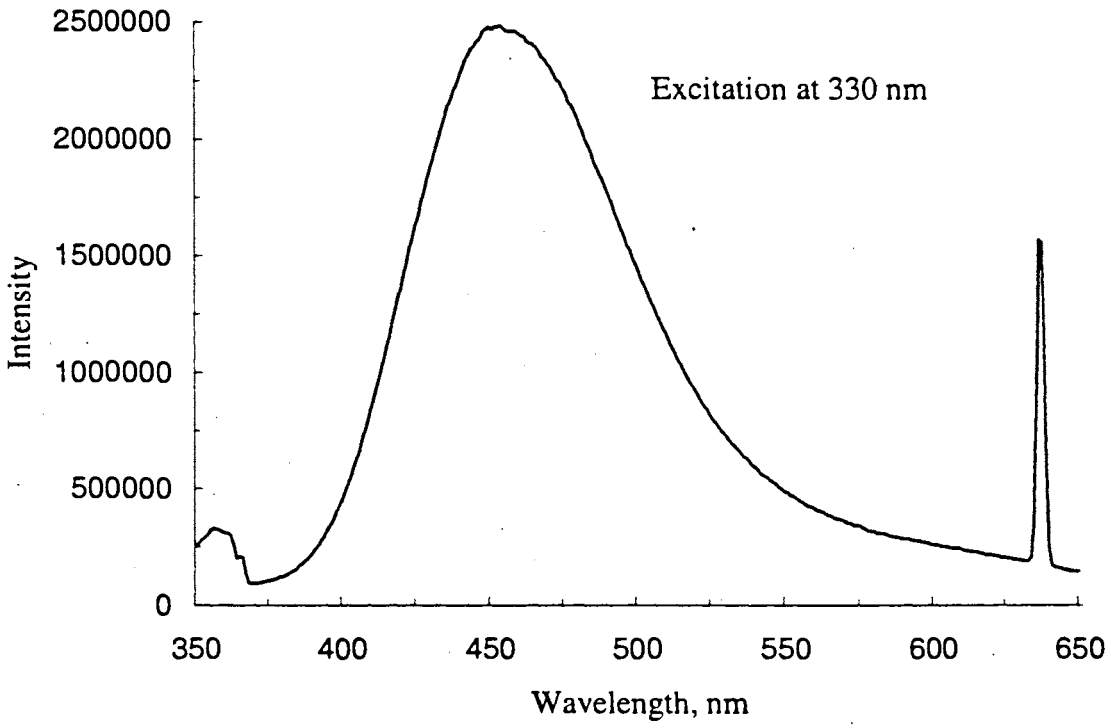


Figure 15. Emission spectrum of $[K(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_4$ (**II**)

TABLE 15

CRYSTAL DATA FOR

$[K(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_4$ (**II**)

Formula	$C_{56}H_{80}Cu_2I_4K_2O_{20}$
Space group	P1bar
A	12.47(3) Å
B	12.66(3) Å
C	12.70(3) Å
α	105.0(2)°
β	93.8(2)°
γ	112.5(2)°
V	1750(7) $Å^3$
Z	1
Mw	1786.1 g $mole^{-1}$
Density (calc.)	1.695 Mg m^{-3}
$\mu(MoK_\alpha)$	2.556 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	884
Collected Reflections	11447
Independent Reflections	10152
Observed Reflections ($F > 5.0\sigma$)	2678
Number of parameters	380
Final R indices	R=6.57 %, R_w=7.21 %
R indices (all data)	R=22.19 %, R_w= 12.82 %
GOF	1.45

TABLE 16

POSITIONAL PARAMETERS FOR

$[K(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_4$ (**II**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.1015(1)	0.0338(1)	0.8168(1)
I(2)	0.1052(1)	0.1806(1)	0.5262(1)
Cu(1)	0.0401(2)	0.0154(2)	0.6207(2)
K(1)	0.2803(2)	0.6296(2)	0.2894(2)
O(1)	0.1451(9)	0.6298(9)	0.0928(8)
C(2)	0.079(2)	0.7006(14)	0.1150(14)
H(2A)	0.0398	0.7004	0.0474
H(2B)	0.1291	0.7822	0.1576
C(3)	-0.0040(13)	0.6438(15)	0.183(2)
H(3A)	-0.0540	0.5629	0.1391
H(3B)	-0.0529	0.6868	0.2021
O(4)	0.0562(8)	0.6428(8)	0.2807(9)
C(5)	-0.015(2)	0.566(2)	0.334(2)
H(5A)	-0.0929	0.5655	0.3283
H(5B)	0.0210	0.6009	0.4109
C(6)	-0.019(2)	0.453(2)	0.309(2)
H(6A)	-0.0568	0.4145	0.2329
H(6B)	-0.0683	0.4101	0.3531
O(7)	0.0911(9)	0.4472(10)	0.3241(10)
C(8)	0.069(2)	0.329(2)	0.278(2)
H(8A)	0.0291	0.2974	0.2027
H(8B)	0.0208	0.2835	0.3210
C(9)	0.183(2)	0.3190(13)	0.283(2)
H(9A)	0.1728	0.2367	0.2638
H(9B)	0.2224	0.3572	0.3593
O(10)	0.2601(9)	0.3802(9)	0.2185(9)
C(11)	0.236(2)	0.322(2)	0.108(2)
H(11A)	0.1520	0.2911	0.0831
H(11B)	0.2575	0.2546	0.0968
C(12)	0.2920(15)	0.395(2)	0.0403(13)
H(12A)	0.2806	0.3488	-0.0360
H(12B)	0.3752	0.4317	0.0702
O(13)	0.2436(8)	0.4864(10)	0.0526(8)
C(14)	0.2810(12)	0.568(2)	0.0022(12)
C(15)	0.224(2)	0.6467(15)	0.0189(12)
C(16)	0.244(2)	0.738(2)	-0.026(2)
H(16A)	0.2063	0.7928	-0.0115

TABLE 16 (Continued)

C(17)	0.329(3)	0.747(2)	-0.100(2)
H(17A)	0.3489	0.8068	-0.1373
C(18)	0.381(2)	0.675(2)	-0.114(2)
H(18A)	0.4403	0.6840	-0.1603
C(19)	0.3593(15)	0.578(2)	-0.0705(13)
H(19A)	0.3955	0.5220	-0.0862
O(21)	0.3397(8)	0.8866(9)	0.4112(10)
C(22)	0.2628(13)	0.8887(14)	0.490(2)
H(22A)	0.1822	0.8459	0.4524
H(22B)	0.2769	0.9711	0.5255
C(23)	0.2843(15)	0.832(2)	0.5705(14)
H(23A)	0.2369	0.8382	0.6265
H(23B)	0.3661	0.8725	0.6055
O(24)	0.2578(8)	0.7127(10)	0.5151(8)
C(25)	0.3072(15)	0.656(2)	0.5758(12)
H(25A)	0.2625	0.5707	0.5448
H(25B)	0.2991	0.6797	0.6520
C(26)	0.4303(12)	0.6770(14)	0.5692(11)
H(26A)	0.4661	0.6494	0.6192
H(26B)	0.4728	0.7625	0.5872
O(27)	0.4347(7)	0.6199(7)	0.4583(7)
C(28)	0.5540(11)	0.6434(12)	0.4411(11)
H(28A)	0.5896	0.6104	0.4858
H(28B)	0.6007	0.7283	0.4615
C(29)	0.5493(11)	0.5909(11)	0.3220(10)
H(29A)	0.4940	0.5082	0.3006
H(29B)	0.6255	0.5929	0.3103
O(30)	0.5134(6)	0.6495(7)	0.2531(6)
C(31)	0.6038(10)	0.7580(10)	0.2533(11)
H(31A)	0.6617	0.7424	0.2130
H(31B)	0.6420	0.8047	0.3284
C(32)	0.5505(10)	0.8298(10)	0.2050(10)
H(32A)	0.5042	0.7812	0.1328
H(32B)	0.6107	0.9020	0.1993
O(33)	0.4774(7)	0.8567(7)	0.2804(7)
C(34)	0.4180(12)	0.9262(12)	0.2559(15)
C(35)	0.3437(12)	0.9424(12)	0.332(2)
C(36)	0.280(2)	1.0059(15)	0.318(2)
H(36A)	0.2278	1.0167	0.3683
C(37)	0.288(2)	1.053(2)	0.236(3)
H(37A)	0.2390	1.0945	0.2272
C(38)	0.366(2)	1.043(2)	0.165(2)
H(38A)	0.3710	1.0802	0.1073
C(39)	0.4320(13)	0.9760(14)	0.178(2)
H(39A)	0.4881	0.9707	0.1304

TABLE 17

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[K(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_4$ (**II**)

I(1)-Cu(1)	2.482 (6)	C(12)-O(13)	1.48 (3)
I(2)-Cu(1)	2.570 (6)	O(13)-C(14)	1.38 (2)
I(2)-Cu(1^i)	2.577 (6)	C(14)-C(15)	1.42 (3)
Cu(1)-I(2^i)	2.577 (6)	C(14)-C(19)	1.38 (2)
Cu(1)...Cu(1^i)	3.040 (8)	C(15)-C(16)	1.37 (3)
K(1)-O(1)	2.922 (13)	C(16)-C(17)	1.44 (4)
K(1)-O(4)	2.858 (13)	C(17)-C(18)	1.29 (5)
K(1)-O(7)	2.756 (13)	C(18)-C(19)	1.42 (4)
K(1)-O(10)	2.954 (13)	O(21)-C(22)	1.44 (2)
K(1)-O(13)	2.984 (11)	O(21)-C(35)	1.37 (2)
K(1)-C(14)	3.53 (2)	C(22)-C(23)	1.46 (3)
K(1)-O(21)	2.986 (12)	C(23)-O(24)	1.38 (2)
K(1)-O(24)	2.858 (12)	O(24)-C(25)	1.43 (3)
K(1)-O(27)	2.847 (12)	C(25)-C(26)	1.47 (2)
K(1)-O(30)	2.900 (11)	C(26)-O(27)	1.42 (2)
K(1)-O(33)	3.021 (11)	O(27)-C(28)	1.44 (2
O(1)-C(2)	1.42 (2)	C(28)-C(29)	1.47 (2)
O(1)-C(15)	1.40 (2)	C(29)-O(30)	1.43 (2)
C(2)-C(3)	1.49 (3)	O(30)-C(31)	1.403 (14)
C(3)-O(4)	1.41 (2)	C(31)-C(32)	1.53 (2)
O(4)-C(5)	1.40 (3)	C(32)-O(33)	1.43 (2)
C(5)-C(6)	1.36 (3)	O(33)-C(34)	1.42 (2)
C(6)-O(7)	1.41 (3)	C(34)-C(35)	1.41 (3)
O(7)-C(8)	1.36 (2)	C(34)-C(39)	1.29 (3)
C(8)-C(9)	1.47 (3)	C(35)-C(36)	1.36 (3)
C(9)-O(10)	1.44 (2)	C(36)-C(37)	1.32 (5)
O(10)-C(11)	1.36 (2)	C(37)-C(38)	1.38 (4)
C(11)-C(12)	1.44 (3)	C(38)-C(39)	1.42 (4)
Cu(1)-I(2)-Cu(1^i)	72.4(2)	O(27)-K(1)-O(33)	88.7(3)
I(1)-Cu(1)-I(2)	127.9(1)	O(30)-K(1)-O(33)	55.6(3)
I(1)-Cu(1)-I(2^i)	124.5(2)	C(2)-O(1)-C(15)	120.7(15)
I(2)-Cu(1)-I(2^i)	107.6(2)	O(1)-C(2)-C(3)	103.6(15)
O(1)-K(1)-O(4)	55.5(4)	C(2)-C(3)-O(4)	111.8(13)
O(1)-K(1)-O(7)	93.2(4)	C(3)-O(4)-C(5)	114.2(12)
O(4)-K(1)-O(7)	61.0(4)	O(4)-C(5)-C(6)	117(2)
O(1)-K(1)-O(10)	100.3(3)	C(5)-C(6)-O(7)	115.3(15)
O(4)-K(1)-O(10)	113.0(3)	C(6)-O(7)-C(8)	105.6(13)
O(7)-K(1)-O(10)	59.7(4)	O(7)-C(8)-C(9)	108.0(13)
O(1)-K(1)-O(13)	50.6(4)	C(8)-C(9)-O(10)	114(2)

TABLE 17 (Continued)

O(4)-K(1)-O(13)	97.2(3)	C(9)-O(10)-C(11)	115.8(11)
O(7)-K(1)-O(13)	91.0(3)	O(10)-C(11)-C(12)	115.1(13)
O(10)-K(1)-O(13)	56.6(4)	C(11)-C(12)-O(13)	106(2)
O(1)-K(1)-O(21)	94.0(4)	C(12)-O(13)-C(14)	119.9(13)
O(4)-K(1)-O(21)	76.2(3)	O(13)-C(14)-C(15)	113.4(14)
O(7)-K(1)-O(21)	120.8(4)	O(13)-C(14)-C(19)	128(2)
O(10)-K(1)-O(21)	165.6(4)	C(15)-C(14)-C(19)	118(2)
O(13)-K(1)-O(21)	135.4(4)	O(1)-C(15)-C(14)	115(2)
O(1)-K(1)-O(24)	127.3(4)	O(1)-C(15)-C(16)	120(2)
O(4)-K(1)-O(24)	74.3(3)	C(14)-C(15)-C(16)	126(2)
O(7)-K(1)-O(24)	73.4(3)	C(15)-C(16)-C(17)	114(2)
O(10)-K(1)-O(24)	114.1(4)	C(16)-C(17)-C(18)	120(3)
O(13)-K(1)-O(24)	164.4(3)	C(17)-C(18)-C(19)	127(2)
O(21)-K(1)-O(24)	56.2(4)	C(14)-C(19)-C(18)	115(2)
O(1)-K(1)-O(27)	171.1(3)	C(22)-O(21)-C(35)	121.5(14)
O(4)-K(1)-O(27)	133.3(3)	O(21)-C(22)-C(23)	110(2)
O(7)-K(1)-O(27)	91.1(4)	C(22)-C(23)-O(24)	108.7(13)
O(10)-K(1)-O(27)	75.1(3)	C(23)-O(24)-C(25)	114.2(12)
O(13)-K(1)-O(27)	121.6(4)	O(24)-C(25)-C(26)	115.5(14)
O(21)-K(1)-O(27)	90.5(3)	C(25)-C(26)-O(27)	108.2(10)
O(24)-K(1)-O(27)	61.5(3)	C(26)-O(27)-C(28)	112.5(9)
O(1)-K(1)-O(30)	110.7(3)	O(27)-C(28)-C(29)	107.9(9)
O(4)-K(1)-O(30)	164.4(4)	C(28)-C(29)-O(30)	113.9(12)
O(7)-K(1)-O(30)	131.7(4)	C(29)-O(30)-C(31)	113.5(9)
O(10)-K(1)-O(30)	74.7(3)	O(30)-C(31)-C(32)	109.6(10)
O(13)-K(1)-O(30)	75.3(3)	C(31)-C(32)-O(33)	104.9(11)
O(21)-K(1)-O(30)	99.3(3)	C(32)-O(33)-C(34)	116.7(12)
O(24)-K(1)-O(30)	116.0(3)	O(33)-C(34)-C(35)	112(2)
O(27)-K(1)-O(30)	60.8(3)	O(33)-C(34)-C(39)	126(2)
O(1)-K(1)-O(33)	88.4(3)	C(35)-C(34)-C(39)	122(2)
O(4)-K(1)-O(33)	113.0(3)	O(21)-C(35)-C(34)	115(2)
O(7)-K(1)-O(33)	170.6(3)	O(21)-C(35)-C(36)	126(2)
O(10)-K(1)-O(33)	129.1(3)	C(34)-C(35)-C(36)	119(2)
O(13)-K(1)-O(33)	97.1(3)	C(35)-C(36)-C(37)	121(2)
C(14)-K(1)-O(33)	78.1(3)	C(36)-C(37)-C(38)	120(3)
O(21)-K(1)-O(33)	49.8(3)	C(37)-C(38)-C(39)	119(3)
O(24)-K(1)-O(33)	98.3(3)	C(34)-C(39)-C(38)	119(2)

Symmetry operation:

^{i} = -x, -y, 1-z

TABLE 18

ANISOTROPIC THERMAL PARAMETERS FOR

$[K(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_4$ (**II**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	115(1)	106(1)	94(1)	-11(1)	20(1)	12(1)
I(2)	65(1)	82(1)	95(1)	20(1)	12(1)	11(1)
Cu(1)	71(1)	100(1)	102(1)	27(1)	27(1)	9(1)
K(1)	45(1)	50(1)	57(2)	17(1)	4(1)	8(1)
O(1)	97(7)	100(7)	88(7)	63(6)	23(6)	39(6)
C(2)	122(14)	85(11)	103(12)	62(11)	-32(11)	18(10)
C(3)	59(10)	110(13)	129(15)	50(10)	-3(11)	-26(12)
O(4)	60(6)	96(7)	116(8)	33(5)	18(6)	25(7)
C(5)	96(14)	123(17)	270(29)	47(13)	110(17)	74(19)
C(6)	95(16)	124(18)	198(22)	13(13)	51(14)	67(16)
O(7)	70(7)	76(8)	166(11)	16(6)	17(7)	43(7)
C(8)	104(15)	97(16)	137(16)	-6(12)	9(12)	30(12)
C(9)	145(17)	70(11)	169(18)	42(11)	62(15)	78(12)
O(10)	108(8)	77(7)	94(8)	48(6)	-8(6)	7(6)
C(11)	139(17)	109(15)	121(17)	86(13)	1(14)	-2(13)
C(12)	107(13)	138(15)	72(11)	83(13)	5(10)	-21(11)
O(13)	80(6)	109(8)	80(6)	54(6)	27(5)	27(6)
C(14)	70(9)	78(11)	74(11)	20(9)	20(8)	15(9)
C(15)	118(14)	68(10)	53(9)	-9(10)	-27(9)	42(9)
C(16)	142(18)	149(21)	63(12)	24(15)	-12(12)	-9(14)
C(17)	206(29)	103(17)	93(17)	33(17)	-60(19)	13(14)
C(18)	145(21)	173(24)	102(16)	-47(18)	32(14)	74(19)
C(19)	95(13)	192(22)	59(10)	45(13)	15(9)	-21(12)
O(21)	68(6)	65(6)	145(9)	37(5)	39(6)	6(7)
C(22)	65(10)	65(10)	155(17)	14(8)	50(11)	-31(11)
C(23)	87(12)	128(17)	94(13)	24(11)	35(10)	-15(13)
O(24)	69(6)	99(8)	68(6)	21(5)	13(5)	-5(6)
C(25)	102(14)	154(16)	48(9)	30(12)	17(9)	21(10)
C(26)	79(11)	127(13)	62(10)	32(9)	7(8)	37(9)
O(27)	70(6)	79(6)	67(6)	24(5)	6(5)	22(5)
C(28)	54(8)	89(10)	91(11)	27(7)	11(7)	32(9)
C(29)	71(9)	65(8)	71(9)	37(7)	18(7)	11(8)
O(30)	57(5)	63(5)	67(5)	30(4)	7(4)	19(5)
C(31)	51(7)	59(8)	101(10)	24(7)	34(7)	22(8)
C(32)	63(8)	58(8)	64(8)	14(7)	15(7)	11(7)
O(33)	65(5)	77(6)	72(6)	35(5)	21(4)	19(5)
C(34)	70(10)	50(9)	113(13)	31(8)	-9(9)	18(9)

TABLE 18 (Continued)

C(35)	52(9)	35(8)	148(16)	18(7)	8(10)	9(9)
C(36)	86(12)	69(12)	218(25)	52(11)	22(14)	10(13)
C(37)	140(22)	103(18)	275(39)	81(17)	-25(22)	50(20)
C(38)	160(22)	85(14)	198(26)	40(15)	-36(18)	61(15)
C(39)	85(11)	55(9)	139(16)	22(9)	-20(10)	32(10)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

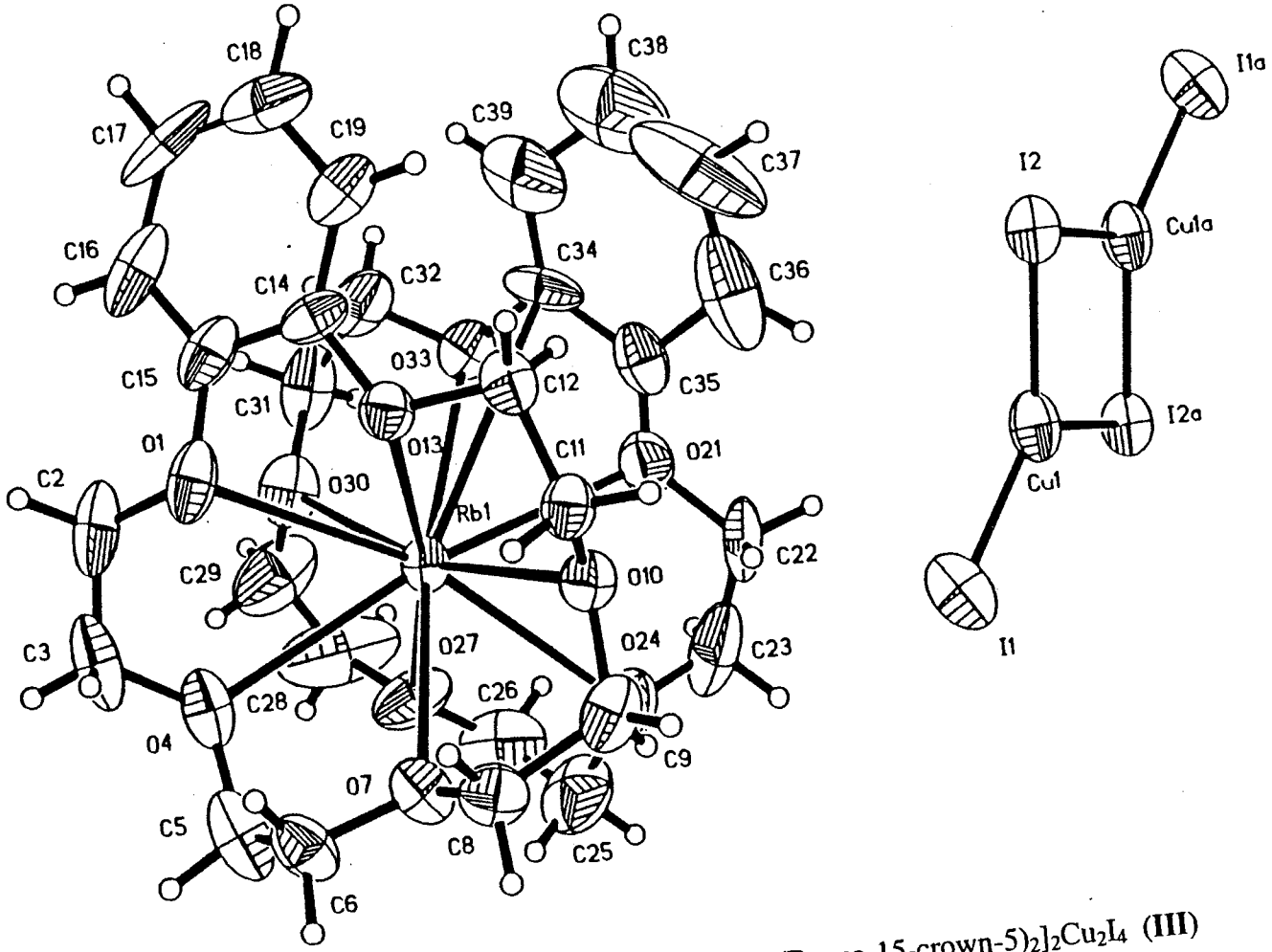


Figure 16. Projection View of $[Rb(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_4$ **(III)**

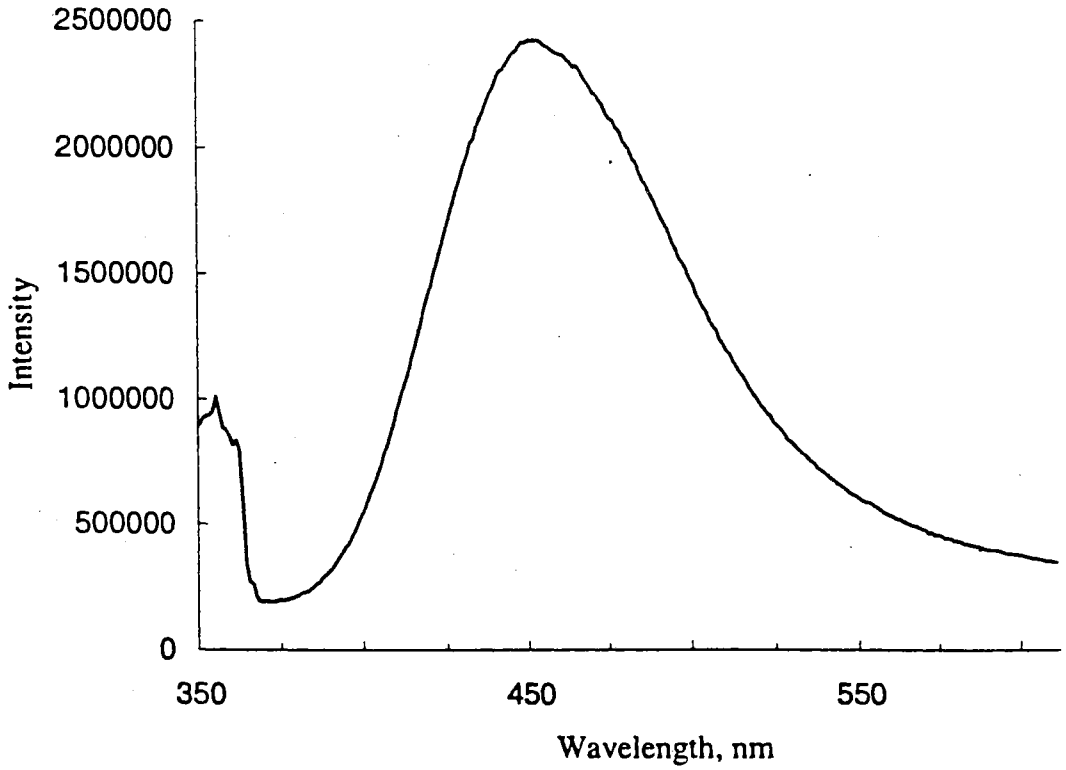


Figure 17. Emission spectrum of $[Rb(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_4$ (**III**)

TABLE 19

CRYSTAL DATA FOR

$[Rb(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_4$ (**III**)

Formula	$C_{56}H_{80}Cu_2I_4O_{20}Rb_2$
Space group	P1bar
a	12.46(6) Å
b	13.94(11) Å
c	12.75(8) Å
α	105.7(6)°
β	93.3(5)°
γ	111.2(4)°
V	1816(20) $Å^3$
Z	1
Mw	1878.8 g $mole^{-1}$
Density (calc.)	1.718 Mg m^{-3}
$\mu(MoK_\alpha)$	3.680 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	920
Collected Reflections	11853
Independent Reflections	10521
Observed Reflections ($F > 4.0\sigma$)	3116
Number of parameters	380
Final R indices	R=6.37%, R_w=6.49%
R indices (all data)	R=22.0%, R_w= 12.06%
GOF	1.35

TABLE 20

POSITIONAL PARAMETERS FOR

$[Rb(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_4$ (**III**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
Cu(1)	0.0396(1)	-0.4852(2)	0.1233(1)
I(1)	0.0996(1)	-0.4695(1)	0.3197(1)
I(2)	0.0985(1)	-0.3218(1)	0.0245(1)
Rb(1)	0.2840(1)	0.1334(1)	0.7879(1)
O(1)	0.3462(6)	0.3916(7)	0.9212(8)
C(2)	0.2628(12)	0.3916(12)	0.9935(14)
H(2A)	0.1849	0.3486	0.9521
H(2B)	0.2713	0.4698	1.0319
C(3)	0.2828(13)	0.334(2)	1.0749(12)
H(3A)	0.2345	0.3375	1.1307
H(3B)	0.3631	0.3743	1.1108
O(4)	0.2602(7)	0.2128(9)	1.0210(7)
C(5)	0.3121(13)	0.155(2)	1.0815(12)
H(5A)	0.2713	0.0722	1.0484
H(5B)	0.3022	0.1757	1.1575
C(6)	0.4387(10)	0.1814(12)	1.0729(9)
H(6A)	0.4776	0.1585	1.1240
H(6B)	0.4756	0.2646	1.0893
O(7)	0.4451(6)	0.1247(7)	0.9643(6)
C(8)	0.5612(10)	0.1468(11)	0.9483(10)
H(8A)	0.5964	0.1148	0.9932
H(8B)	0.6056	0.2295	0.9698
C(9)	0.5610(10)	0.0971(11)	0.8249(11)
H(9A)	0.5082	0.0166	0.8014
H(9B)	0.6378	0.1005	0.8145
O(10)	0.5244(6)	0.1555(7)	0.7560(6)
C(11)	0.6129(9)	0.2653(10)	0.7580(10)
H(11A)	0.6697	0.2510	0.7148
H(11B)	0.6524	0.3110	0.8323
C(12)	0.5564(10)	0.3338(10)	0.7117(9)
H(12A)	0.5069	0.2851	0.6419
H(12B)	0.6143	0.4015	0.7014
O(13)	0.4868(6)	0.3666(7)	0.7889(6)
C(14)	0.4221(10)	0.4287(10)	0.7659(12)
C(15)	0.3446(11)	0.4436(11)	0.8363(14)
C(16)	0.2736(13)	0.5001(14)	0.819(2)
H(16A)	0.2217	0.5130	0.8687

TABLE 20 (Continued)

C(17)	0.282(2)	0.5470(15)	0.729(2)
H(17A)	0.2311	0.5836	0.7142
C(18)	0.361(2)	0.5354(14)	0.661(2)
H(18A)	0.3668	0.5661	0.6000
C(19)	0.4287(11)	0.4751(12)	0.6793(14)
H(19A)	0.4862	0.4684	0.6339
O(21)	0.2415(8)	-0.0193(10)	0.5473(7)
C(22)	0.2953(14)	-0.104(2)	0.5388(12)
H(22A)	0.3763	-0.0648	0.5725
H(22B)	0.2901	-0.1477	0.4631
C(23)	0.238(2)	-0.181(2)	0.606(2)
H(23A)	0.2607	-0.2463	0.5940
H(23B)	0.1556	-0.2098	0.5812
O(24)	0.2589(9)	-0.1240(9)	0.7142(9)
C(25)	0.179(2)	-0.1851(14)	0.781(2)
H(25A)	0.2167	-0.1536	0.8574
H(25B)	0.1651	-0.2667	0.7568
C(26)	0.069(2)	-0.169(2)	0.776(2)
H(26A)	0.0175	-0.2146	0.8141
H(26B)	0.0328	-0.1955	0.6996
O(27)	0.0875(9)	-0.0542(10)	0.8235(10)
C(28)	-0.013(2)	-0.030(3)	0.824(2)
H(28A)	-0.0576	-0.0639	0.8748
H(28B)	-0.0556	-0.0761	0.7511
C(29)	-0.024(2)	0.060(2)	0.821(2)
H(29A)	0.0010	0.0990	0.8993
H(29B)	-0.1027	0.0518	0.8035
O(30)	0.0499(7)	0.1397(8)	0.7767(9)
C(31)	-0.0065(12)	0.1485(13)	0.6802(15)
H(31A)	-0.0533	0.1927	0.7031
H(31B)	-0.0580	0.0717	0.6344
C(32)	0.0758(15)	0.2002(13)	0.6129(12)
H(32A)	0.1282	0.2777	0.6564
H(32B)	0.0353	0.2040	0.5486
O(33)	0.1368(7)	0.1244(7)	0.5806(7)
C(34)	0.2219(15)	0.1473(15)	0.5135(11)
C(35)	0.2755(12)	0.064(2)	0.5010(11)
C(36)	0.3683(14)	0.089(2)	0.4294(13)
H(36A)	0.4081	0.0368	0.4143
C(37)	0.388(3)	0.192(3)	0.392(3)
H(37A)	0.4538	0.2074	0.3542
C(38)	0.337(3)	0.257(3)	0.400(3)
H(38A)	0.3584	0.3168	0.3652
C(39)	0.247(2)	0.240(2)	0.4711(13)
H(39A)	0.2056	0.2904	0.4831

TABLE 21

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[Rb(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_4$ (**III**)

Cu(1)-I(1)	2.50 (2)	C(9)-O(10)	1.45 (2)
Cu(1)-I(2)	2.65 (2)	O(10)-C(11)	1.44 (2)
Cu(1)-I(2^i)	2.59 (2)	C(11)-C(12)	1.52 (2)
I(2)-Cu(1^i)	2.59 (2)	C(12)-O(13)	1.43 (2)
Rb(1)-O(1)	3.09 (3)	O(13)-C(14)	1.40 (2)
Rb(1)-O(4)	2.94 (3)	C(14)-C(15)	1.38 (2)
Rb(1)-C(5)	3.66 (3)	C(14)-C(19)	1.38 (3)
Rb(1)-O(7)	2.98 (3)	C(15)-C(16)	1.38 (3)
Rb(1)-C(9)	3.67 (3)	C(16)-C(17)	1.42 (4)
Rb(1)-O(10)	2.97 (3)	C(17)-C(18)	1.37 (4)
Rb(1)-O(13)	3.15 (3)	C(18)-C(19)	1.39 (3)
Rb(1)-C(14)	3.68 (3)	O(21)-C(22)	1.47 (3)
Rb(1)-C(15)	3.67 (3)	O(21)-C(35)	1.32 (3)
Rb(1)-O(21)	3.06 (3)	C(22)-C(23)	1.50 (3)
Rb(1)-O(24)	3.10 (3)	C(23)-O(24)	1.33 (2)
Rb(1)-O(27)	2.92 (3)	O(24)-C(25)	1.50 (3)
Rb(1)-C(28)	3.67 (4)	C(25)-C(26)	1.47 (4)
Rb(1)-C(29)	3.68 (4)	C(26)-O(27)	1.37 (3)
Rb(1)-O(30)	2.94 (3)	O(27)-C(28)	1.40 (3)
Rb(1)-O(33)	3.08 (3)	C(28)-C(29)	1.23 (5)
Rb(1)-C(34)	3.60 (3)	C(29)-O(30)	1.38 (3)
Rb(1)-C(35)	3.51 (3)	O(30)-C(31)	1.43 (2)
O(1)-C(2)	1.43 (2)	C(31)-C(32)	1.47 (3)
O(1)-C(15)	1.42 (2)	C(32)O(33)	1.44 (3)
C(2)-C(3)	1.49 (3)	O(33)-C(34)	1.40 (2)
C(3)-O(4)	1.44 (2)	C(34)-C(35)	1.44 (3)
O(4)-C(5)	1.48 (3)	C(34)-C(39)	1.39 (3)
C(5)-C(6)	1.51 (2)	C(35)-C(36)	1.51 (3)
C(6)-O(7)	1.40 (2)	C(36)-C(37)	1.48 (5)
O(7)-C(8)	1.41 (2)	C(37)-C(38)	1.22 (7)
C(8)-C(9)	1.53 (2)	C(38)-C(39)	1.47 (5)
Cu(1)-I(2)-Cu(1^i)	73.0(5)	O(30)-Rb(1)-O(33)	54.6(6)
I(1)-Cu(1)-I(2)	129.5(5)	C(2)-O(1)-C(15)	118.0(13)
I(1)-Cu(1)-I(2^i)	123.5(5)	O(1)-C(2)-C(3)	107.8(15)
I(2)-Cu(1)-I(2^i)	107.0(5)	C(2)-C(3)-O(4)	111.2(12)
O(1)-Rb(1)-O(4)	56.2(6)	C(3)-O(4)-C(5)	117.3(11)
O(1)-Rb(1)-O(7)	88.0(5)	O(4)-C(5)-C(6)	112.9(14)
O(4)-Rb(1)-O(7)	60.0(5)	C(5)-C(6)-O(7)	108.5(10)

TABLE 21 (Continued)

O(1)-Rb(1)-O(10)	97.2(5)	C(6)-O(7)-C(8)	112.2(9)
O(4)-Rb(1)-O(10)	113.8(5)	O(7)-C(8)-C(9)	108.6(10)
O(7)-Rb(1)-O(10)	59.8(5)	C(8)-C(9)-O(10)	114.4(13)
C(9)-Rb(1)-O(10)	22.2(6)	C(9)-O(10)-C(11)	114.6(9)
O(1)-Rb(1)-O(13)	48.1(5)	O(10)-C(11)-C(12)	109.6(10)
O(4)-Rb(1)-O(13)	96.7(5)	C(11)-C(12)-O(13)	107.0(11)
O(7)-Rb(1)-O(13)	86.9(5)	C(12)-O(13)-C(14)	119.3(11)
O(10)-Rb(1)-O(13)	55.7(5)	O(13)-C(14)-C(15)	116.1(15)
O(1)-Rb(1)-O(21)	139.2(6)	O(13)-C(14)-C(19)	125.7(14)
O(4)-Rb(1)-O(21)	161.3(5)	C(15)-C(14)-C(19)	118(2)
O(7)-Rb(1)-O(21)	121.7(6)	O(1)-C(15)-C(14)	112.4(14)
O(10)-Rb(1)-O(21)	78.4(5)	O(1)-C(15)-C(16)	127(2)
O(13)-Rb(1)-O(21)	102.0(5)	C(14)-C(15)-C(16)	121(2)
O(1)-Rb(1)-O(24)	164.0(6)	C(15)-C(16)-C(17)	120(2)
O(4)-Rb(1)-O(24)	111.8(6)	C(16)-C(17)-C(18)	120(2)
O(7)-Rb(1)-O(24)	76.3(5)	C(17)-C(18)-C(19)	119(2)
O(10)-Rb(1)-O(24)	77.5(5)	C(14)-C(19)-C(18)	122(2)
O(13)-Rb(1)-O(24)	132.2(5)	C(22)-O(21)-C(35)	123.0(14)
O(21)-Rb(1)-O(24)	55.2(6)	O(21)-C(22)-C(23)	108(2)
O(1)-Rb(1)-O(27)	121.2(6)	C(22)-C(23)-O(24)	113.4(14)
O(4)-Rb(1)-O(27)	73.2(5)	C(23)-O(24)-C(25)	115.7(13)
O(7)-Rb(1)-O(27)	91.3(6)	O(24)-C(25)-C(26)	112(2)
O(10)-Rb(1)-O(27)	131.8(6)	C(25)-C(26)-O(27)	111.0(14)
O(13)-Rb(1)-O(27)	169.1(5)	C(26)-O(27)-C(28)	115(2)
O(21)-Rb(1)-O(27)	88.1(6)	O(27)-C(28)-C(29)	128(2)
O(24)-Rb(1)-O(27)	57.4(6)	C(28)-C(29)-O(30)	124(2)
O(1)-Rb(1)-O(30)	79.5(5)	C(29)-O(30)-C(31)	113.8(13)
O(4)-Rb(1)-O(30)	76.0(5)	O(30)-C(31)-C(32)	113.1(13)
O(7)-Rb(1)-O(30)	133.4(5)	C(31)-C(32)-O(33)	105.5(15)
O(10)-Rb(1)-O(30)	165.8(6)	C(32)-O(33)-C(34)	120.8(14)
O(13)-Rb(1)-O(30)	114.7(5)	O(33)-C(34)-C(35)	110(2)
O(21)-Rb(1)-O(30)	94.9(6)	O(33)-C(34)-C(39)	110(2)
O(24)-Rb(1)-O(30)	109.2(5)	O(33)-C(34)-C(39)	122(2)
O(27)-Rb(1)-O(30)	59.6(6)	C(35)-C(34)-C(39)	128(2)
O(1)-Rb(1)-O(33)	97.9(5)	O(21)-C(35)-C(34)	121.1(14)
O(4)-Rb(1)-O(33)	128.7(6)	O(21)-C(35)-C(36)	129(2)
O(7)-Rb(1)-O(33)	171.2(5)	C(34)-C(35)-C(36)	110(2)
O(10)-Rb(1)-O(33)	112.8(5)	C(35)-C(36)-C(37)	116(2)
O(13)-Rb(1)-O(33)	92.2(5)	C(36)-C(37)-C(38)	132(4)
O(21)-Rb(1)-O(33)	50.0(6)	C(37)-C(38)-C(39)	115(4)
O(24)-Rb(1)-O(33)	98.1(5)	C(34)-C(39)-C(38)	119(3
O(27)-Rb(1)-O(33)	91.2(6)		

Symmetry operation:

^{i} = -x, -1-y, -z

TABLE 22

ANISOTROPIC THERMAL PARAMETERS FOR

$[Rb(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_4$ (**III**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	104(1)	109(1)	95(1)	14(1)	19(1)	11(1)
I(2)	62(1)	86(1)	95(1)	14(1)	9(1)	6(1)
Cu(1)	66(1)	108(1)	104(1)	23(1)	25(1)	8(1)
Rb(1)	42(1)	54(1)	56(1)	12(1)	1(1)	4(1)
O(1)	54(5)	65(6)	123(7)	23(4)	30(5)	-2(5)
C(2)	72(10)	73(10)	144(15)	23(8)	44(10)	-18(10)
C(3)	78(10)	137(16)	78(11)	26(10)	31(8)	-21(10)
O(4)	66(6)	99(7)	70(6)	21(5)	13(5)	-9(5)
C(5)	96(12)	140(15)	74(10)	20(10)	27(9)	2(10)
C(6)	71(9)	125(12)	55(8)	33(8)	1(6)	23(8)
O(7)	49(5)	94(6)	63(5)	15(4)	4(4)	20(4)
C(8)	63(8)	93(10)	81(9)	26(7)	0(7)	32(8)
C(9)	49(7)	69(9)	117(12)	20(6)	15(7)	16(8)
O(10)	58(5)	70(5)	71(5)	25(4)	8(4)	17(4)
C(11)	56(7)	64(8)	76(8)	23(7)	17(6)	14(6)
C(12)	57(7)	63(8)	67(8)	8(6)	16(6)	12(6)
O(13)	58(5)	75(5)	70(5)	30(4)	19(4)	24(4)
C(14)	57(8)	41(7)	98(10)	9(6)	-3(7)	29(7)
C(15)	52(8)	41(7)	138(14)	12(6)	17(9)	14(8)
C(16)	79(10)	66(10)	194(19)	45(9)	16(11)	5(11)
C(17)	142(18)	66(11)	267(30)	70(12)	-6(18)	54(15)
C(18)	143(17)	80(12)	149(17)	33(12)	-6(13)	61(11)
C(19)	71(9)	60(9)	125(13)	26(7)	2(8)	21(9)
O(21)	100(7)	124(9)	77(7)	64(7)	21(5)	27(6)
C(22)	118(13)	168(18)	68(10)	108(14)	-2(9)	-27(10)
C(23)	158(18)	118(17)	162(21)	89(15)	7(16)	-26(15)
O(24)	107(8)	92(7)	100(8)	49(6)	-14(6)	-8(6)
C(25)	164(19)	71(11)	176(19)	39(12)	40(17)	39(12)
C(26)	133(18)	129(19)	151(17)	27(14)	-10(13)	64(14)
O(27)	96(8)	81(7)	190(11)	27(6)	32(7)	80(7)
C(28)	111(16)	359(44)	446(43)	145(25)	163(22)	331(40)
C(29)	105(14)	150(19)	287(28)	75(14)	84(17)	113(19)
O(30)	50(5)	92(7)	118(8)	20(5)	14(5)	17(6)
C(31)	50(8)	105(12)	130(14)	33(8)	-14(9)	-25(10)
C(32)	121(13)	98(12)	95(11)	60(11)	-37(10)	2(9)
O(33)	73(6)	78(6)	90(6)	29(5)	7(5)	21(5)
C(34)	108(12)	82(11)	48(8)	-11(10)	-25(8)	32(8)

TABLE 22 (Continued)

C(35)	65(9)	108(13)	54(9)	22(9)	-3(7)	-8(9)
C(36)	85(13)	236(26)	81(12)	31(14)	-14(10)	-59(14)
C(37)	176(31)	261(47)	111(20)	-126(33)	-8(19)	81(29)
C(38)	263(42)	193(34)	92(19)	0(26)	-33(22)	29(21)
C(39)	164(19)	125(17)	58(11)	-1(14)	-35(11)	-4(11)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

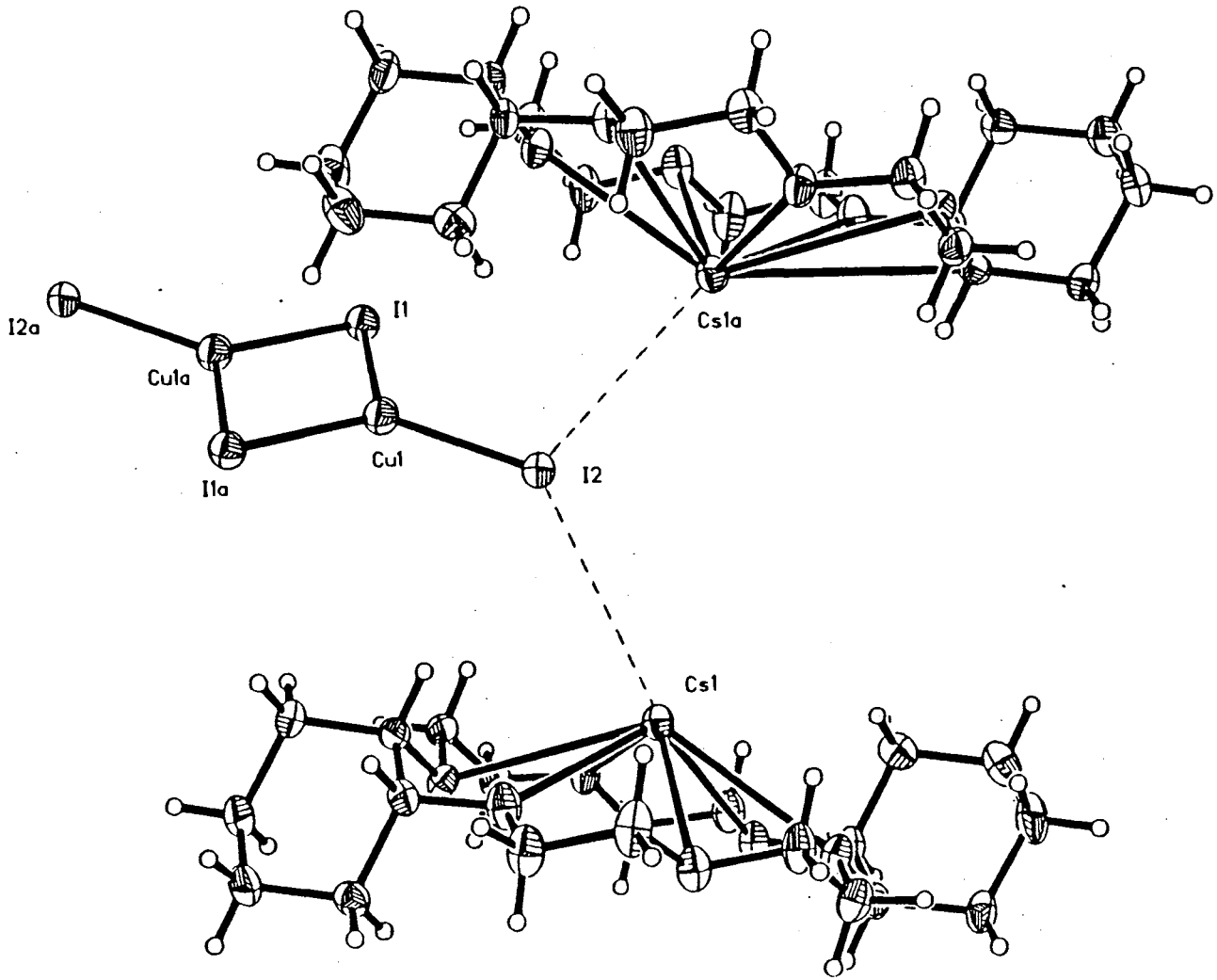


Figure 18. Projection View of $[Cs(Dicyclohexano\text{-}18\text{-}crown\text{-}6)]_2Cu_2I_4$ (**IV**)

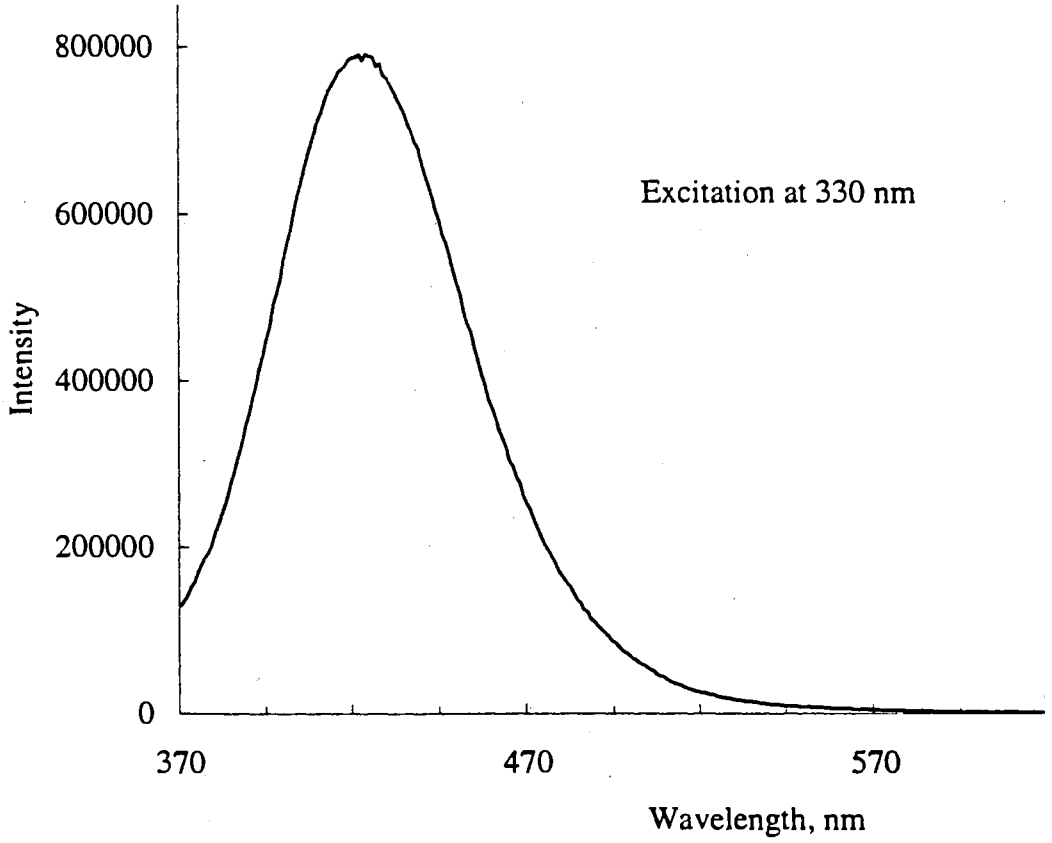


Figure 19. Emission spectrum of $[Cs(Dicyclohexano\text{-}18\text{-}crown\text{-}6)]_2Cu_2I_4$ (**IV**)

TABLE 23

CRYSTAL DATA FOR

$[Cs(Dicyclohexano\text{-}18\text{-}crown\text{-}6)]_2Cu_2I_4$ (**IV**)

Formula	$C_{40}H_{72}Cs_2Cu_2I_4O_{12}$
Space group	$P2_1/c$
a	12.502(3) Å
b	8.664(2) Å
c	25.117(6) Å
β	94.330(10)°
V	2719.1(11) $Å^3$
Z	2
Mw	1645.5 g $mole^{-1}$
Density (calc.)	2.010 Mg m^{-3}
$\mu(MoK_\alpha)$	4.423 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	1576
Collected Reflections	10033
Independent Reflections	7955
Observed Reflections ($F > 4.0\sigma$)	4186
Number of parameters	272
Final R indices	R=6.32 %, R_w=6.95 %
R indices (all data)	R=11.20 %, R_w= 8.51 %
GOF	1.35

TABLE 24

POSITIONAL PARAMETERS FOR

$[Cs(Dicyclohexano\text{-}18\text{-}crown\text{-}6)]_2Cu_2I_4$ (**IV**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.6888(1)	1.0101(1)	0.0132(1)
I(2)	1.0041(1)	1.2501(1)	0.0081(1)
Cu(1)	0.8897(1)	1.0008(2)	0.0050(1)
Cs(1)	0.4782(1)	0.8031(1)	0.1054(1)
O(1)	0.3904(5)	0.9302(8)	0.2104(2)
C(2)	0.4566(8)	1.0495(14)	0.2326(4)
H(2A)	0.4249	1.0916	0.2630
H(2B)	0.4624	1.1307	0.2070
C(3)	0.5662(7)	0.9895(12)	0.2492(4)
H(3A)	0.5609	0.9079	0.2747
H(3B)	0.6101	1.0699	0.2655
O(4)	0.6136(5)	0.9319(9)	0.2024(2)
C(5)	0.7226(7)	0.8844(12)	0.2138(4)
H(5A)	0.7284	0.8135	0.2432
H(5B)	0.7652	0.9738	0.2233
C(6)	0.7635(7)	0.8091(13)	0.1651(4)
H(6A)	0.8395	0.7926	0.1704
H(6B)	0.7501	0.8761	0.1348
O(7)	0.7116(5)	0.6650(8)	0.1546(2)
C(8)	0.7418(7)	0.5897(12)	0.1067(3)
H(8A)	0.7238	0.6549	0.0765
C(9)	0.8629(7)	0.5530(14)	0.1089(4)
H(9A)	0.9031	0.6470	0.1140
H(9B)	0.8806	0.5074	0.0759
C(10)	0.8936(8)	0.4428(15)	0.1550(4)
H(10A)	0.8820	0.4928	0.1882
H(10B)	0.9685	0.4180	0.1552
C(11)	0.8273(9)	0.2941(14)	0.1509(4)
H(11A)	0.8462	0.2302	0.1814
H(11B)	0.8447	0.2387	0.1196
C(12)	0.7058(8)	0.3288(12)	0.1470(4)
H(12A)	0.6858	0.3730	0.1798
H(12B)	0.6668	0.2343	0.1408
C(13)	0.6773(7)	0.4414(12)	0.1000(3)
H(13A)	0.6957	0.3922	0.0677
O(14)	0.5658(5)	0.4774(9)	0.0944(3)

TABLE 24 (Continued)

C(15)	0.4976(8)	0.3536(13)	0.0785(5)
H(15A)	0.4891	0.2884	0.1088
H(15B)	0.5289	0.2936	0.0515
C(16)	0.3898(8)	0.4140(15)	0.586(4)
H(16A)	0.3990	0.4826	0.0293
H(16B)	0.3435	0.3312	0.0461
O(17)	0.3427(5)	0.4934(8)	0.0997(3)
C(18)	0.2380(7)	0.5543(14)	0.0815(4)
H(18A)	0.1935	0.4727	0.0664
H(18B)	0.2449	0.6318	0.0546
C(19)	0.1891(8)	0.6225(14)	0.1288(4)
H(19A)	0.1940	0.5501	0.1579
H(19B)	0.1146	0.6448	0.1200
O(20)	0.2446(5)	0.7606(9)	0.1447(3)
C(21)	0.2125(7)	0.8278(13)	0.1931(4)
H(21A)	0.2284	0.7564	0.2218
C(22)	0.0929(7)	0.8695(15)	0.1895(4)
H(22A)	0.0733	0.9063	0.2235
H(22B)	0.0521	0.7780	0.1808
C(23)	0.0644(9)	0.991(2)	0.1464(4)
H(23A)	-0.0101	1.0179	0.1462
H(23B)	0.0768	0.9500	0.1119
C(24)	0.1321(9)	1.1325(15)	0.1568(4)
H(24A)	0.1151	1.1787	0.1898
H(24B)	0.1159	1.2060	0.1287
C(25)	0.2535(8)	1.0924(13)	0.1596(3)
H(25A)	0.2957	1.1834	0.1672
H(25B)	0.2723	1.0510	0.1259
C(26)	0.2780(7)	0.9756(13)	0.2037(4)
H(26A)	0.2584	1.0193	0.2368

TABLE 25

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[Cs(Dicyclohexano\text{-}18\text{-}crown\text{-}6)]_2Cu_2I_4$ (**IV**)

I(1)-Cu(1)	2.536 (2)	C(8)-C(13)	1.507 (15)
I(2)-Cu(1)	2.588 (2)	C(9)-C(10)	1.53 (2)
I(2)-Cu(1^i)	2.583 (2)	C(10)-C(11)	1.53 (2)
Cu(1)-I(2^i)	2.583 (2)	C(11)-C(12)	1.54 (2)
Cu(1)...Cu(1^i)	2.790 (3)	C(12)-C(13)	1.549 (14)
Cs(1)-O(1)	3.131 (7)	C(13)-O(14)	1.436 (12)
Cs(1)-O(4)	3.066 (6)	O(14)-C(15)	1.412 (14)
Cs(1)-O(7)	3.303 (6)	C(15)-C(16)	1.483 (15)
Cs(1)-O(14)	3.040 (8)	C(16)-O(17)	1.404 (14)
Cs(1)-O(17)	3.173 (7)	O(17)-C(18)	1.450 (12)
Cs(1)-O(20)	3.173 (7)	C(18)-C(19)	1.48 (2)
O(1)-C(2)	1.421 (14)	C(19)-O(20)	1.417 (14)
O(1)-C(26)	1.456 (11)	O(20)-C(21)	1.434 (12)
C(2)-C(3)	1.488 (15)	C(21)-C(22)	1.533 (14)
C(3)-O(4)	1.446 (12)	C(21)-C(26)	1.537 (15)
O(4)-C(5)	1.432 (11)	C(22)-C(23)	1.53 (2)
C(5)-C(6)	1.506 (15)	C(23)-C(24)	1.50 (2)
C(6)-O(7)	1.425 (13)	C(24)-C(25)	1.55 (2)
O(7)-C(8)	1.450 (12)	C(25)-C(26)	1.520 (14)
C(8)-C(9)	1.545 (14)		
Cu(1)-I(2)-Cu(1^i)	65.3(1)	O(7)-C(8)-C(13)	108.2(8)
I(1)-Cu(1)-I(2)	121.3(1)	C(9)-C(8)-C(13)	110.3(9)
I(1)-Cu(1)-I(2^i)	124.0(1)	C(8)-C(9)-C(10)	109.6(9)
I(2)-Cu(1)-I(2^i)	114.7(1)	C(9)-C(10)-C(11)	112.3(9)
O(1)-Cs(1)-O(4)	53.9(2)	C(10)-C(11)-C(12)	111.3(10)
O(1)-Cs(1)-O(7)	99.6(2)	C(11)-C(12)-C(13)	110.2(9)
O(4)-Cs(1)-O(7)	54.2(2)	C(8)-C(13)-C(12)	111.1(8)
O(1)-Cs(1)-O(14)	123.6(2)	C(8)-C(13)-O(14)	109.1(8)
O(4)-Cs(1)-O(14)	103.2(2)	C(12)-C(13)-O(14)	112.4(8)
O(7)-Cs(1)-O(14)	52.2(2)	C(13)-O(14)-C(15)	115.0(8)
O(1)-Cs(1)-O(17)	96.6(2)	O(14)-C(15)-C(16)	110.2(10)
O(4)-Cs(1)-O(17)	127.1(2)	C(15)-C(16)-O(17)	110.7(9)
O(7)-Cs(1)-O(17)	99.5(2)	C(16)-O(17)-C(18)	112.0(8)
O(14)-Cs(1)-O(17)	53.6(2)	O(17)-C(18)-C(19)	108.4(8)
O(1)-Cs(1)-O(20)	52.4(2)	C(18)-C(19)-O(20)	110.5(9)
O(4)-Cs(1)-O(20)	105.2(2)	C(19)-O(20)-C(21)	114.8(8)
O(7)-Cs(1)-O(20)	130.5(2)	O(20)-C(21)-C(22)	112.4(8)
O(14)-Cs(1)-O(20)	105.4(2)	O(20)-C(21)-C(26)	107.8(8)
O(17)-Cs(1)-O(20)	54.2(2)	C(22)-C(21)-C(26)	108.4(9)

TABLE 25 (Continued)

C(2)-O(1)-C(26)	112.4(8)	C(21)-C(22)-C(23)	112.1(9)
O(1)-C(2)-C(3)	110.6(10)	C(22)-C(23)-C(24)	110.1(9)
C(2)-C(3)-O(4)	108.4(8)	C(23)-C(24)-C(25)	111.0(11)
C(3)-O(4)-C(5)	112.2(7)	C(24)-C(25)-C(26)	109.0(9)
O(4)-C(5)-C(6)	109.7(8)	O(1)-C(26)-C(21)	106.9(8)
C(5)-C(6)-O(7)	110.7(8)	O(1)-C(26)-C(25)	113.8(8)
C(6)-O(7)-C(8)	114.4(7)	C(21)-C(26)-C(25)	110.8(8)
O(7)-C(8)-C(9)	112.2(7)		

Symmetry operation:

^{i} = 2-x, 2-y, -z

TABLE 26

ANISOTROPIC THERMAL PARAMETERS FOR

$[Cs(Dicyclohexano\text{-}18\text{-}crown\text{-}6)]_2Cu_2I_4$ (**IV**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	46(1)	59(1)	62(1)	4(1)	7(1)	4(1)
I(2)	53(1)	50(1)	66(1)	-1(1)	7(1)	-2(1)
Cu(1)	51(1)	62(1)	62(1)	1(1)	6(1)	0(1)
Cs(1)	42(1)	52(1)	52(1)	2(1)	1(1)	-3(1)
O(1)	41(4)	48(4)	61(4)	4(4)	-1(3)	-15(3)
C(2)	51(6)	58(7)	76(7)	7(6)	4(5)	-15(6)
C(3)	45(5)	48(6)	56(5)	-1(5)	-5(4)	-11(5)
O(4)	37(3)	65(5)	53(4)	2(4)	2(3)	-9(3)
C(5)	36(5)	47(6)	64(6)	-8(5)	-2(4)	-2(5)
C(6)	41(5)	48(6)	74(7)	-3(6)	9(5)	11(5)
O(7)	40(3)	42(4)	57(4)	-3(3)	13(3)	-4(3)
C(8)	52(6)	53(7)	42(5)	15(5)	12(4)	4(4)
C(9)	43(5)	61(7)	67(6)	11(6)	17(5)	3(6)
C(10)	45(6)	79(9)	74(7)	23(7)	1(5)	12(7)
C(11)	63(7)	57(8)	77(7)	25(7)	13(6)	3(6)
C(12)	58(6)	43(6)	58(6)	6(6)	8(5)	-2(5)
C(13)	45(5)	42(6)	53(5)	11(5)	4(4)	0(4)
O(14)	51(4)	50(5)	77(5)	6(4)	-1(3)	-12(4)
C(15)	54(6)	49(7)	90(8)	0(6)	3(6)	-24(6)
C(16)	50(6)	68(8)	75(7)	4(6)	-2(5)	-33(6)
O(17)	44(4)	49(5)	71(4)	1(4)	-6(3)	-15(3)
C(18)	37(5)	61(7)	78(7)	1(6)	-7(5)	-20(6)
C(19)	41(5)	62(8)	71(7)	-13(6)	1(5)	-9(6)
O(20)	37(3)	56(5)	62(4)	-1(4)	5(3)	-9(3)
C(21)	40(5)	63(7)	53(5)	6(6)	2(4)	-3(5)
C(22)	41(5)	82(9)	52(5)	13(6)	7(4)	-11(5)
C(23)	51(6)	100(11)	66(7)	21(8)	-16(5)	-15(7)
C(24)	72(8)	74(9)	61(7)	22(8)	-11(6)	-1(6)
C(25)	65(7)	52(7)	47(5)	0(6)	0(5)	-7(5)
C(26)	39(5)	56(7)	48(5)	10(5)	2(4)	-13(4)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

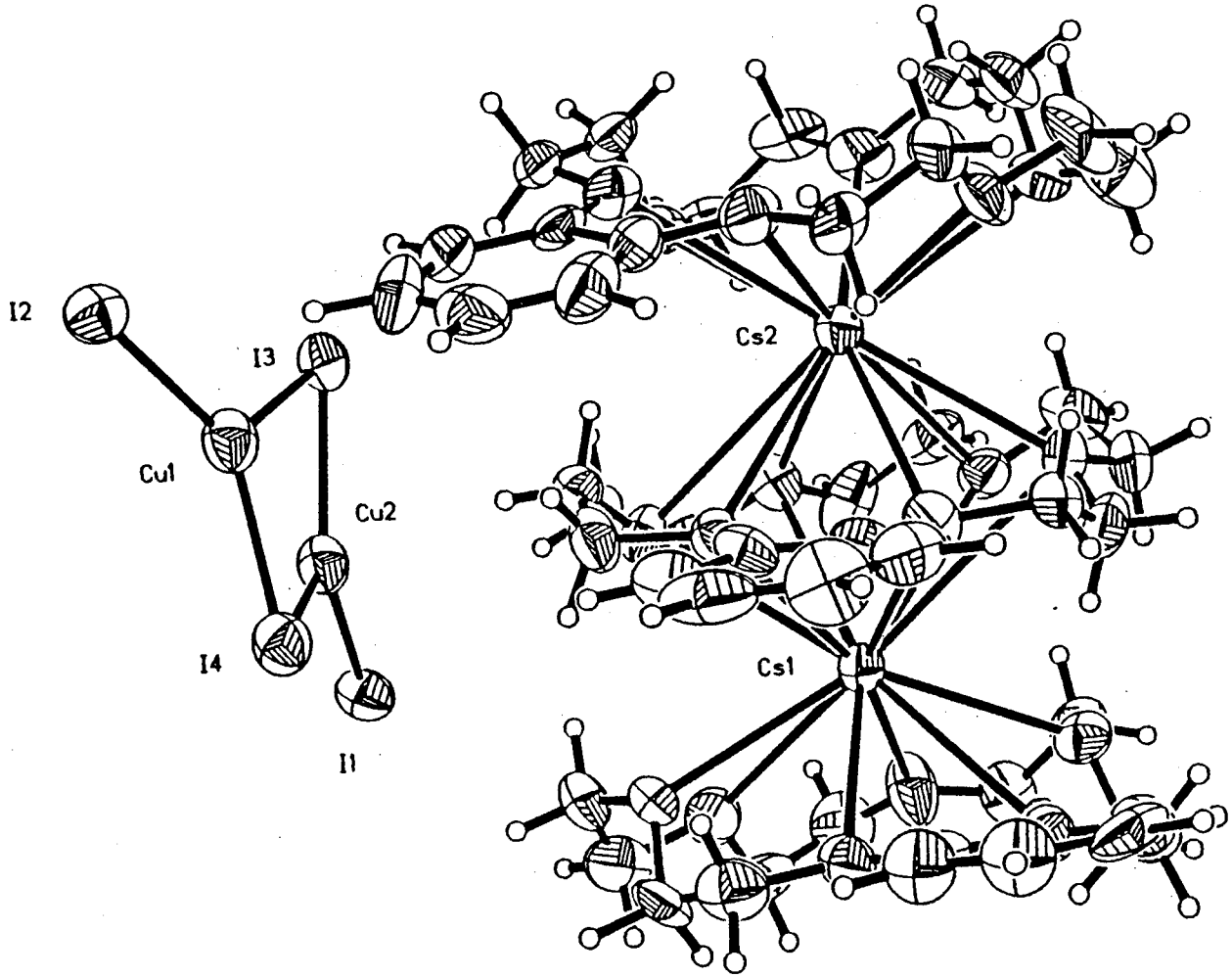


Figure 20. Projection View of $[Cs_2(Benzo\text{-}18\text{-}crown\text{-}6)_3]Cu_2I_4$ (V)

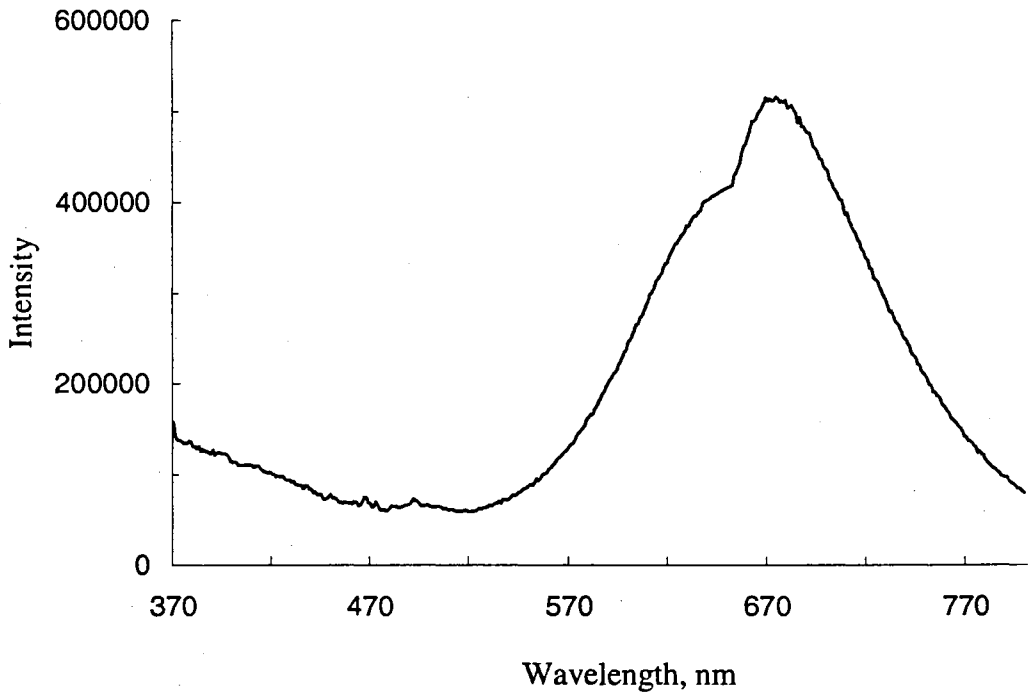


Figure 21. Emission spectrum of $[Cs_2(Benzo\text{-}18\text{-}crown\text{-}6)_3]Cu_2I_4$ (V)

TABLE 27

CRYSTAL DATA FOR

$[Cs_2(Benzo\text{-}18\text{-}crown\text{-}6)_3]Cu_2I_4$ (**V**)

Formula	$C_{48}H_{72}Cs_2Cu_2I_4O_{18}$
Space group	$P2_1/c$
a	22.882(8) Å
b	19.725(5) Å
c	13.980(6) Å
β	99.49(4)°
V	6229(4) $Å^3$
Z	4
Mw	1837.6 g mol^{-1}
Density (calc.)	1.960 Mg m^{-3}
$\mu(MoK_\alpha)$	3.880 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	3536
Collected Reflections	21273
Independent Reflections	18171
Observed Reflections ($F > 4.0\sigma$)	3867
Number of parameters	668
Final R indices	$R = 6.37$ %, $R_w = 7.00$ %
R indices (all data)	$R = 25.02$ %, $R_w = 14.15$ %
GOF	1.28

TABLE 28

POSITIONAL PARAMETERS FOR

$[Cs_2(Benzo\text{-}18\text{-}crown\text{-}6)_3]Cu_2I_4$ (**V**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.3843(1)	0.6175(1)	0.2997(2)
I(2)	0.1257(1)	0.3869(1)	0.1215(1)
I(3)	0.1821(1)	0.5851(1)	0.2387(1)
I(4)	0.3082(1)	0.4189(1)	0.3008(2)
Cu(1)	0.2919(2)	0.5475(2)	0.2742(2)
Cu(2)	0.2048(2)	0.4571(2)	0.2177(3)
Cs(1)	0.3451(1)	0.5467(1)	0.7860(1)
Cs(2)	0.1596(1)	0.5601(1)	0.7195(1)
O(1)	0.0796(7)	0.4217(10)	0.6635(14)
C(2)	0.0788(12)	0.3812(14)	0.748(2)
H(2A)	0.1184	0.3733	0.7818
H(2B)	0.0601	0.3383	0.7311
C(3)	0.0477(14)	0.422(2)	0.812(2)
H(3A)	0.0402	0.3955	0.8664
H(3B)	0.0102	0.4342	0.7745
O(4)	0.0769(8)	0.4814(11)	0.8443(15)
C(5)	0.050(2)	0.515(2)	0.910(3)
H(5A)	0.0459	0.4863	0.9638
H(5B)	0.0110	0.5269	0.8784
C(6)	0.075(2)	0.577(2)	0.938(3)
H(6A)	0.1139	0.5661	0.9726
H(6B)	0.0532	0.5985	0.9822
O(7)	0.0850(9)	0.6269(12)	0.865(2)
C(8)	0.0357(14)	0.654(2)	0.821(2)
H(8A)	0.0109	0.6659	0.8672
H(8B)	0.0158	0.6187	0.7801
C(9)	0.0422(13)	0.710(2)	0.757(2)
H(9A)	0.0606	0.7461	0.7964
H(9B)	0.0046	0.7253	0.7228
O(10)	0.0794(8)	0.6896(9)	0.688(2)
C(11)	0.0722(12)	0.7306(12)	0.606(2)
H(11A)	0.0761	0.7776	0.6238
H(11B)	0.0333	0.7233	0.5700
C(12)	0.1173(11)	0.707(2)	0.545(2)
H(12A)	0.1558	0.7173	0.5806
H(12B)	0.1122	0.7328	0.4856

TABLE 28 (Continued)

O(13)	0.1149(8)	0.6368(11)	0.5201(14)
C(14)	0.0602(11)	0.6143(15)	0.474(2)
H(14A)	0.0450	0.6444	0.4219
H(14B)	0.0327	0.6129	0.5189
C(15)	0.0669(10)	0.543(2)	0.436(2)
H(15A)	0.1002	0.5420	0.4018
H(15B)	0.0323	0.5283	0.3920
O(16)	0.0776(7)	0.5013(10)	0.5193(12)
C(17)	0.0878(9)	0.437(2)	0.498(2)
C(18)	0.0895(11)	0.390(2)	0.581(2)
C(19)	0.1029(13)	0.324(2)	0.567(2)
H(19A)	0.1076	0.2947	0.6222
C(20)	0.1123(12)	0.300(2)	0.484(4)
H(20A)	0.1184	0.2520	0.4766
C(21)	0.1090(14)	0.343(2)	0.403(2)
H(21A)	0.1173	0.3260	0.3422
C(22)	0.0969(10)	0.406(2)	0.414(2)
H(22A)	0.0943	0.4350	0.3580
O(31)	0.4128(6)	0.3988(8)	0.8277(13)
C(32)	0.4174(12)	0.3589(13)	0.7432(2)
H(32A)	0.3788	0.3435	0.7137
H(32B)	0.4426	0.3203	0.7596
C(33)	0.4399(11)	0.4045(15)	0.673(2)
H(33A)	0.4504	0.3794	0.6195
H(33B)	0.4751	0.4254	0.7075
O(34)	0.3981(7)	0.4528(9)	0.6403(12)
C(35)	0.4116(15)	0.496(2)	0.565(2)
H(35A)	0.3768	0.5226	0.5421
H(35B)	0.4193	0.4680	0.5128
C(36)	0.4594(14)	0.541(2)	0.590(2)
H(36A)	0.4686	0.5640	0.5339
H(36B)	0.4936	0.5162	0.6195
O(37)	0.4449(8)	0.5938(11)	0.6586(14)
C(38)	0.4926(11)	0.632(2)	0.701(2)
H(38A)	0.5121	0.6510	0.6516
H(38B)	0.5203	0.6033	0.7414
C(39)	0.474(2)	0.686(2)	0.762(3)
H(39A)	0.4487	0.7168	0.7213
H(39B)	0.5081	0.7112	0.7932
O(40)	0.4439(9)	0.6609(10)	0.829(2)
C(41)	0.4539(13)	0.6956(13)	0.915(2)
H(41A)	0.4567	0.7435	0.9049
H(41B)	0.4908	0.6803	0.9518
C(42)	0.4081(12)	0.6798(15)	0.972(2)
H(42A)	0.3723	0.6996	0.9376

TABLE 28 (Continued)

H(42B)	0.4166	0.7008	1.0343
O(43)	0.3975(7)	0.6111(9)	0.9855(12)
C(44)	0.4433(10)	0.5746(14)	1.044(2)
H(44A)	0.4563	0.6003	1.1019
H(45B)	0.4760	0.5697	1.0096
C(45)	0.4245(10)	0.5088(12)	1.069(2)
H(45A)	0.3894	0.5132	1.0978
H(45B)	0.4543	0.4864	1.1145
O(46)	0.4122(7)	0.4701(7)	0.9824(11)
C(47)	0.3972(10)	0.4067(13)	0.989(2)
C(48)	0.3967(10)	0.362(2)	0.906(2)
C(49)	0.3832(13)	0.2944(13)	0.914(3)
H(49A)	0.3844	0.2661	0.8583
C(50)	0.369(2)	0.269(2)	0.997(3)
H(50A)	0.3616	0.2215	1.0015
C(51)	0.3677(13)	0.313(2)	1.070(2)
H(51A)	0.3532	0.2948	1.1248
C(52)	0.3834(11)	0.380(2)	1.070(2)
H(52A)	0.3853	0.4071	1.1274
O(61)	0.2417(7)	0.4412(8)	0.8484(12)
C(62)	0.2307(10)	0.4480(15)	0.948(2)
H(62A)	0.2484	0.4102	0.9851
H(62B)	0.1889	0.4479	0.9492
C(63)	0.2564(12)	0.510(2)	0.986(2)
H(63A)	0.2978	0.5103	0.9817
H(63B)	0.2528	0.5140	1.0534
O(64)	0.2301(7)	0.5661(10)	0.9343(12)
C(65)	0.2434(13)	0.625(2)	0.985(2)
H(65A)	0.2855	0.6271	1.0054
H(65B)	0.2246	0.6269	1.0418
C(66)	0.2262(12)	0.6843(14)	0.921(2)
H(66A)	0.2316	0.7265	0.9560
H(66B)	0.1849	0.6794	0.8950
O(67)	0.2614(7)	0.6826(8)	0.8468(13)
C(68)	0.2507(12)	0.738(2)	0.785(2)
H(68A)	0.2568	0.7789	0.8212
H(68B)	0.2104	0.7364	0.7522
C(69)	0.2877(15)	0.7348(15)	0.712(2)
H(69A)	0.3276	0.7267	0.7435
H(69B)	0.2868	0.7760	0.6750
O(70)	0.2672(8)	0.6796(10)	0.6510(14)
C(71)	0.3007(11)	0.6665(12)	0.578(2)
H(71A)	0.3398	0.6517	0.6053
H(71B)	0.3039	0.7072	0.5413
C(72)	0.2706(11)	0.6106(15)	0.512(2)

TABLE 28 (Continued)

H(72A)	0.2896	0.6031	0.4572
H(72B)	0.2300	0.6230	0.4904
O(73)	0.2727(7)	0.5517(9)	0.5692(10)
C(74)	0.2378(10)	0.5020(13)	0.521(2)
H(74A)	0.2434	0.5020	0.4540
H(74B)	0.1970	0.5121	0.5223
C(75)	0.2523(11)	0.4355(13)	0.562(2)
H(75A)	0.2914	0.4224	0.5525
H(75B)	0.2246	0.4025	0.5308
O(76)	0.2489(6)	0.4361(7)	0.6657(10)
C(77)	0.2447(10)	0.3759(12)	0.710(2)
C(78)	0.2400(9)	0.3790(14)	0.805(2)
C(79)	0.2327(11)	0.318(2)	0.8553(2)
H(79A)	0.2278	0.3189	0.9222
C(80)	0.2344(15)	0.258(2)	0.808(3)
H(80A)	0.2265	0.2161	0.8400
C(81)	0.2427(12)	0.257(2)	0.7154(3)
H(81A)	0.2467	0.2139	0.6847
C(82)	0.2482(11)	0.3147(13)	0.667(2)
H(82A)	0.2544	0.3129	0.6008

TABLE 29

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[Cs_2(Benzo\text{-}18\text{-}crown\text{-}6)_3]Cu_2I_4$ (**V**)

I(1)-Cu(1)	2.500 (4)	C(18)-C(19)	1.35 (6)
I(2)-Cu(2)	2.489 (4)	C(19)-C(20)	1.31 (6)
I(3)-Cu(1)	2.589 (4)	C(20)-C(21)	1.41 (6)
I(3)-Cu(2)	2.604 (4)	O(21)-C(22)	1.30 (5)
I(4)-Cu(1)	2.581 (4)	O(31)-C(32)	1.44 (4)
I(4)-Cu(2)	2.572 (4)	O(31)-C(48)	1.41 (3)
Cu(1)-Cu(2)	2.695 (5)	C(32)-C(33)	1.48 (4)
Cs(1)-Cs(2)	4.202 (3)	C(33)-O(34)	1.37 (3)
Cs(1)-O(31)	3.309 (15)	O(34)-C(35)	1.43 (4)
Cs(1)-O(34)	3.14 (2)	C(35)-C(36)	1.41 (5)
Cs(1)-O(37)	3.25 (2)	C(36)-O(37)	1.48 (4)
Cs(1)-O(40)	3.18 (2)	O(37)-C(38)	1.38 (3)
Cs(1)-O(43)	3.12 (2)	C(38)-C(39)	1.47 (5)
Cs(1)-O(46)	3.285 (15)	C(39)-O(40)	1.34 (4)
Cs(1)-O(61)	3.37 (2)	O(40)-C(41)	1.38 (4)
Cs(1)-O(64)	3.63 (2)	C(41)-C(42)	1.44 (4)
Cs(1)-O(67)	3.48 (2)	C(42)-O(43)	1.40 (3)
Cs(1)-O(70)	3.54 (2)	O(43)-C(44)	1.42 (3)
Cs(1)-O(73)	3.207 (14)	C(44)-C(45)	1.43 (4)
Cs(1)-O(76)	3.349 (13)	C(45)-O(46)	1.42 (3)
Cs(2)-O(1)	3.31 (2)	O(46)-C(47)	1.30 (3)
Cs(2)-O(4)	3.18 (2)	C(47)-C(48)	1.46 (4)
Cs(2)-O(7)	3.16 (2)	C(47)-C(52)	1.33 (4)
Cs(2)-O(10)	3.13 (2)	C(48)-C(49)	1.37 (4)
Cs(2)-O(13)	3.19 (2)	C(49)-C(50)	1.36 (6)
Cs(2)-O(16)	3.31 (2)	C(50)-C(51)	1.34 (6)
Cs(2)-O(61)	3.341 (15)	C(51)-C(52)	1.37 (6)
Cs(2)-O(64)	3.168 (15)	O(61)-C(62)	1.46 (3)
Cs(2)-O(67)	3.612 (2)	O(61)-C(78)	1.36 (3)
Cs(2)-O(70)	3.65 (2)	C(62)-C(63)	1.43 (4)
Cs(2)-O(73)	3.60 (2)	C(63)-O(64)	1.40 (3)
Cs(2)-O(76)	3.350 (14)	O(64)-C(65)	1.37 (4)
O(1)-C(2)	1.44 (3)	C(65)-C(66)	1.48 (4)
O(1)-C(18)	1.37 (4)	C(66)-O(67)	1.42 (4)
C(2)-C(3)	1.47 (4)	O(67)-C(68)	1.38 (4)
C(3)-O(4)	1.39 (4)	C(68)-C(69)	1.43 (5)
O(4)-C(5)	1.36 (5)	C(69)-O(70)	1.41 (4)
C(5)-C(6)	1.38 (6)	O(70)-C(71)	1.40 (4)
C(6)-O(7)	1.46 (5)	C(71)-C(72)	1.52 (4)
O(7)-C(8)	1.30 (4)	C(72)-O(73)	1.40 (3)

TABLE 29 (Continued)

C(8)-C(9)	1.45 (5)	O(73)-C(74)	1.37 (3)
C(9)-O(10)	1.44 (4)	C(74)-C(75)	1.45 (4)
O(10)-C(11)	1.38 (4)	C(75)-C(76)	1.47 (3)
C(11)-C(12)	1.52 (4)	C(76)-C(77)	1.35 (3)
C(12)-O(13)	1.43 (4)	C(77)-C(78)	1.36 (4)
O(13)-C(14)	1.38 (3)	C(77)-C(82)	1.36 (4)
C(14)-C(15)	1.53 (4)	C(78)-C(79)	1.42 (4)
C(15)-O(16)	1.42 (3)	C(79)-C(80)	1.36 (5)
O(16)-C(17)	1.33 (4)	C(80)-C(81)	1.35 (6)
C(17)-C(18)	1.48 (4)	C(81)-C(82)	1.34 (5)
C(17)-C(22)	1.36 (4)		
Cu(1)-I(3)-Cu(2)	62.5(1)	O(7)-Cs(2)-O(67)	77.1(5)
Cu(1)-I(4)-Cu(2)	63.1(1)	O(10)-Cs(2)-O(67)	80.8(4)
I(1)-Cu(1)-I(3)	129.7(2)	O(13)-Cs(2)-O(67)	101.6(5)
I(1)-Cu(1)-I(4)	115.1(1)	O(16)-Cs(2)-O(67)	151.6(4)
I(3)-Cu(1)-I(4)	114.9(1)	O(61)-Cs(2)-O(67)	86.8(4)
I(2)-Cu(2)-I(3)	117.3(1)	O(64)-Cs(2)-O(67)	47.3(4)
I(2)-Cu(2)-I(4)	127.9(2)	O(1)-Cs(2)-O(70)	147.3(5)
I(3)-Cu(2)-I(4)	114.7(1)	O(4)-Cs(2)-O(70)	161.3(5)
O(31)-Cs(1)-O(34)	51.3(4)	O(7)-Cs(2)-O(70)	111.1(5)
O(31)-Cs(1)-O(37)	89.9(5)	O(10)-Cs(2)-O(70)	80.8(5)
O(34)-Cs(1)-O(37)	55.4(5)	O(13)-Cs(2)-O(70)	66.2(5)
O(31)-Cs(1)-O(40)	107.1(4)	O(16)-Cs(2)-O(70)	108.5(4)
O(34)-Cs(1)-O(40)	101.6(5)	O(61)-Cs(2)-O(70)	104.5(4)
O(37)-Cs(1)-O(40)	50.2(5)	O(64)-Cs(2)-O(70)	87.9(4)
O(31)-Cs(1)-O(43)	95.8(4)	O(67)-Cs(2)-O(70)	44.7(4)
O(34)-Cs(1)-O(43)	133.4(4)	O(1)-Cs(2)-O(73)	104.3(4)
O(37)-Cs(1)-O(43)	99.9(5)	O(4)-Cs(2)-O(73)	148.0(5)
O(40)-Cs(1)-O(43)	52.1(5)	O(7)-Cs(2)-O(73)	156.2(5)
O(31)-Cs(1)-O(46)	46.1(4)	O(10)-Cs(2)-O(73)	114.6(5)
O(34)-Cs(1)-O(46)	95.4(4)	O(13)-Cs(2)-O(73)	70.7(4)
O(37)-Cs(1)-O(46)	108.4(4)	O(16)-Cs(2)-O(73)	81.5(4)
O(40)-Cs(1)-O(46)	87.0(5)	O(61)-Cs(2)-O(73)	83.5(4)
O(43)-Cs(1)-O(46)	51.8(4)	O(64)-Cs(2)-O(73)	104.6(4)
O(31)-Cs(1)-O(61)	74.8(4)	O(67)-Cs(2)-O(73)	81.4(4)
O(34)-Cs(1)-O(61)	99.6(4)	O(70)-Cs(2)-O(73)	45.1(4)
O(37)-Cs(1)-O(61)	154.6(5)	O(1)-Cs(2)-O(76)	71.2(4)
O(40)-Cs(1)-O(61)	153.7(5)	O(4)-Cs(2)-O(76)	102.0(5)
O(43)-Cs(1)-O(61)	101.7(4)	O(7)-Cs(2)-O(76)	149.9(5)
O(46)-Cs(1)-O(61)	75.6(4)	O(10)-Cs(2)-O(76)	158.1(5)
O(31)-Cs(1)-O(64)	110.8(4)	O(13)-Cs(2)-O(76)	105.6(4)
O(34)-Cs(1)-O(64)	145.8(4)	O(16)-Cs(2)-O(76)	80.6(4)
O(37)-Cs(1)-O(64)	157.4(5)	O(61)-Cs(2)-O(76)	45.5(4)
O(40)-Cs(1)-O(64)	112.2(5)	O(64)-Cs(2)-O(76)	90.3(4)

TABLE 29 (Continued)

O(43)-Cs(1)-O(64)	69.8(4)	O(67)-Cs(2)-O(76)	103.3(3)
O(46)-Cs(1)-O(64)	81.6(4)	O(70)-Cs(2)-O(76)	87.1(4)
O(61)-Cs(1)-O(64)	46.5(4)	O(73)-Cs(2)-O(76)	46.5(4)
O(31)-Cs(1)-O(67)	153.7(4)	O(1)-C(2)-C(3)	106(2)
O(34)-Cs(1)-O(67)	154.1(4)	C(2)-C(3)-O(4)	114(3)
O(37)-Cs(1)-O(67)	112.2(5)	C(3)-O(4)-C(5)	112(3)
O(40)-Cs(1)-O(67)	79.1(5)	O(4)-C(5)-C(6)	114(4)
O(43)-Cs(1)-O(67)	67.3(4)	C(5)-C(6)-O(7)	120(3)
O(46)-Cs(1)-O(67)	110.5(4)	C(6)-O(7)-C(8)	113(3)
O(61)-Cs(1)-O(67)	88.5(4)	O(7)-C(8)-C(9)	116(3)
O(64)-Cs(1)-O(67)	45.5(4)	C(8)-C(9)-O(10)	109(3)
O(31)-Cs(1)-O(70)	158.1(5)	C(9)-O(10)-C(11)	112(2)
O(34)-Cs(1)-O(70)	107.8(5)	O(10)-C(11)-C(12)	107(2)
O(37)-Cs(1)-O(70)	80.4(5)	C(11)-C(12)-O(13)	115(2)
O(40)-Cs(1)-O(70)	81.7(5)	C(12)-O(13)-C(14)	115(2)
O(43)-Cs(1)-O(70)	105.1(4)	O(13)-C(14)-C(15)	109(2)
O(46)-Cs(1)-O(70)	155.8(4)	C(14)-C(15)-O(16)	105(2)
O(61)-Cs(1)-O(70)	106.4(4)	C(15)-O(16)-C(17)	112(2)
O(64)-Cs(1)-O(70)	83.0(4)	O(16)-C(17)-C(18)	114(2)
O(67)-Cs(1)-O(70)	46.4(4)	O(16)-C(17)-C(22)	132(3)
O(31)-Cs(1)-C(71)	138.6(5)	C(18)-C(17)-C(22)	114(3)
O(34)-Cs(1)-C(71)	87.3(5)	O(1)-C(18)-C(17)	112(3)
O(37)-Cs(1)-C(71)	61.4(5)	O(1)-C(18)-C(19)	130(3)
O(40)-Cs(1)-C(71)	78.1(5)	C(17)-C(18)-C(19)	118(3)
O(43)-Cs(1)-C(71)	116.8(5)	C(18)-C(19)-C(20)	124(4)
O(46)-Cs(1)-C(71)	165.1(4)	C(19)-C(20)-C(21)	120(4)
O(61)-Cs(1)-C(71)	118.5(5)	C(20)-C(21)-C(22)	118(4)
O(64)-Cs(1)-C(71)	104.3(5)	C(17)-C(22)-C(21)	127(3)
O(67)-Cs(1)-C(71)	67.4(5)	C(32)-O(31)-C(48)	114(2)
O(70)-Cs(1)-C(71)	21.8(5)	O(31)-C(32)-C(33)	107(2)
O(31)-Cs(1)-O(73)	110.3(4)	C(32)-C(33)-O(34)	110(2)
O(34)-Cs(1)-O(73)	66.4(4)	C(33)-O(34)-C(35)	116(2)
O(37)-Cs(1)-O(73)	76.9(4)	O(34)-C(35)-C(36)	117(2)
O(40)-Cs(1)-O(73)	113.4(5)	C(35)-C(36)-O(37)	111(3)
O(43)-Cs(1)-O(73)	153.5(4)	C(36)-O(37)-C(38)	114(2)
O(46)-Cs(1)-O(73)	154.4(4)	O(37)-C(38)-C(39)	111(2)
O(61)-Cs(1)-O(73)	89.3(4)	C(38)-C(39)-O(40)	111(3)
O(64)-Cs(1)-O(73)	103.1(4)	C(39)-O(40)-C(41)	113(2)
O(67)-Cs(1)-O(73)	89.3(4)	O(40)-C(41)-C(42)	110(2)
O(70)-Cs(1)-O(73)	48.4(4)	C(41)-C(42)-O(43)	116(2)
O(31)-Cs(1)-O(76)	76.4(3)	C(42)-O(43)-C(44)	116(2)
O(34)-Cs(1)-O(76)	65.3(4)	O(43)-C(44)-C(45)	112(2)
O(37)-Cs(1)-O(76)	111.9(4)	C(44)-C(45)-O(46)	108(2)
O(40)-Cs(1)-O(76)	160.9(5)	C(45)-O(46)-C(47)	118(2)
O(43)-Cs(1)-O(76)	147.0(4)	O(46)-C(47)-C(48)	120(2)

TABLE 29 (Continued)

O(46)-Cs(1)-O(76)	107.3(3)	O(46)-C(47)-C(52)	122(3)
O(61)-Cs(1)-O(76)	45.3(4)	C(48)-C(47)-C(52)	118(3)
O(64)-Cs(1)-O(76)	82.9(4)	O(31)-C(48)-C(47)	109(2)
O(67)-Cs(1)-O(76)	106.4(3)	O(31)-C(48)-C(49)	131(3)
O(70)-Cs(1)-O(76)	89.0(4)	C(47)-C(48)-C(49)	120(3)
O(73)-Cs(1)-O(76)	49.5(4)	C(48)-C(49)-C(50)	121(3)
O(1)-Cs(2)-O(4)	51.1(5)	C(49)-C(50)-C(51)	117(4)
O(1)-Cs(2)-O(7)	99.3(5)	C(50)-C(51)-C(52)	126(4)
O(4)-Cs(2)-O(7)	54.2(6)	C(47)-C(52)-C(51)	118(3)
O(1)-Cs(2)-O(10)	110.6(4)	C(62)-O(61)-C(78)	120(2)
O(4)-Cs(2)-O(10)	95.0(5)	O(61)-C(62)-C(63)	108(2)
O(7)-Cs(2)-O(10)	52.0(6)	C(62)-C(63)-O(64)	112(2)
O(1)-Cs(2)-O(13)	95.7(5)	C(63)-O(64)-C(65)	111(2)
O(4)-Cs(2)-O(13)	125.2(5)	O(64)-C(65)-C(66)	110(2)
O(7)-Cs(2)-O(13)	103.7(5)	C(65)-C(66)-O(67)	107(2)
O(10)-Cs(2)-O(13)	52.7(6)	C(66)-O(67)-C(68)	112(2)
O(1)-Cs(2)-O(16)	45.3(5)	O(67)-C(68)-C(69)	111(2)
O(4)-Cs(2)-O(16)	89.3(5)	C(68)-C(69)-O(70)	106(3)
O(7)-Cs(2)-O(16)	113.6(5)	C(69)-O(70)-C(71)	114(2)
O(10)-Cs(2)-O(16)	85.9(5)	O(70)-C(71)-C(72)	109(2)
O(13)-Cs(2)-O(16)	51.1(5)	C(71)-C(72)-O(73)	107(2)
O(1)-Cs(2)-O(61)	77.8(4)	C(72)-O(73)-C(74)	110(2)
O(4)-Cs(2)-O(61)	72.2(5)	O(73)-C(74)-C(75)	112(2)
O(7)-Cs(2)-O(61)	105.1(5)	C(74)-C(75)-O(76)	110(2)
O(10)-Cs(2)-O(61)	155.9(5)	C(75)-O(76)-C(77)	118(2)
O(13)-Cs(2)-O(61)	151.1(5)	O(76)-C(77)-C(78)	116(2)
O(16)-Cs(2)-O(61)	113.6(4)	O(76)-C(77)-C(82)	124(3)
O(1)-Cs(2)-O(64)	115.5(5)	C(78)-C(77)-C(82)	120(3)
O(4)-Cs(2)-O(64)	75.8(5)	O(61)-C(78)-C(77)	118(2)
O(7)-Cs(2)-O(64)	67.5(5)	O(61)-C(78)-C(79)	123(3)
O(10)-Cs(2)-O(64)	107.3(5)	C(77)-C(78)-C(79)	119(3)
O(13)-Cs(2)-O(64)	148.3(5)	C(78)-C(79)-C(80)	119(3)
O(16)-Cs(2)-O(64)	160.6(5)	C(79)-C(80)-C(81)	120(3)
O(61)-Cs(2)-O(64)	50.3(4)	C(80)-C(81)-C(82)	121(3)
O(1)-Cs(2)-O(67)	162.7(4)	C(77)-C(82)-C(81)	121(3)
O(4)-Cs(2)-O(67)	116.7(5)		

TABLE 30

ANISOTROPIC THERMAL PARAMETERS FOR

$[Cs_2(Benzo\text{-}18\text{-}crown\text{-}6)_3]Cu_2I_4$ (**V**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	74(1)	85(1)	109(2)	-2(1)	26(1)	-3(1)
I(2)	78(1)	88(1)	88(1)	-8(1)	14(1)	12(1)
I(3)	93(1)	76(1)	69(1)	1(1)	23(1)	1(1)
I(4)	102(1)	76(1)	92(2)	4(1)	16(1)	-12(1)
Cu(1)	91(2)	86(2)	73(2)	-12(2)	24(2)	-8(2)
Cu(2)	98(3)	94(3)	76(2)	-16(2)	26(2)	-4(2)
Cs(1)	60(1)	77(1)	54(1)	-1(1)	10(1)	0(1)
Cs(2)	65(1)	93(1)	56(1)	16(1)	12(1)	6(1)
O(1)	70(11)	115(15)	72(13)	-6(10)	9(10)	25(13)
C(2)	82(19)	106(21)	50(16)	-8(17)	8(15)	50(17)
C(3)	93(23)	207(40)	58(20)	31(27)	39(19)	67(25)
O(4)	87(14)	118(16)	86(15)	9(12)	55(12)	14(13)
C(5)	144(33)	188(38)	125(36)	47(31)	96(30)	94(34)
C(6)	173(42)	133(32)	167(42)	17(31)	93(35)	53(34)
O(7)	62(12)	165(21)	100(17)	25(13)	23(12)	0(16)
C(8)	74(21)	164(33)	111(27)	-19(22)	55(21)	-12(25)
C(9)	73(19)	153(33)	113(27)	38(21)	21(19)	-35(25)
O(10)	97(14)	65(12)	125(17)	53(10)	13(13)	22(13)
C(11)	86(20)	36(14)	177(34)	46(14)	-2(22)	22(19)
C(12)	53(17)	139(28)	90(22)	24(18)	-17(15)	9(20)
O(13)	69(13)	113(17)	88(15)	10(12)	11(11)	21(13)
C(14)	59(18)	127(24)	57(18)	-6(17)	-10(15)	14(18)
C(15)	47(14)	147(28)	52(17)	-17(16)	3(12)	-4(20)
O(16)	67(11)	96(14)	57(12)	1(10)	7(9)	42(12)
C(17)	42(12)	96(23)	45(16)	4(14)	-13(11)	19(18)
C(18)	56(16)	95(23)	76(25)	-18(16)	5(16)	-31(22)
C(19)	93(23)	136(37)	72(24)	-17(23)	2(19)	16(24)
C(20)	63(17)	128(32)	165(41)	-13(18)	17(25)	-58(34)
O(21)	129(28)	138(34)	64(24)	1(26)	-7(20)	-36(25)
C(22)	62(15)	97(22)	66(21)	-9(15)	3(14)	-7(18)
O(31)	65(10)	77(11)	82(12)	-2(8)	10(9)	-28(10)
C(32)	81(19)	69(18)	128(27)	5(14)	7(18)	-9(19)
C(33)	57(15)	138(25)	108(23)	39(17)	17(16)	-55(20)
O(34)	66(10)	119(13)	65(11)	26(11)	22(9)	-8(11)
C(35)	104(25)	183(34)	77(23)	31(24)	46(21)	-6(25)
C(36)	102(25)	171(32)	93(22)	41(25)	41(20)	72(23)
O(37)	75(12)	166(18)	81(13)	-14(13)	20(11)	2(13)

TABLE 30 (Continued)

C(38)	48(15)	182(33)	117(26)	-28(20)	-4(18)	61(25)
C(39)	134(32)	127(29)	121(31)	-21(23)	25(25)	-9(25)
O(40)	133(17)	129(17)	89(15)	-43(14)	55(14)	-12(14)
C(41)	117(25)	73(19)	98(24)	-2(17)	34(21)	9(18)
C(42)	92(22)	102(26)	79(20)	6(18)	-16(17)	-21(19)
O(43)	66(11)	73(11)	83(13)	-16(9)	0(10)	-12(10)
C(44)	59(15)	133(24)	44(14)	4(17)	-9(12)	-36(16)
C(45)	64(15)	65(16)	80(19)	-3(13)	7(14)	3(15)
O(46)	88(11)	56(10)	65(11)	-1(8)	27(9)	-6(9)
C(47)	59(15)	74(20)	73(19)	-14(13)	14(14)	8(16)
C(48)	42(13)	132(27)	63(19)	21(15)	-3(13)	9(20)
C(49)	128(27)	32(14)	199(38)	18(16)	-40(25)	-77(21)
C(50)	136(31)	112(30)	191(42)	-17(24)	0(30)	148(33)
C(51)	54(16)	221(49)	84(25)	10(25)	-37(17)	29(30)
C(52)	72(18)	122(26)	123(28)	-34(18)	34(18)	26(23)
O(61)	89(12)	63(10)	80(12)	9(9)	26(10)	11(10)
C(62)	69(16)	154(27)	50(15)	9(19)	30(13)	54(19)
C(63)	87(20)	133(25)	40(16)	-27(20)	0(15)	11(19)
O(64)	90(12)	101(14)	45(11)	0(11)	10(9)	-13(11)
C(65)	113(24)	140(28)	50(18)	19(22)	18(16)	-20(21)
C(66)	76(19)	92(22)	141(29)	-10(16)	28(20)	-77(22)
O(67)	80(12)	73(12)	73(12)	18(9)	-3(10)	-11(10)
C(68)	88(22)	91(23)	114(27)	8(19)	-24(21)	-21(22)
C(69)	177(34)	78(20)	74(22)	-4(22)	-28(23)	54(19)
O(70)	92(13)	114(16)	87(14)	6(12)	23(12)	-4(13)
C(71)	92(19)	60(16)	84(20)	7(15)	-7(17)	48(16)
C(72)	69(16)	146(25)	31(13)	24(17)	8(12)	-8(18)
O(73)	82(11)	78(11)	45(10)	-21(10)	5(8)	10(10)
C(74)	56(15)	100(21)	59(17)	15(15)	16(13)	9(17)
C(75)	93(19)	102(22)	70(19)	-13(16)	39(15)	-17(16)
O(76)	60(9)	56(9)	55(10)	-9(7)	9(7)	-5(8)
C(77)	55(15)	54(18)	105(22)	2(12)	29(16)	-9(16)
C(78)	49(13)	80(20)	96(23)	13(13)	26(14)	13(19)
C(79)	74(18)	103(23)	109(24)	-9(16)	9(17)	51(22)
C(80)	134(27)	47(20)	152(34)	-21(18)	23(26)	16(23)
C(81)	63(18)	74(24)	217(45)	12(15)	-18(27)	-51(29)
C(82)	94(20)	39(15)	124(25)	12(13)	13(18)	12(17)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

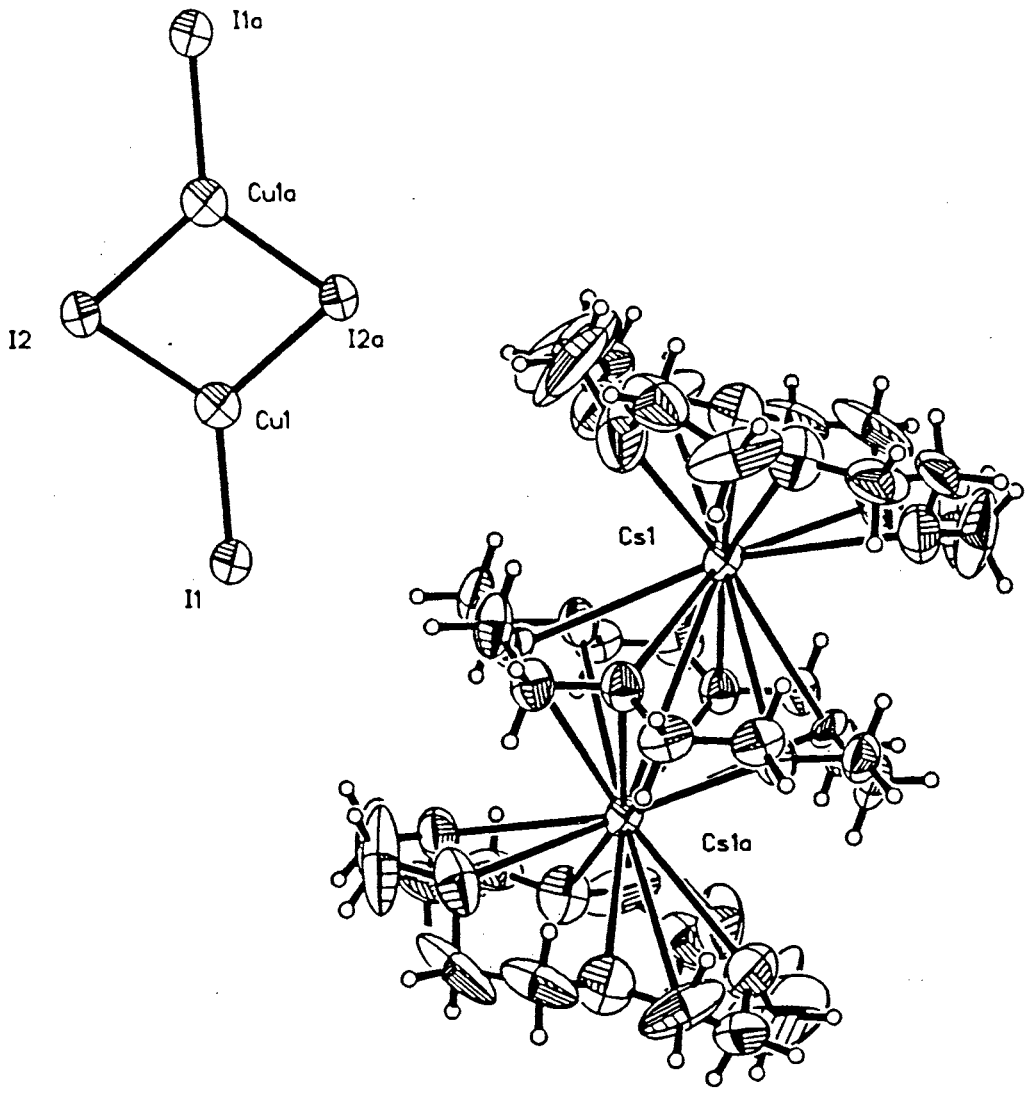


Figure 22. Projection View of $[Cs_2(18\text{-Crown-6})_3]Cu_2I_4$ (**VI**)

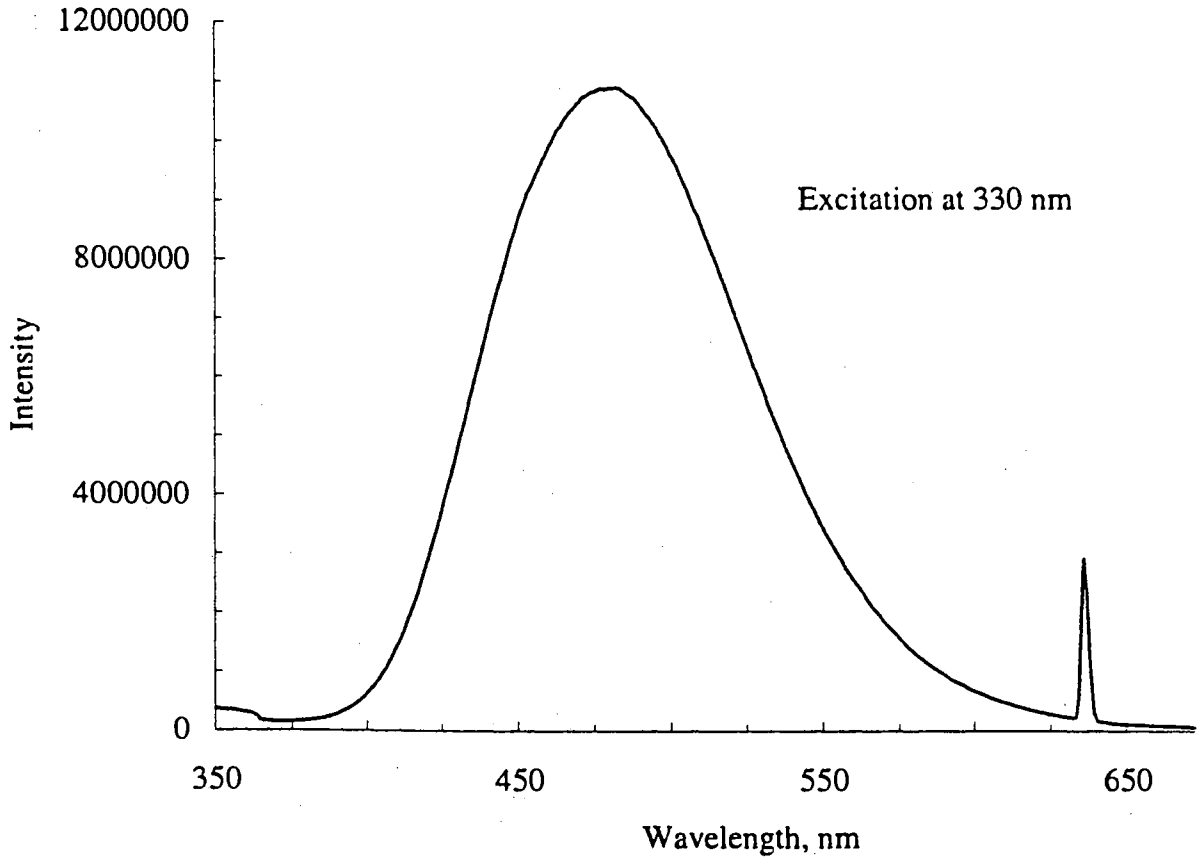


Figure 23. Emission spectrum of $[Cs_2(18\text{-Crown-}6)_3]Cu_2I_4$ (**VI**)

TABLE 31

CRYSTAL DATA FOR

$[Cs_2(18\text{-Crown-}6)_3]Cu_2I_4$ (**VI**)

Formula	$C_{36}H_{72}Cs_2Cu_2I_4O_{18}$
Space group	C2/m
a	15.991(4) Å
b	13.580(4) Å
c	12.990(5) Å
β	96.61(3)°
V	2807.4(15) $Å^3$
Z	2
Mw	1693.4 g $mole^{-1}$
Density (calc.)	2.003 Mg m^{-3}
$\mu(MoK_\alpha)$	4.295 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	1624
Collected Reflections	5012
Independent Reflections	4253
Number of parameters	151
Observed Reflections ($F > 4.0\sigma$)	2145
Final R indices	R = 5.91 %, R_w = 7.47 %
R indices (all data)	R = 10.67 %, R_w = 9.68 %
GOF	1.64

TABLE 32

POSITIONAL PARAMETERS FOR

$[Cs_2(18\text{-Crown-6})_3]Cu_2I_4$ (**VI**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	-0.4610(1)	0.0	0.3139(1)
I(2)	-0.6258(1)	0.0	0.0046(1)
Cu(1)	-0.4856(1)	0.0	0.1216(1)
Cs(1)	0.0377(1)	0.0	0.3382(1)
C(1)	-0.1374(14)	0.030(3)	0.076(2)
H(1A)	-0.1204	0.0510	0.0105
H(1B)	-0.1945	0.0510	0.0768
O(1)	-0.0935(6)	0.0995(10)	0.1601(10)
C(2)	-0.0753(11)	0.177(2)	0.1102(12)
H(2A)	-0.1250	0.2163	0.0929
H(2B)	-0.0570	0.1542	0.0467
C(3)	-0.0024(13)	0.2339(9)	0.1664(12)
H(3A)	-0.0188	0.2566	0.2311
H(3B)	0.0079	0.2900	0.1247
O(4)	0.0670(6)	0.1788(6)	0.1832(8)
C(5)	0.1397(12)	0.2285(12)	0.2066(10)
H(5A)	0.1386	0.2514	0.2764
H(5B)	0.1436	0.2851	0.1631
C(6)	0.2152(11)	0.1733(16)	0.2115(13)
H(6A)	0.2653	0.2128	0.2167
H(6B)	0.2110	0.1372	0.1476
O(7)	0.2152(4)	0.1035(6)	0.2964(8)
C(8)	0.2875(6)	0.0442(12)	0.312(2)
H(8A)	0.3196	0.0638	0.3752
H(8B)	0.3196	0.0638	0.2569
O(11)	-0.1670(5)	0.0	0.4374(7)
C(12)	-0.2011(5)	0.0869(8)	0.3887(11)
H(12A)	-0.2613	0.0861	0.3863
H(12B)	-0.1871	0.0892	0.3188
C(13)	-0.1677(5)	0.1704(7)	0.4436(9)
H(13A)	-0.1923	0.2282	0.4102
H(13B)	-0.1838	0.1684	0.5125
O(14)	-0.0804(4)	0.1777(4)	0.4494(5)
C(15)	-0.0450(7)	0.2594(7)	0.4951(9)
H(15A)	-0.0658	0.3163	0.4563
H(15B)	-0.0622	0.2649	0.5633

TABLE 33

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[Cs_2(18\text{-Crown-}6)_3]Cu_2I_4$ (**VI**)

Cs(1)-O(1)	3.235 (12)	C(1)-C(1^{ii})	0.81 (9)
Cs(1)-O(4)	3.223 (9)	O(1)-C(2)	1.29 (2)
Cs(1)-O(7)	3.268 (8)	C(2)-C(3)	1.51 (2)
Cs(1)-O(11)	3.653 (8)	C(3)-O(4)	1.33 (2)
Cs(1)-O(14)	3.479 (6)	O(4)-C(5)	1.35 (2)
Cs(1)-Cs(1^{i})	4.505 (2)	C(5)-C(6)	1.42 (3)
Cs(1)-O(1^{ii})	3.235 (12)	C(6)-O(7)	1.45 (2)
Cs(1)-O(4^{ii})	3.223 (9)	O(7)-C(8)	1.406 (15)
Cs(1)-O(7^{ii})	3.268 (8)	C(8)-C(8^{ii})	1.20 (3)
Cs(1)-O(11^{ii})	3.375 (8)	O(11)-C(12)	1.417 (12)
Cs(1)-O(14^{iii})	3.670 (7)	O(11)-Cs(1^{i})	3.375 (8)
Cs(1)-O(14^{iv})	3.670 (7)	O(11)-C(12^{ii})	1.417 (12)
Cs(1)-O(14^{ii})	3.479 (6)	C(15)-O(14)	1.352 (11)
I(1)-Cu(1)	2.484 (2)	C(15)-C(15^{iv})	1.43 (2)
I(2)-Cu(1)	2.559 (2)	O(14)-C(13)	1.393 (10)
I(2)-Cu(1^{v})	2.556 (2)	O(14)-Cs(1^{i})	3.670 (7)
Cu(1)-I(2^{v})	2.556 (2)	C(13)-C(12)	1.411 (15)
C(1)-O(1)	1.56 (3)		

O(1)-Cs(1)-O(4)	50.8(3)	O(4'')-Cs(1)-O(14^{iii})	86.9(2)
O(1)-Cs(1)-O(7)	101.9(3)	O(7'')-Cs(1)-O(14^{iii})	75.6(2)
O(4)-Cs(1)-O(7)	51.7(2)	O(11'')-Cs(1)-O(14^{iii})	46.2(1)
O(1)-Cs(1)-O(11)	73.6(2)	O(1)-Cs(1)-O(14^{iv})	108.2(3)
O(4)-Cs(1)-O(11)	114.9(2)	O(4)-Cs(1)-O(14^{iv})	86.9(2)
O(7)-Cs(1)-O(11)	152.8(2)	O(7)-Cs(1)-O(14^{iv})	75.6(2)
O(1)-Cs(1)-O(14)	70.7(3)	O(11)-Cs(1)-O(14^{iv})	80.3(1)
O(4)-Cs(1)-O(14)	82.1(2)	O(14)-Cs(1)-O(14^{iv})	45.1(2)
O(7)-Cs(1)-O(14)	107.1(2)	O(1'')-Cs(1)-O(14^{iv})	149.5(2)
O(11)-Cs(1)-O(14)	45.8(1)	O(4'')-Cs(1)-O(14^{iv})	159.6(2)
O(1)-Cs(1)-O(1^{ii})	49.4(5)	O(7'')-Cs(1)-O(14^{iv})	108.5(2)
O(4)-Cs(1)-O(1^{ii})	89.8(3)	O(11'')-Cs(1)-O(14^{iv})	46.2(1)
O(7)-Cs(1)-O(1^{ii})	124.4(3)	O(14''')-Cs(1)-O(14^{iv})	82.2(2)
O(11)-Cs(1)-O(1^{ii})	73.6(2)	O(1)-Cs(1)-O(14^{ii})	104.4(2)
O(14)-Cs(1)-O(1^{ii})	104.4(2)	O(4)-Cs(1)-O(14^{ii})	155.1(2)
O(1)-Cs(1)-O(4^{ii})	89.8(3)	O(7)-Cs(1)-O(14^{ii})	152.9(2)
O(4)-Cs(1)-O(4^{ii})	97.8(3)	O(11)-Cs(1)-O(14^{ii})	45.8(1)
O(7)-Cs(1)-O(4^{ii})	91.7(2)	O(14)-Cs(1)-O(14^{ii})	87.8(2)
O(11)-Cs(1)-O(4^{ii})	114.9(2)	O(1'')-Cs(1)-O(14^{ii})	70.7(3)
O(14)-Cs(1)-O(4^{ii})	155.1(2)	O(4'')-Cs(1)-O(14^{ii})	82.1(2)
O(1'')-Cs(1)-O(4^{ii})	50.8(3)	O(7'')-Cs(1)-O(14^{ii})	107.1(2)

TABLE 33 (Continued)

O(1)-Cs(1)-O(7^{ii})	124.4(3)	O(11^{ii})-Cs(1)-O(14^{ii})	87.1(1)
O(4)-Cs(1)-O(7^{ii})	91.7(2)	O(14^{iii})-Cs(1)-O(14^{ii})	45.1(2)
O(7)-Cs(1)-O(7^{ii})	51.0(3)	O(14^{iv})-Cs(1)-O(14^{ii})	101.9(1)
O(11)-Cs(1)-O(7^{ii})	152.8(2)	Cu(1)-I(2)-Cu(1^{v})	75.7(1)
O(14)-Cs(1)-O(7^{ii})	152.9(2)	I(1)-Cu(1)-I(2)	128.5(1)
O(1^{ii})-Cs(1)-O(7^{ii})	101.9(3)	I(1)-Cu(1)-I(2^{v})	127.1(1)
O(4^{ii})-Cs(1)-O(7^{ii})	51.7(2)	I(2)-Cu(1)-I(2^{v})	104.3(1)
O(1)-Cs(1)-O(11^{ii})	154.2(2)	O(1)-C(1)-C(1^{ii})	127.5(14)
O(4)-Cs(1)-O(11^{ii})	114.9(2)	C(1)-O(1)-C(2)	105(2)
O(7)-Cs(1)-O(11^{ii})	71.7(2)	O(1)-C(2)-C(3)	112.3(13)
O(11)-Cs(1)-O(11^{ii})	100.4(2)	C(2)-C(3)-O(4)	112.0(12)
O(14)-Cs(1)-O(11^{ii})	87.1(1)	C(3)-O(4)-C(5)	115.8(11)
O(1^{ii})-Cs(1)-O(11^{ii})	154.2(2)	O(4)-C(5)-C(6)	117.0(14)
C(3A)-Cs(1)-O(11^{ii})	122.6(2)	C(5)-C(6)-O(7)	107.7(14)
O(4^{ii})-Cs(1)-O(11^{ii})	114.9(2)	C(6)-O(7)-C(8)	114.0(12)
O(7^{ii})-Cs(1)-O(11^{ii})	71.7(2)	O(7)-C(8)-C(8^{ii})	125.0(7)
O(1)-Cs(1)-O(14^{iii})	149.5(2)	C(12)-O(11)-C(12^{ii})	112.7(11)
O(4)-Cs(1)-O(14^{iii})	159.6(2)	O(14)-C(15)-C(15^{iv})	113.9(7)
O(7)-Cs(1)-O(14^{iii})	108.5(2)	C(15)-O(14)-C(13)	116.6(8)
O(11)-Cs(1)-O(14^{iii})	80.3(1)	O(14)-C(13)-C(12)	113.8(8)
O(14)-Cs(1)-O(14^{iii})	101.9(1)	O(11)-C(12)-C(13)	109.8(9)
O(1^{ii})-Cs(1)-O(14^{iii})	108.2(3)		

Symmetry operations:

^{i} = -x, 0, 1-z
^{ii} = x, -y, z
^{iii} = -x, -y, 1-z
^{iv} = -x, y, 1-z
^{v} = -1-x, 0, -z

TABLE 34

ANISOTROPIC THERMAL PARAMETERS FOR

$[Cs_2(18\text{-Crown-}6)_3]Cu_2I_4$ (**VI**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	74(1)	79(1)	85(1)	0	6(1)	0
I(2)	65(1)	186(1)	85(1)	0	16(1)	0
Cu(1)	92(1)	69(1)	90(1)	0	17(1)	0
Cs(1)	68(1)	68(1)	77(1)	0	-4(1)	0
C(1)	329(33)	1017(140)	316(33)	-328(72)	-252(29)	174(74)
O(1)	111(7)	276(13)	192(11)	-8(8)	-3(7)	117(11)
C(2)	165(14)	246(21)	111(10)	75(14)	40(11)	78(13)
C(3)	325(25)	81(9)	122(11)	80(13)	-78(13)	-8(8)
O(4)	142(7)	86(5)	164(7)	-14(5)	16(6)	17(5)
C(5)	227(18)	177(15)	89(8)	-116(15)	64(11)	-17(9)
C(6)	235(22)	353(31)	133(12)	-217(23)	127(15)	-112(16)
O(7)	90(5)	142(7)	176(8)	-28(5)	42(5)	-60(6)
C(8)	64(7)	232(25)	440(36)	3(8)	25(12)	-204(24)
O(11)	66(5)	106(8)	95(7)	-25(13)	-3(5)	-61(13)
C(12)	57(5)	106(8)	159(11)	9(5)	-7(5)	42(8)
C(13)	71(5)	89(7)	112(7)	27(5)	5(5)	10(6)
O(14)	79(4)	80(4)	113(5)	3(3)	16(4)	-7(4)
C(15)	122(8)	64(6)	91(6)	8(4)	2(7)	-2(5)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

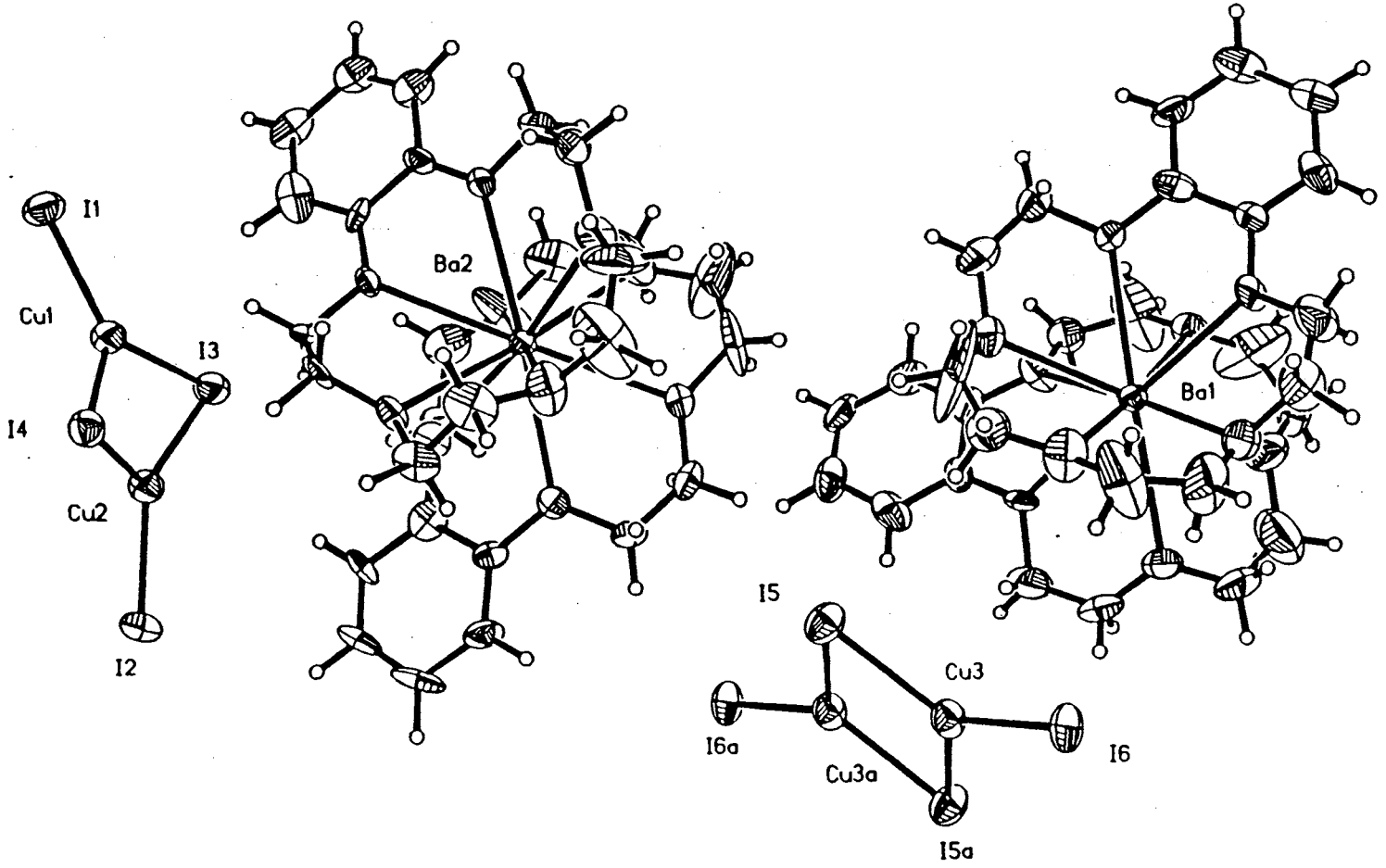


Figure 24. Projection View of $[Ba(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ **(VII)**

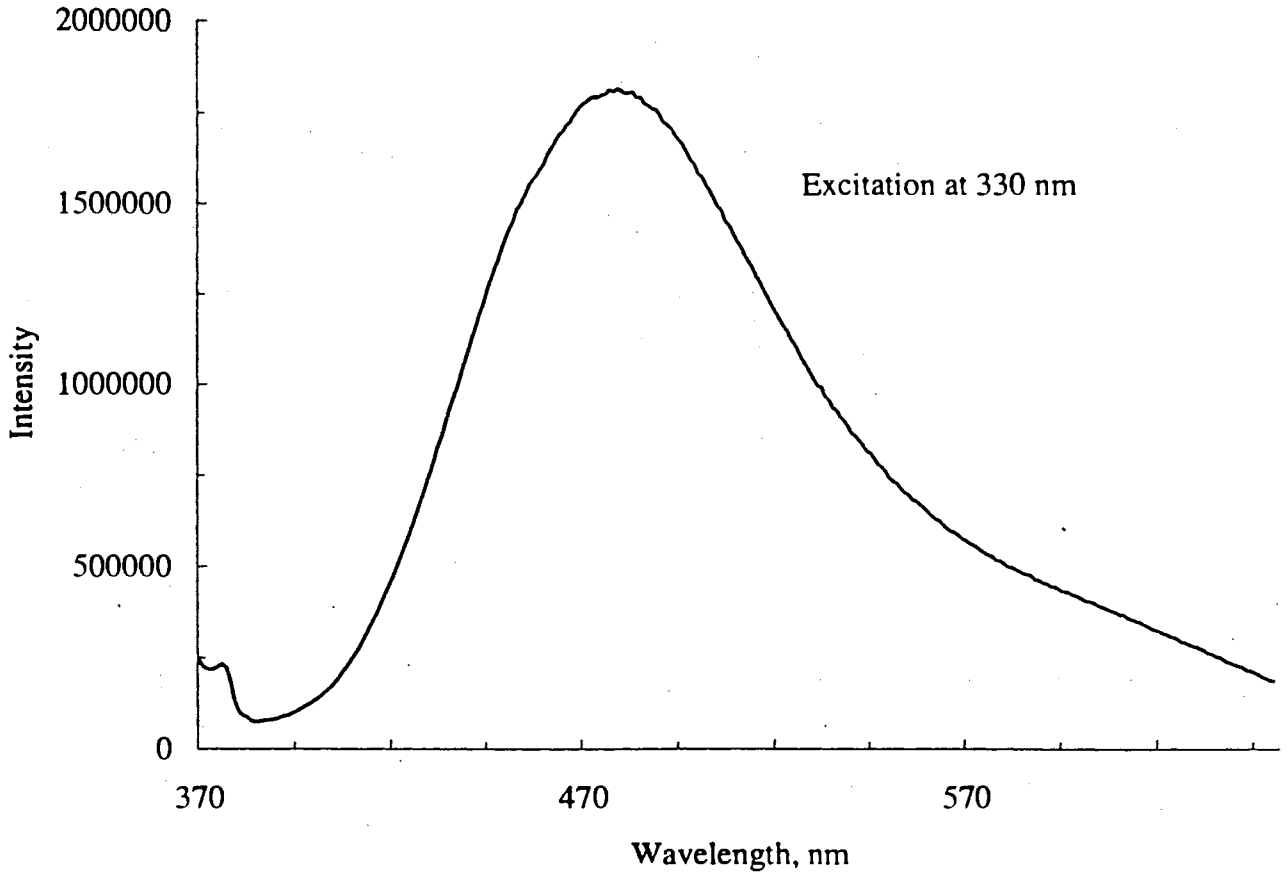


Figure 25. Emission Spectrum of $[Ba(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ **(VII)**

TABLE 35

CRYSTAL DATA FOR

$[Ba(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ (**VII**)

Formula	$C_{84}H_{120}Ba_3Cu_6I_{12}O_{30}$
Space group	C2/c
a	34.00(3) Å
b	20.75(2) Å
c	23.14(3) Å
β	132.34(5)°
V	12048(22) $Å^3$
Z	4
Mw	3925.8 g $mole^{-1}$
Density (calc.)	2.164 Mg m^{-3}
$\mu(MoK_\alpha)$	5.139 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	7368
Collected Reflections	14300
Independent Reflections	13017
Observed Reflections ($F > 4.0\sigma$)	4354
Number of parameters	610
Final R indices	R = 6.37 %, R_w = 7.19 %
R indices (all data)	R = 18.59 %, R_w = 13.09 %
GOF	1.47

TABLE 36

POSITIONAL PARAMETERS FOR

$[Ba(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ (**VII**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.5777(1)	-0.4077(1)	1.0880(1)
I(2)	0.6734(1)	-0.1271(1)	1.0084(1)
I(3)	0.5568(1)	-0.2889(1)	0.9061(1)
I(4)	0.6111(1)	-0.1929(1)	1.1192(1)
I(5)	0.1517(1)	0.3686(1)	0.4713(1)
I(6)	0.2526(1)	0.1948(1)	0.5857(1)
Cu(1)	0.5846(1)	-0.3016(1)	1.0433(2)
Cu(2)	0.6168(1)	-0.2011(1)	1.0125(2)
Cu(3)	0.2155(1)	0.2909(1)	0.4894(2)
Ba(1)	0.0	0.1159(1)	0.25
Ba(2)	0.3361(1)	-0.1131(1)	0.7592(1)
O(1)	0.4038(4)	-0.2001(6)	0.8837(7)
C(2)	0.4568(7)	-0.1801(9)	0.9467(11)
H(2A)	0.4741	-0.1711	0.9276
H(2B)	0.4762	-0.2131	0.9858
C(3)	0.4539(7)	-0.1170(10)	0.9741(12)
H(3A)	0.4882	-0.1004	1.0187
H(3B)	0.4334	-0.1246	0.9882
O(4)	0.4274(5)	-0.0735(7)	0.9124(7)
C(5)	0.4229(10)	-0.0082(11)	0.9311(14)
H(5A)	0.4232	0.0191	0.8979
H(5B)	0.4538	0.0014	0.9845
C(6)	0.3720(12)	-0.0017(12)	0.9134(15)
H(6A)	0.3705	0.0416	0.9264
H(6B)	0.3690	-0.0315	0.9420
O(7)	0.3286(7)	-0.0100(8)	0.8284(10)
C(8)	0.2787(13)	-0.004(2)	0.803(2)
H(8A)	0.2584	0.0320	0.7688
H(8B)	0.2899	0.0080	0.8526
C(9)	0.2473(15)	-0.052(2)	0.787(3)
H(9A)	0.2124	-0.0361	0.7437
H(9B)	0.2475	-0.0646	0.8270
O(10)	0.2530(6)	-0.1090(9)	0.7558(9)
C(11)	0.2367(9)	-0.1667(13)	0.773(2)
H(11A)	0.1993	-0.1645	0.7447
H(11B)	0.2557	-0.1676	0.8279

TABLE 36 (Continued)

C(12)	0.2508(9)	-0.2234(11)	0.7617(14)
H(12A)	0.2278	-0.2264	0.7059
H(12B)	0.2448	-0.2604	0.7799
O(13)	0.3042(5)	-0.2207(7)	0.7929(8)
C(14)	0.3346(8)	-0.2742(11)	0.8201(11)
C(15)	0.3902(8)	-0.2658(10)	0.8665(11)
C(16)	0.4238(10)	-0.3170(15)	0.8974(14)
H(16A)	0.4614	-0.3099	0.9380
C(17)	0.4048(12)	-0.3806(11)	0.879(2)
H(17A)	0.4290	-0.4160	0.8982
C(18)	0.3476(11)	-0.3897(11)	0.8267(14)
H(18A)	0.3332	-0.4326	0.8105
C(19)	0.3156(11)	-0.3413(11)	0.8005(14)
H(19A)	0.2788	-0.3485	0.7734
O(21)	0.4304(5)	-0.1259(7)	0.7830(8)
C(22)	0.4273(9)	-0.1707(12)	0.732(2)
H(22A)	0.4633	-0.1846	0.7618
H(22B)	0.4150	-0.1510	0.6850
C(23)	0.3950(13)	-0.2261(13)	0.714(2)
H(23A)	0.4134	-0.2537	0.7587
H(23B)	0.3891	-0.2499	0.6730
O(24)	0.3463(8)	-0.2098(10)	0.6870(12)
C(25)	0.2989(14)	-0.2418(14)	0.624(2)
H(25A)	0.2912	-0.2672	0.6499
H(25B)	0.3041	-0.2713	0.5975
C(26)	0.2515(13)	-0.206(2)	0.576(2)
H(26A)	0.2196	-0.2313	0.5464
H(26B)	0.2538	-0.1871	0.5400
O(27)	0.2464(7)	-0.1612(9)	0.6125(9)
C(28)	0.206(2)	-0.121(2)	0.560(2)
H(28A)	0.1920	-0.1169	0.5845
H(28B)	0.1785	-0.1386	0.5089
C(29)	0.2144(10)	-0.063(2)	0.560(2)
H(29A)	0.1864	-0.0342	0.5445
H(29B)	0.2141	-0.0636	0.5184
O(30)	0.2659(6)	-0.0299(8)	0.6275(9)
C(31)	0.2895(10)	0.0078(12)	0.6035(14)
H(31A)	0.2648	0.0391	0.5643
H(31B)	0.3006	-0.0192	0.5830
C(32)	0.3395(9)	0.0379(12)	0.6788(14)
H(32A)	0.3308	0.0595	0.7057
H(32B)	0.3551	0.0680	0.6678
O(33)	0.3746(6)	-0.0168(7)	0.7248(9)
C(34)	0.4302(9)	-0.0109(10)	0.7714(12)
C(35)	0.4585(10)	-0.0698(11)	0.7995(12)

TABLE 36 (Continued)

C(36)	0.5141(8)	-0.0674(12)	0.8497(12)
H(36A)	0.5332	-0.1072	0.8730
C(37)	0.5389(10)	-0.0132(14)	0.8652(15)
H(37A)	0.5767	-0.0114	0.8966
C(38)	0.5135(12)	0.0485(15)	0.841(2)
H(38A)	0.5320	0.0880	0.8514
C(39)	0.4588(10)	0.0475(10)	0.7949(15)
H(39A)	0.4401	0.0878	0.7770
O(41)	0.0426(6)	0.0118(7)	0.2264(9)
C(42)	0.0089(10)	-0.0281(12)	0.156(2)
H(42A)	0.0190	-0.0727	0.1672
H(42B)	0.0168	-0.0120	0.1254
C(43)	-0.0424(14)	-0.012(2)	0.105(2)
H(43A)	-0.0505	-0.0381	0.1296
H(43B)	-0.0622	-0.0286	0.0530
O(44)	-0.0645(7)	0.0434(9)	0.1086(10)
C(45)	-0.096(2)	0.074(2)	0.047(2)
H(45A)	-0.1307	0.0554	0.0123
H(45B)	-0.0800	0.0640	0.0255
C(46)	-0.0977(12)	0.1395(14)	0.0363(15)
H(46A)	-0.1310	0.1493	0.0217
H(46B)	-0.0990	0.1563	-0.0037
O(47)	-0.0624(8)	0.1754(10)	0.1038(11)
C(48)	-0.0410(15)	0.233(2)	0.096(2)
H(48A)	-0.0709	0.2604	0.0592
H(48B)	-0.0233	0.2243	0.0781
C(49)	0.0025(15)	0.2608(14)	0.161(2)
H(49A)	-0.0185	0.2765	0.1715
H(49B)	0.0156	0.2980	0.1535
O(50)	0.0396(7)	0.2269(8)	0.2316(11)
C(51)	0.0901(13)	0.2241(14)	0.260(2)
H(51A)	0.1064	0.2637	0.2882
H(51B)	0.0893	0.2247	0.2175
C(52)	0.1232(12)	0.1750(14)	0.302(2)
H(52A)	0.1392	0.1863	0.3541
H(52B)	0.1513	0.1713	0.3019
O(53)	0.0997(5)	0.1154(7)	0.2966(9)
C(54)	0.1278(9)	0.0598(12)	0.3155(12)
C(55)	0.0967(10)	0.0029(13)	0.2773(14)
C(56)	0.1233(12)	-0.0552(11)	0.297(2)
H(56A)	0.1025	-0.0940	0.2790
C(57)	0.1781(12)	-0.0598(14)	0.350(2)
H(57A)	0.1957	-0.0998	0.3591
C(58)	0.2080(11)	-0.0037(15)	0.3883(15)
H(58A)	0.2461	-0.0044	0.4281

TABLE 36 (Continued)

C(59)	0.1814(10)	0.0561(15)	0.3683(15)
H(59A)	0.2005	0.0958	0.3917

TABLE 37

BOND DISTANCES () AND BOND ANGLES (°) FOR

$[Ba(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ (**VII**)

I(1)-Cu(1)	2.508 (5)	C(14)-C(15)	1.42 (3)
I(2)-Cu(2)	2.513 (6)	C(14)-C(19)	1.47 (3)
I(3)-Cu(1)	2.645 (6)	C(15)-C(16)	1.36 (4)
I(3)-Cu(2)	2.603 (4)	C(16)-C(17)	1.40 (4)
I(4)-Cu(1)	2.618 (5)	C(17)-C(18)	1.45 (4)
I(4)-Cu(2)	2.608 (6)	C(18)-C(19)	1.29 (4)
I(5)-Cu(3)	2.502 (5)	O(21)-C(22)	1.44 (4)
I(6)-Cu(3)	2.596 (5)	O(21)-C(35)	1.39 (3)
I(6)-Cu(3^{i})	2.609 (7)	C(22)-C(23)	1.44 (4)
Cu(1)...Cu(2)	2.666 (6)	C(23)-O(24)	1.36 (5)
Cu(3)-I(6i)	2.609 (7)	O(24)-C(25)	1.42 (3)
Cu(3)...Cu(3^{i})	2.658 (8)	C(25)-C(26)	1.40 (5)
Ba(1)-O(41)	2.85 (2)	C(26)-O(27)	1.35 (5)
Ba(1)-O(44)	2.85 (2)	O(27)-C(28)	1.35 (4)
Ba(1)-O(47)	2.79 (2)	C(28)-C(29)	1.24 (5)
Ba(1)-O(50)	2.84 (2)	C(29)-O(30)	1.51 (3)
Ba(1)-O(53)	2.78 (2)	O(30)-C(31)	1.47 (4)
Ba(1)-O(41^{ii})	2.85 (2)	C(31)-C(32)	1.52 (3)
Ba(1)-O(44^{ii})	2.85 (2)	C(32)-O(33)	1.46 (3)
Ba(1)-O(47^{ii})	2.79 (2)	O(33)-C(34)	1.42 (3)
Ba(1)-O(50^{ii})	2.84 (2)	C(34)-C(35)	1.41 (3)
Ba(1)-O(53^{ii})	2.78 (2)	C(34)-C(39)	1.41 (3)
Ba(2)-O(1)	2.816 (12)	C(35)-C(36)	1.40 (3)
Ba(2)-O(4)	2.838 (11)	C(36)-C(37)	1.30 (4)
Ba(2)-O(7)	2.78 (2)	C(37)-C(38)	1.43 (4)
Ba(2)-O(10)	2.77 (2)	C(38)-C(39)	1.39 (4)
Ba(2)-O(13)	2.81 (2)	O(41)-C(42)	1.47 (3)
Ba(2)-O(21)	2.88 (2)	O(41)-C(55)	1.37 (3)
Ba(2)-O(24)	2.78 (3)	C(42)-C(43)	1.34 (4)
Ba(2)-O(27)	2.805 (14)	C(43)-O(44)	1.40 (5)
Ba(2)-O(30)	2.857 (15)	O(44)-C(45)	1.24 (4)
Ba(2)-O(33)	2.78 (2)	C(45)-C(46)	1.37 (5)
O(1)-C(2)	1.42 (2)	C(46)-O(47)	1.38 (3)
O(1)-C(15)	1.41 (2)	O(47)-C(48)	1.46 (6)
C(2)-C(3)	1.49 (3)	C(48)-C(49)	1.33 (4)
C(3)-O(4)	1.39 (2)	C(49)-O(50)	1.41 (4)
O(4)-C(5)	1.46 (3)	O(50)-C(51)	1.37 (5)
C(5)-C(6)	1.49 (6)	C(51)-C(52)	1.33 (4)
C(6)-O(7)	1.47 (3)	C(52)-O(53)	1.43 (4)
C(7)-C(8)	1.38 (5)	O(53)-C(54)	1.37 (3)

TABLE 37 (Continued)

C(8)-C(9)	1.33 (6)	C(54)-C(55)	1.43 (3)
C(9)-O(10)	1.45 (6)	C(54)-C(59)	1.35 (3)
O(10)-C(11)	1.48 (4)	C(55)-C(56)	1.39 (4)
C(11)-C(12)	1.36 (4)	C(56)-C(57)	1.38 (4)
C(12)-O(13)	1.44 (3)	C(57)-C(58)	1.40 (4)
O(13)-C(14)	1.35 (3)	C(58)-C(59)	1.42 (4)
Cu(1)-I(3)-Cu(2)	61.0(1)	O(4)-Ba(2)-O(30)	125.6(4)
Cu(1)-I(4)-Cu(2)	61.3(2)	O(7)-Ba(2)-O(30)	79.4(5)
Cu(3)-I(6)-Cu(3^{i})	61.4(2)	O(10)-Ba(2)-O(30)	81.3(6)
I(1)-Cu(1)-I(3)	121.6(2)	O(13)-Ba(2)-O(30)	125.0(4)
I(1)-Cu(1)-I(4)	124.5(2)	O(21)-Ba(2)-O(30)	106.4(6)
I(3)-Cu(1)-I(4)	113.7(2)	O(24)-Ba(2)-O(30)	98.5(6)
I(2)-Cu(2)-I(3)	121.6(2)	O(27)-Ba(2)-O(30)	58.6(5)
I(2)-Cu(2)-I(4)	122.8(1)	O(1)-Ba(2)-O(33)	122.3(4)
I(3)-Cu(2)-I(4)	115.5(2)	O(4)-Ba(2)-O(33)	79.6(5)
I(5)-Cu(3)-I(6)	120.3(2)	O(7)-Ba(2)-O(33)	81.8(7)
I(5)-Cu(3)-I(6^{i})	121.1(2)	O(10)-Ba(2)-O(33)	129.6(6)
I(6)-Cu(3)-I(6^{i})	118.6(2)	O(13)-Ba(2)-O(33)	173.2(6)
O(41)-Ba(1)-O(44)	58.5(5)	O(21)-Ba(2)-O(33)	56.1(5)
O(41)-Ba(1)-O(47)	100.0(7)	O(24)-Ba(2)-O(33)	94.2(8)
O(44)-Ba(1)-O(47)	58.2(5)	O(27)-Ba(2)-O(33)	104.3(6)
O(41)-Ba(1)-O(50)	103.4(7)	O(30)-Ba(2)-O(33)	58.5(5)
O(44)-Ba(1)-O(50)	109.4(7)	C(2)-O(1)-C(15)	121.6(13)
O(47)-Ba(1)-O(50)	60.7(6)	O(1)-C(2)-C(3)	107(2)
O(41)-Ba(1)-O(53)	55.1(5)	C(2)-C(3)-O(4)	108(2)
O(44)-Ba(1)-O(53)	103.7(6)	C(3)-O(4)-C(5)	115(2)
O(47)-Ba(1)-O(53)	101.8(8)	O(4)-C(5)-C(6)	110(2)
O(50)-Ba(1)-O(53)	58.9(5)	C(5)-C(6)-O(7)	107(3)
O(41)-Ba(1)-O(41^{ii})	81.4(9)	C(6)-O(7)-C(8)	113(3)
O(44)-Ba(1)-O(41^{ii})	73.9(6)	O(7)-C(8)-C(9)	125(4)
O(47)-Ba(1)-O(41^{ii})	119.8(6)	C(8)-C(9)-O(10)	114(6)
O(50)-Ba(1)-O(41^{ii})	175.0(7)	C(9)-O(10)-C(11)	109(4)
O(53)-Ba(1)-O(41^{ii})	124.5(5)	O(10)-C(11)-C(12)	114(4)
O(41)-Ba(1)-O(44^{ii})	73.9(6)	C(11)-C(12)-O(13)	111(2)
O(44)-Ba(1)-O(44^{ii})	116.3(7)	C(12)-O(13)-C(14)	121(2)
O(47)-Ba(1)-O(44^{ii})	173.7(7)	O(13)-C(14)-C(15)	118(2)
O(50)-Ba(1)-O(44^{ii})	121.6(5)	O(13)-C(14)-C(19)	126(2)
O(53)-Ba(1)-O(44^{ii})	76.0(6)	C(15)-C(14)-C(19)	116(2)
O(41^{ii})-Ba(1)-O(44^{ii})	58.5(5)	O(1)-C(15)-C(14)	110(2)
O(41)-Ba(1)-O(47^{ii})	119.8(6)	O(1)-C(15)-C(16)	128(2)
O(44)-Ba(1)-O(47^{ii})	173.7(7)	C(14)-C(15)-C(16)	121(2)
O(47)-Ba(1)-O(47^{ii})	127.5(8)	C(15)-C(16)-C(17)	122(2)
O(50)-Ba(1)-O(47^{ii})	76.9(7)	C(16)-C(17)-C(18)	117(2)
O(53)-Ba(1)-O(47^{ii})	78.4(8)	C(17)-C(18)-C(19)	121(2)

TABLE 37 (Continued)

O(41^{ii})-Ba(1)-O(47^{ii})	100.0(7)	C(14)-C(19)-C(18)	122(3)
O(44^{ii})-Ba(1)-O(47^{ii})	58.2(5)	C(22)-O(21)-C(35)	115(3)
O(41)-Ba(1)-O(50^{ii})	175.0(7)	O(21)-C(22)-C(23)	112(4)
O(44)-Ba(1)-O(50^{ii})	121.6(5)	C(22)-C(23)-O(24)	113(2)
O(47)-Ba(1)-O(50^{ii})	76.9(7)	C(23)-O(24)-C(25)	123(3)
O(50)-Ba(1)-O(50^{ii})	71.7(11)	O(24)-C(25)-C(26)	118(3)
O(53)-Ba(1)-O(50^{ii})	121.5(5)	C(25)-C(26)-O(27)	115(3)
O(41^{ii})-Ba(1)-O(50^{ii})	103.4(7)	C(26)-O(27)-C(28)	110(3)
O(44^{ii})-Ba(1)-O(50^{ii})	109.4(7)	O(27)-C(28)-C(29)	121(3)
O(47^{ii})-Ba(1)-O(50^{ii})	60.7(6)	C(28)-C(29)-O(30)	123(2)
O(41)-Ba(1)-O(53^{ii})	124.5(5)	C(29)-O(30)-C(31)	113(2)
O(44)-Ba(1)-O(53^{ii})	76.0(6)	O(30)-C(31)-C(32)	105(2)
O(47)-Ba(1)-O(53^{ii})	78.4(8)	C(31)-C(32)-O(33)	104(2)
O(50)-Ba(1)-O(53^{ii})	121.5(5)	C(32)-O(33)-C(34)	120(2)
O(53)-Ba(1)-O(53^{ii})	179.6(6)	O(33)-C(34)-C(35)	115(2)
O(41^{ii})-Ba(1)-O(53^{ii})	55.1(5)	O(33)-C(34)-C(39)	126(2)
O(44^{ii})-Ba(1)-O(53^{ii})	103.7(6)	C(35)-C(34)-C(39)	119(2)
O(47^{ii})-Ba(1)-O(53^{ii})	101.8(8)	O(21)-C(35)-C(34)	118(2)
O(50^{ii})-Ba(1)-O(53^{ii})	58.9(5)	O(21)-C(35)-C(36)	124(2)
O(1)-Ba(2)-O(4)	57.0(4)	C(34)-C(35)-C(36)	118(2)
O(1)-Ba(2)-O(7)	103.4(5)	C(35)-C(36)-C(37)	121(2)
O(4)-Ba(2)-O(7)	60.4(5)	C(36)-C(37)-C(38)	124(3)
O(1)-Ba(2)-O(10)	99.4(5)	C(37)-C(38)-C(39)	116(3)
O(4)-Ba(2)-O(10)	105.3(6)	C(34)-C(39)-C(38)	122(2)
O(7)-Ba(2)-O(10)	60.5(6)	C(42)-O(41)-C(55)	118(2)
O(1)-Ba(2)-O(13)	53.8(4)	O(41)-C(42)-C(43)	114(3)
O(4)-Ba(2)-O(13)	100.7(4)	C(42)-C(43)-O(44)	126(3)
O(7)-Ba(2)-O(13)	104.4(7)	C(43)-O(44)-C(45)	115(4)
O(10)-Ba(2)-O(13)	57.1(5)	O(44)-C(45)-C(46)	128(3)
O(1)-Ba(2)-O(21)	73.0(5)	C(45)-C(46)-O(47)	116(2)
O(4)-Ba(2)-O(21)	69.3(5)	C(46)-O(47)-C(48)	115(3)
O(7)-Ba(2)-O(21)	118.9(6)	O(47)-C(48)-C(49)	119(4)
O(10)-Ba(2)-O(21)	172.2(5)	C(48)-C(49)-O(50)	122(3)
O(13)-Ba(2)-O(21)	117.5(5)	C(49)-O(50)-C(51)	115(4)
O(1)-Ba(2)-O(24)	78.7(6)	O(50)-C(51)-C(52)	124(4)
O(4)-Ba(2)-O(24)	119.0(5)	C(51)-C(52)-O(53)	117(3)
O(7)-Ba(2)-O(24)	175.9(8)	C(52)-O(53)-C(54)	118(2)
O(10)-Ba(2)-O(24)	122.8(7)	O(53)-C(54)-C(55)	116(2)
O(13)-Ba(2)-O(24)	79.7(8)	O(53)-C(54)-C(59)	124(2)
O(21)-Ba(2)-O(24)	58.3(6)	C(55)-C(54)-C(59)	120(2)
O(1)-Ba(2)-O(27)	118.9(4)	O(41)-C(55)-C(54)	115(2)
O(4)-Ba(2)-O(27)	175.7(5)	O(41)-C(55)-C(56)	127(2)
O(7)-Ba(2)-O(27)	121.5(6)	C(54)-C(55)-C(56)	118(2)
O(10)-Ba(2)-O(27)	73.7(7)	C(55)-C(56)-C(57)	123(2)
O(13)-Ba(2)-O(27)	75.2(5)	C(56)-C(57)-C(58)	118(3)

TABLE 37 (Continued)

O(21)-Ba(2)-O(27)	111.3(6)	C(57)-C(58)-C(59)	119(2)
O(24)-Ba(2)-O(27)	59.4(6)	C(54)-C(59)-C(58)	121(3)
O(1)-Ba(2)-O(30)	177.1(5)		

Symmetry operations:

[i] = 0.5-x, 0.5-y, 1-z

[ii] = -x, y, 0.5-z

TABLE 38

ANISOTROPIC THERMAL PARAMETERS FOR

$[Ba(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ (**VII**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	100(1)	62(1)	85(1)	-14(1)	62(1)	2(1)
I(2)	67(1)	61(1)	93(1)	-18(1)	61(1)	-19(1)
I(3)	72(1)	67(1)	67(1)	15(1)	44(1)	-6(1)
I(4)	62(1)	68(1)	65(1)	3(1)	42(1)	2(1)
I(5)	68(1)	82(1)	84(1)	31(1)	51(1)	13(1)
I(6)	92(1)	66(1)	92(1)	20(1)	70(1)	15(1)
Cu(1)	60(2)	63(2)	82(2)	3(2)	45(2)	13(2)
Cu(2)	56(2)	65(2)	79(2)	0(2)	45(2)	6(2)
Cu(3)	56(2)	59(2)	69(2)	7(1)	39(2)	-7(1)
Ba(1)	41(1)	39(1)	45(1)	0	31(1)	0
Ba(2)	34(1)	38(1)	36(1)	-3(1)	22(1)	-2(1)
O(1)	27(7)	39(8)	47(8)	-1(6)	12(7)	0(7)
C(2)	34(12)	55(14)	43(12)	-21(10)	16(11)	11(10)
C(3)	21(10)	56(15)	53(13)	-19(11)	7(10)	-21(12)
O(4)	33(8)	54(10)	50(9)	-5(7)	22(7)	-19(8)
C(5)	92(20)	42(15)	80(19)	-33(14)	45(17)	-47(14)
C(6)	111(25)	80(19)	102(21)	-3(17)	86(21)	-35(15)
O(7)	80(13)	75(12)	82(13)	20(10)	41(11)	-21(10)
C(8)	115(31)	161(39)	244(49)	22(27)	116(34)	-107(37)
C(9)	153(36)	102(31)	307(56)	-15(27)	190(42)	27(34)
O(10)	65(10)	78(13)	102(13)	12(9)	68(10)	2(10)
C(11)	50(15)	104(23)	113(22)	20(15)	60(16)	40(19)
C(12)	60(16)	63(17)	107(19)	-9(13)	63(16)	11(14)
O(13)	36(9)	51(9)	78(11)	4(8)	29(8)	20(8)
C(14)	42(13)	56(15)	36(12)	-24(11)	19(11)	-12(10)
C(15)	55(14)	39(13)	40(12)	24(11)	30(11)	23(10)
C(16)	72(18)	134(27)	54(16)	26(19)	49(15)	-9(17)
C(17)	117(24)	37(14)	103(20)	31(15)	93(20)	8(14)
C(18)	101(21)	40(15)	78(18)	-15(15)	60(17)	-18(13)
C(19)	96(20)	40(14)	80(18)	0(14)	62(16)	-8(13)
O(21)	67(10)	53(10)	65(10)	4(8)	54(9)	-17(8)
C(22)	56(16)	61(17)	113(22)	6(13)	59(16)	8(15)
C(23)	132(29)	75(21)	117(25)	-2(21)	93(24)	-12(18)
O(24)	86(14)	161(20)	159(19)	-73(14)	94(15)	-138(17)
C(25)	152(33)	66(21)	159(30)	-31(23)	118(28)	-62(22)
C(26)	90(26)	170(42)	115(28)	-27(26)	56(24)	-73(29)
O(27)	64(12)	82(13)	44(10)	-30(10)	17(9)	-20(10)

TABLE 38 (Continued)

C(28)	258(61)	113(36)	83(28)	-47(39)	-67(31)	11(29)
C(29)	41(18)	179(38)	68(20)	45(22)	-12(15)	-23(24)
O(30)	43(10)	75(12)	73(11)	-3(8)	18(9)	22(9)
C(31)	70(18)	61(17)	72(17)	15(14)	31(15)	31(14)
C(32)	69(18)	69(18)	77(18)	-22(15)	34(16)	22(15)
O(33)	45(10)	72(12)	83(11)	6(8)	43(9)	22(9)
C(34)	61(15)	53(14)	56(14)	-4(12)	51(13)	3(11)
C(35)	85(19)	56(16)	53(15)	0(14)	54(15)	-20(12)
C(36)	20(11)	89(19)	61(15)	-12(12)	18(11)	-14(14)
C(37)	49(16)	95(22)	90(20)	-43(16)	46(15)	-33(17)
C(38)	92(23)	82(22)	126(25)	-71(19)	73(21)	-54(19)
C(39)	73(18)	32(13)	110(21)	3(12)	66(17)	6(13)
O(41)	54(11)	72(11)	89(12)	-11(9)	45(10)	-40(10)
C(42)	77(20)	52(17)	101(22)	-10(15)	48(18)	-16(16)
C(43)	109(32)	196(42)	173(38)	8(30)	51(29)	-134(34)
O(44)	64(11)	83(13)	52(10)	-13(10)	34(9)	-9(9)
C(45)	332(71)	153(43)	52(24)	-156(47)	22(33)	-39(27)
C(46)	90(22)	98(25)	53(18)	20(19)	27(16)	3(17)
O(47)	108(16)	91(15)	80(14)	-9(12)	57(13)	20(12)
C(48)	83(29)	242(54)	137(38)	-20(32)	39(27)	31(39)
C(49)	127(34)	61(22)	167(36)	-24(22)	65(30)	29(25)
O(50)	76(13)	59(11)	103(14)	-9(10)	64(12)	3(10)
C(51)	114(30)	59(20)	182(34)	-13(20)	95(28)	31(21)
C(52)	84(23)	84(24)	211(40)	-8(20)	99(27)	18(26)
O(53)	49(9)	49(10)	100(12)	-11(8)	55(9)	9(9)
C(54)	45(14)	64(16)	48(14)	10(13)	31(12)	4(12)
C(55)	68(19)	70(18)	73(17)	26(15)	54(16)	28(15)
C(56)	103(23)	35(15)	111(22)	3(15)	77(20)	-10(14)
C(57)	101(24)	64(20)	128(27)	44(18)	87(23)	57(20)
C(58)	80(20)	97(23)	81(20)	38(19)	60(18)	26(18)
C(59)	60(18)	133(27)	81(19)	-8(18)	58(17)	0(19)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

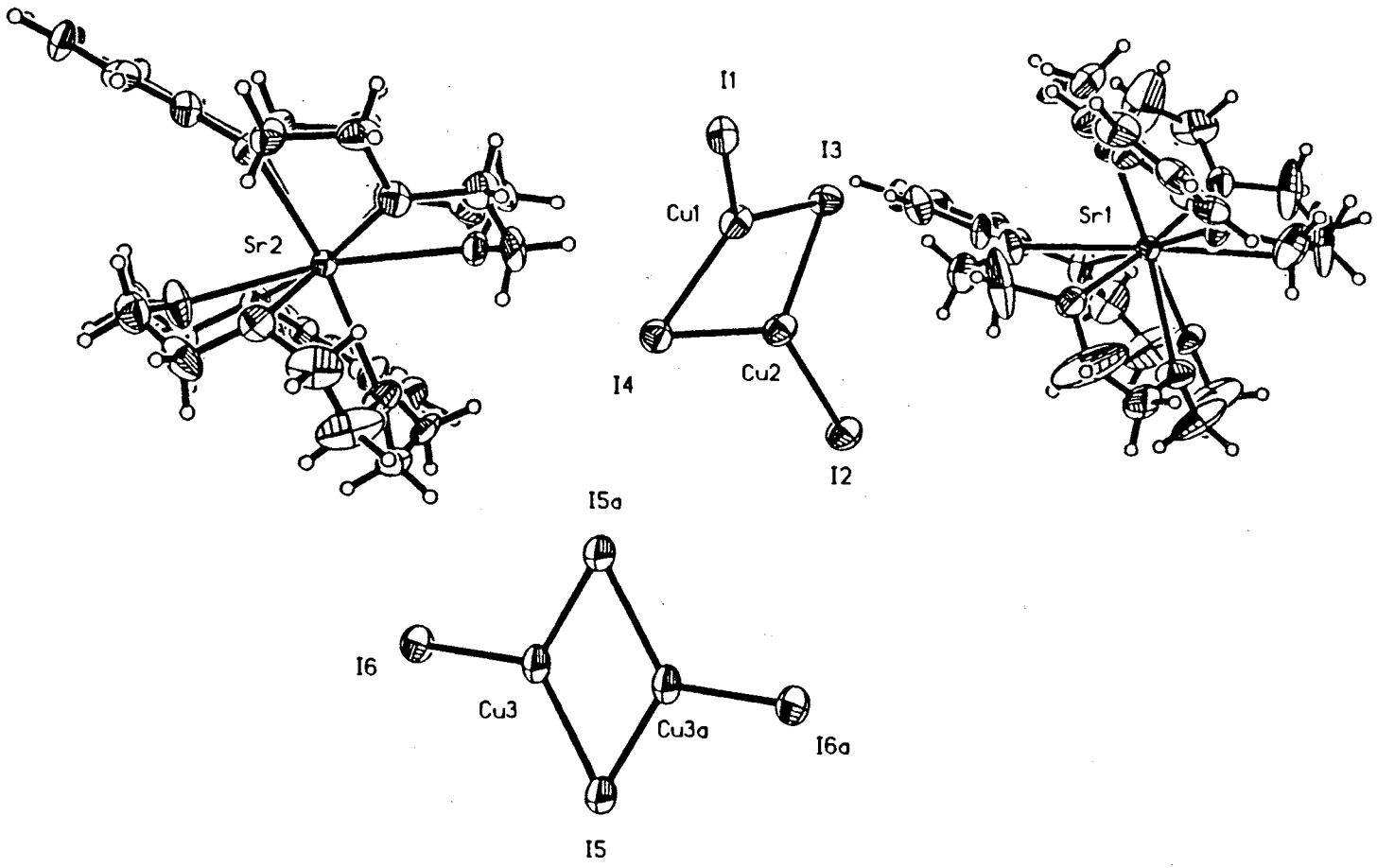


Figure 26. Projection View of $[Sr(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ **(VIII)**

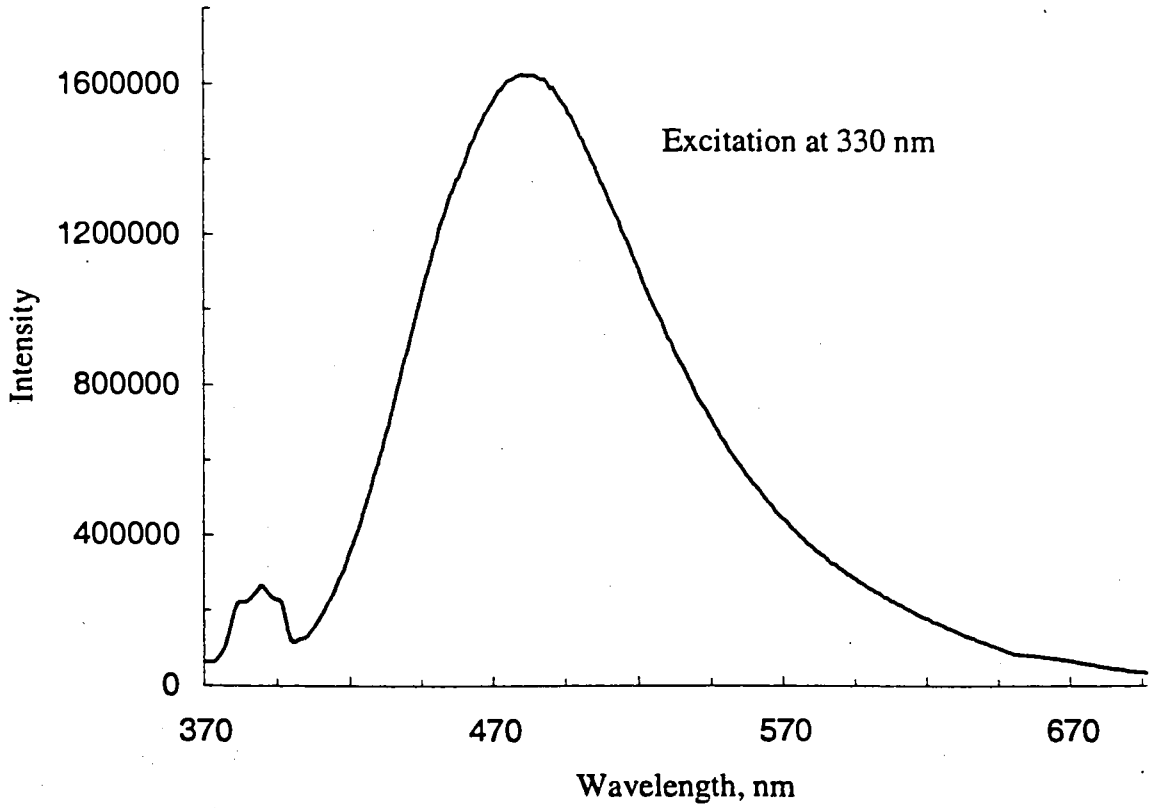


Figure 27. Emission spectrum of of $[Sr(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ (**VIII**)

TABLE 39

CRYSTAL DATA FOR

$[Sr(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ (**VIII**)

Formula	$C_{84}H_{120}Sr_3Cu_6I_{12}O_{30}$
Space group	C2/c
a	33.581(16) Å
b	20.715(7) Å
c	22.497(8) Å
β	131.31(2)°
V	11758(8) $Å^3$
Z	4
Mw	3776.8 g $mole^{-1}$
Density (calc.)	2.133 Mg m^{-3}
$\mu(MoK_\alpha)$	5.629 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	7152
Collected Reflections	18876
Independent Reflections	17144
Observed Reflections ($F > 4.0\sigma$)	3368
Number of parameters	610
Final R indices	$R = 5.08\ \%$, $R_w = 5.12\ \%$
R indices (all data)	$R = 25.14\ \%$, $R_w = 10.50\ \%$
GOF	0.94

TABLE 40

POSITIONAL PARAMETERS FOR

$[Sr(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ (**VIII**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.1766(1)	0.8706(1)	0.5123(1)
I(2)	0.0780(1)	0.5908(1)	0.5897(1)
I(3)	0.0557(1)	0.7120(1)	0.4040(1)
I(4)	0.1093(1)	0.8071(1)	0.6204(1)
I(5)	0.2519(1)	0.6955(1)	0.10871(1)
I(6)	0.1523(1)	0.8712(1)	0.9711(1)
Cu(1)	0.1169(1)	0.7982(1)	0.5128(2)
Cu(2)	0.0834(1)	0.6976(1)	0.5435(2)
Cu(3)	0.2159(1)	0.7919(1)	0.9901(2)
Sr(1)	0.0	0.3836(1)	0.2500
Sr(2)	0.1638(1)	1.1138(1)	0.7405(1)
O(1)	0.1944(5)	1.2229(7)	0.7128(8)
C(2)	0.2488(9)	1.2259(10)	0.7474(13)
H(2A)	0.2726	1.2261	0.8041
H(2B)	0.2546	1.2643	0.7301
C(3)	0.2605(10)	1.1664(13)	0.7220(13)
H(3A)	0.2973	1.1628	0.7478
H(3B)	0.2402	1.1694	0.6660
O(4)	0.2431(5)	1.1094(8)	0.7385(8)
C(5)	0.2492(9)	1.0538(14)	0.7076(14)
H(5A)	0.2861	1.0466	0.7357
H(5B)	0.2311	1.0605	0.6528
C(6)	0.2256(10)	0.9963(13)	0.7140(15)
H(6A)	0.2475	0.9857	0.7691
H(6B)	0.2251	0.9598	0.6873
O(7)	0.1733(6)	1.0089(7)	0.6817(9)
C(8)	0.1324(9)	0.9985(11)	0.5974(13)
H(8A)	0.1353	0.9561	0.5833
H(8B)	0.1361	1.0298	0.5698
C(9)	0.0800(10)	1.0081(12)	0.5734(13)
H(9A)	0.0772	0.9766	0.6018
H(9B)	0.0518	1.0005	0.5178
O(10)	0.0759(5)	1.0736(7)	0.5947(7)
C(11)	0.0467(7)	1.1179(10)	0.5288(10)
H(11A)	0.0119	1.1015	0.4861
H(11B)	0.0656	1.1232	0.5107

TABLE 40 (Continued)

C(12)	0.0441(8)	1.1818(10)	0.5577(11)
H(12A)	0.0242	1.1764	0.5740
H(12B)	0.0272	1.2142	0.5172
O(13)	0.0978(5)	1.2005(7)	0.6238(7)
C(14)	0.1102(9)	1.2662(10)	0.6351(11)
C(15)	0.1641(9)	1.2789(11)	0.6831(12)
C(16)	0.1858(10)	1.3405(11)	0.7047(12)
H(16A)	0.2235	1.3463	0.7408
C(17)	0.1480(11)	1.3922(12)	0.6716(14)
H(17A)	0.1606	1.4359	0.6834
C(18)	0.0943(11)	1.3789(11)	0.6215(13)
H(18A)	0.0699	1.4144	0.6001
C(19)	0.0742(9)	1.3158(10)	0.6038(13)
H(19A)	0.0369	1.3070	0.5694
O(21)	0.1222(6)	1.0173(6)	0.7654(8)
C(22)	0.1553(8)	0.9626(11)	0.8133(13)
H(22A)	0.1631	0.9382	0.7858
H(22B)	0.1377	0.9349	0.8240
C(23)	0.2066(10)	0.9869(12)	0.8870(13)
H(23A)	0.2304	0.9525	0.9204
H(23B)	0.1988	1.0110	0.9147
O(24)	0.2301(6)	1.0307(8)	0.8676(8)
C(25)	0.2804(10)	1.0557(15)	0.939(2)
H(25A)	0.3072	1.0229	0.9666
H(25B)	0.2747	1.0710	0.9734
C(26)	0.2945(10)	1.1097(15)	0.9225(15)
H(26A)	0.2993	1.0948	0.8872
H(26B)	0.3275	1.1272	0.9689
O(27)	0.2531(6)	1.1599(8)	0.8798(8)
C(28)	0.2506(11)	1.1986(15)	0.9273(15)
H(28A)	0.2826	1.2232	0.9638
H(28B)	0.2462	1.1715	0.9572
C(29)	0.2013(10)	1.2428(12)	0.8734(14)
H(29A)	0.2075	1.2742	0.8488
H(29B)	0.1952	1.2651	0.9041
O(30)	0.1570(7)	1.2033(8)	0.8169(9)
C(31)	0.1066(9)	1.2242(12)	0.7896(13)
H(31A)	0.0893	1.2512	0.7438
H(31B)	0.1119	1.2488	0.8304
C(32)	0.0720(8)	1.1669(10)	0.7671(12)
H(32A)	0.0370	1.1798	0.7445
H(32B)	0.0875	1.1425	0.8142
O(33)	0.0703(5)	1.1274(7)	0.7143(7)
C(34)	0.0421(9)	1.0701(11)	0.6963(11)
C(35)	0.0668(9)	1.0106(12)	0.7206(12)

TABLE 40 (Continued)

C(36)	0.0399(11)	0.9539(10)	0.7006(14)
H(36A)	0.0589	0.9137	0.7185
C(37)	-0.0135(10)	0.9574(12)	0.6556(14)
H(37A)	-0.0332	0.9181	0.6410
C(38)	-0.0414(9)	1.0140(15)	0.6305(12)
H(38A)	-0.0790	1.0141	0.5996
C(39)	-0.0132(8)	1.0734(12)	0.6513(12)
H(39A)	-0.0309	1.1144	0.6354
O(41)	-0.0983(5)	0.3835(8)	0.1993(8)
C(42)	-0.1238(11)	0.3228(14)	0.190(2)
H(42A)	-0.1425	0.3082	0.1366
H(42B)	-0.1491	0.3295	0.1959
C(43)	-0.0877(14)	0.2775(16)	0.2404(19)
H(43A)	-0.1024	0.2359	0.2167
H(43B)	-0.0843	0.2799	0.2861
O(44)	-0.0388(8)	0.2769(9)	0.2656(11)
C(45)	-0.026(15)	0.239(2)	0.335(2)
H(45A)	0.0116	0.2058	0.3239
H(45B)	-0.0226	0.2181	0.3459
C(46)	0.0383(13)	0.268(2)	0.396(2)
H(46A)	0.0665	0.2373	0.4296
H(46B)	0.0273	0.2818	0.4245
O(47)	0.0596(7)	0.3234(8)	0.3911(9)
C(48)	0.0953(12)	0.356(2)	0.4619(15)
H(48A)	0.1306	0.3478	0.4826
H(48B)	0.0930	0.3403	0.4996
C(49)	0.093(2)	0.417(2)	0.451(2)
H(49A)	0.1272	0.4360	0.4906
H(49B)	0.0725	0.4264	0.4659
O(50)	0.0643(6)	0.4543(7)	0.3855(8)
C(51)	0.0424(12)	0.512(2)	0.385(2)
H(51A)	0.0522	0.5418	0.3637
H(51B)	0.0613	0.5252	0.4388
C(52)	-0.0102(10)	0.5278(12)	0.3376(15)
H(52A)	-0.0198	0.5721	0.3220
H(52B)	-0.0185	0.5162	0.3697
O(53)	-0.0405(6)	0.4866(7)	0.2694(8)
C(54)	-0.0949(10)	0.4951(13)	0.2190(13)
C(55)	-0.1271(10)	0.4396(14)	0.1788(12)
C(56)	-0.1806(10)	0.4433(12)	0.1262(14)
H(56A)	-0.2014	0.4051	0.0993
C(57)	-0.2041(10)	0.504(2)	0.1125(14)
H(57A)	-0.2421	0.5063	0.0741
C(58)	-0.1750(13)	0.5568(13)	0.150(2)
H(58A)	-0.1932	0.5961	0.1415

TABLE 40 (Continued)

C(59)	-0.1194(12)	0.556(2)	0.2026(15)
H(59A)	-0.0986	0.5950	0.2260

TABLE 41

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[Sr(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ (**VIII**)

I(1)-Cu(1)	2.509 (5)	C(14)-C(15)	1.39 (3)
I(2)-Cu(2)	2.502 (4)	C(14)-C(19)	1.38 (3)
I(3)-Cu(1)	2.602 (3)	C(15)-C(16)	1.39 (3)
I(3)-Cu(2)	2.637 (4)	C(16)-C(17)	1.44 (4)
I(4)-Cu(1)	2.603 (5)	C(17)-C(18)	1.39 (4)
I(4)-Cu(2)	2.627 (4)	C(18)-C(19)	1.40 (3)
I(5)-Cu(3)	2.593 (4)	O(21)-C(22)	1.45 (2)
I(6)-Cu(3)	2.497 (4)	O(21)-C(35)	1.42 (3)
I(5)-Cu(3^i)	2.595 (5)	C(22)-C(23)	1.48 (3)
Cu(1)...Cu(2)	2.667 (5)	C(23)-O(24)	1.45 (4)
Cu(3)-I(5^i)	2.595 (5)	O(24)-C(25)	1.46 (2)
Cu(3)...Cu(3^i)	2.667 (7)	C(25)-C(26)	1.36 (5)
Sr(1)-O(41)	2.69 (2)	C(26)-O(27)	1.47 (3)
Sr(1)-O(44)	2.70 (2)	O(27)-C(28)	1.38 (4)
Sr(1)-O(47)	2.69 (2)	C(28)-C(29)	1.55 (4)
Sr(1)-O(50)	2.722 (14)	C(29)-O(30)	1.42 (3)
Sr(1)-O(53)	2.72(2)	O(30)-C(31)	1.43 (4)
Sr(1)-O(41^{ii})	2.69 (2)	C(31)-C(32)	1.50 (4)
Sr(1)-O(44^{ii})	2.70 (2)	C(32)-O(33)	1.41 (3)
Sr(1)-O(47^{ii})	2.69 (2)	O(33)-C(34)	1.40 (3)
Sr(1)-O(50^{ii})	2.722 (14)	C(34)-C(35)	1.38 (3)
Sr(1)-O(53^{ii})	2.72 (2)	C(34)-C(39)	1.41 (4)
Sr(2)-O(1)	2.72 (2)	C(35)-C(36)	1.36 (4)
Sr(2)-O(4)	2.70 (2)	C(36)-C(37)	1.36 (4)
Sr(2)-O(7)	2.67 (2)	C(37)-C(38)	1.37 (4)
Sr(2)-O(10)	2.717 (11)	C(38)-C(39)	1.43 (4)
Sr(2)-O(13)	2.711 (12)	O(41)-C(42)	1.45 (4)
Sr(2)-O(21)	2.70 (2)	O(41)-C(55)	1.38 (3)
Sr(2)-O(24)	2.773 (14)	C(42)-C(43)	1.35 (4)
Sr(2)-O(27)	2.706 (12)	C(43)-O(44)	1.34 (5)
Sr(2)-O(30)	2.64 (2)	O(44)-C(45)	1.42 (4)
Sr(2)-O(33)	2.80 (2)	C(45)-C(46)	1.28 (4)
O(1)-C(2)	1.44 (3)	C(46)-O(47)	1.40 (5)
O(1)-C(15)	1.39 (3)	O(47)-C(48)	1.38 (3)
C(2)-C(3)	1.52 (4)	C(48)-C(49)	1.27 (5)
C(3)-O(4)	1.47 (4)	C(49)-O(50)	1.36 (4)
O(4)-C(5)	1.43 (4)	O(50)-C(51)	1.40 (5)
C(5)-C(6)	1.49 (5)	C(51)-C(52)	1.37 (4)
C(6)-O(7)	1.41 (4)	C(52)-O(53)	1.43 (3)
O(7)-C(8)	1.45 (2)	O(53)-C(54)	1.38 (3)

TABLE 41 (Continued)

C(8)-C(9)	1.47 (5)	C(54)-C(55)	1.42 (4)
C(9)-O(10)	1.48 (3)	C(54)-C(59)	1.42 (4)
O(10)-C(11)	1.44 (2)	C(55)-C(56)	1.35 (4)
C(11)-C(12)	1.50 (3)	C(56)-C(57)	1.40 (4)
C(12)-O(13)	1.440 (2)	C(57)-C(58)	1.34 (4)
O(13)-C(14)	1.40 (2)	C(58)-C(59)	1.40 (4)
Cu(1)-I(3)-Cu(2)	61.2(1)	O(4)-Sr(2)-O(30)	123.1(6)
Cu(1)-I(4)-Cu(2)	61.3(1)	O(7)-Sr(2)-O(30)	170.0(6)
Cu(3)-I(5)-Cu(3^{i})	61.9(1)	O(10)-Sr(2)-O(30)	120.7(5)
I(1)-Cu(1)-I(3)	122.9(2)	O(13)-Sr(2)-O(30)	78.4(5)
I(1)-Cu(1)-I(4)	122.2(1)	O(21)-Sr(2)-O(30)	96.1(7)
I(3)-Cu(1)-I(4)	114.9(2)	O(24)-Sr(2)-O(30)	97.0(5)
I(2)-Cu(2)-I(3)	122.0(1)	O(27)-Sr(2)-O(30)	60.3(6)
I(2)-Cu(2)-I(4)	124.9(2)	O(1)-Sr(2)-O(33)	114.1(5)
I(3)-Cu(2)-I(4)	113.0(1)	O(4)-Sr(2)-O(33)	169.4(4)
I(5)-Cu(3)-I(6)	121.4(2)	O(7)-Sr(2)-O(33)	117.5(5)
I(5)-Cu(3)-I(5^{i})	118.1(1)	O(10)-Sr(2)-O(33)	66.7(5)
I(6)-Cu(3)-I(5^{i})	120.4(1)	O(13)-Sr(2)-O(33)	69.1(5)
O(41)-Sr(1)-O(44)	59.5(6)	O(21)-Sr(2)-O(33)	57.1(5)
O(41)-Sr(1)-O(47)	104.4(7)	O(24)-Sr(2)-O(33)	107.8(6)
O(44)-Sr(1)-O(47)	61.0(5)	O(27)-Sr(2)-O(33)	116.1(6)
O(41)-Sr(1)-O(50)	108.6(6)	O(30)-Sr(2)-O(33)	60.0(5)
O(44)-Sr(1)-O(50)	112.8(6)	C(2)-O(1)-C(15)	119(2)
O(47)-Sr(1)-O(50)	60.4(5)	O(1)-C(2)-C(3)	108(2)
O(41)-Sr(1)-O(53)	57.6(5)	C(2)-C(3)-O(4)	108(3)
O(44)-Sr(1)-O(53)	106.6(8)	C(3)-O(4)-C(5)	108(2)
O(47)-Sr(1)-O(53)	103.6(6)	O(4)-C(5)-C(6)	110(3)
O(50)-Sr(1)-O(53)	60.6(5)	C(5)-C(6)-O(7)	111(2)
O(41)-Sr(1)-O(41^{ii})	180.0(8)	C(6)-O(7)-C(8)	115(3)
O(44)-Sr(1)-O(41^{ii})	120.4(6)	O(7)-C(8)-C(9)	109(3)
O(47)-Sr(1)-O(41^{ii})	75.5(7)	C(8)-C(9)-O(10)	110(2)
O(50)-Sr(1)-O(41^{ii})	71.4(6)	C(9)-O(10)-C(11)	113(2)
O(53)-Sr(1)-O(41^{ii})	122.5(5)	O(10)-C(11)-C(12)	108(2)
O(41)-Sr(1)-O(44^{ii})	120.4(6)	C(11)-C(12)-O(13)	107(2)
O(44)-Sr(1)-O(44^{ii})	70.4(12)	C(12)-O(13)-C(14)	118.1(14)
O(47)-Sr(1)-O(44^{ii})	74.2(7)	O(13)-C(14)-C(15)	114(2)
O(50)-Sr(1)-O(44^{ii})	119.4(5)	O(13)-C(14)-C(19)	125(2)
O(53)-Sr(1)-O(44^{ii})	176.8(8)	C(15)-C(14)-C(19)	120(2)
O(41^{ii})-Sr(1)-O(44^{ii})	59.5(6)	O(1)-C(15)-C(14)	112(2)
O(41)-Sr(1)-O(47^{ii})	75.5(7)	O(1)-C(15)-C(16)	123(2)
O(44)-Sr(1)-O(47^{ii})	74.2(7)	C(14)-C(15)-C(16)	124(2)
O(47)-Sr(1)-O(47^{ii})	124.9(7)	C(15)-C(16)-C(17)	115(2)
O(50)-Sr(1)-O(47^{ii})	172.9(7)	C(16)-C(17)-C(18)	120(2)
O(53)-Sr(1)-O(47^{ii})	119.4(5)	C(17)-C(18)-C(19)	123(2)

TABLE 41 (Continued)

O(41^{ii})-Sr(1)-O(47^{ii})	104.4(7)	C(14)-C(19)-C(18)	117(2)
O(44^{ii})-Sr(1)-O(47^{ii})	61.0(5)	C(22)-O(21)-C(35)	117(2)
O(41)-Sr(1)-O(50^{ii})	71.4(6)	O(21)-C(22)-C(23)	109(2)
O(44)-Sr(1)-O(50^{ii})	119.4(5)	C(22)-C(23)-O(24)	110(2)
O(47)-Sr(1)-O(50^{ii})	172.9(7)	C(23)-O(24)-C(25)	111(2)
O(50)-Sr(1)-O(50^{ii})	114.9(6)	O(24)-C(25)-C(26)	110(2)
O(53)-Sr(1)-O(50^{ii})	69.3(6)	C(25)-C(26)-O(27)	114(3)
O(41^{ii})-Sr(1)-O(50^{ii})	108.6(6)	C(26)-O(27)-C(28)	115(2)
O(44^{ii})-Sr(1)-O(50^{ii})	112.8(6)	O(27)-C(28)-C(29)	108(2)
O(47^{ii})-Sr(1)-O(50^{ii})	60.4(5)	C(28)-C(29)-O(30)	108(2)
O(41)-Sr(1)-O(53^{ii})	122.5(5)	C(29)-O(30)-C(31)	117(2)
O(44)-Sr(1)-O(53^{ii})	176.8(8)	O(30)-C(31)-C(32)	110(2)
O(47)-Sr(1)-O(53^{ii})	119.4(5)	C(31)-C(32)-O(33)	110(3)
O(50)-Sr(1)-O(53^{ii})	69.3(6)	C(32)-O(33)-C(34)	112(2)
O(53)-Sr(1)-O(53^{ii})	76.5(9)	O(33)-C(34)-C(35)	122(2)
O(41^{ii})-Sr(1)-O(53^{ii})	57.6(5)	O(33)-C(34)-C(39)	119(2)
O(44^{ii})-Sr(1)-O(53^{ii})	106.6(8)	C(35)-C(34)-C(39)	119(2)
O(47^{ii})-Sr(1)-O(53^{ii})	103.6(6)	O(21)-C(35)-C(34)	111(2)
O(50^{ii})-Sr(1)-O(53^{ii})	60.6(5)	O(21)-C(35)-C(36)	126(2)
O(1)-Sr(2)-O(4)	59.8(5)	C(34)-C(35)-C(36)	123(2)
O(1)-Sr(2)-O(7)	112.0(7)	C(35)-C(36)-C(37)	117(2)
O(4)-Sr(2)-O(7)	61.4(6)	C(36)-C(37)-C(38)	124(2)
O(1)-Sr(2)-O(10)	104.6(4)	C(37)-C(38)-C(39)	118(2)
O(4)-Sr(2)-O(10)	105.4(5)	C(34)-C(39)-C(38)	118(2)
O(7)-Sr(2)-O(10)	62.7(5)	C(42)-O(41)-C(55)	118(2)
O(1)-Sr(2)-O(13)	54.5(4)	O(41)-C(42)-C(43)	111(2)
O(4)-Sr(2)-O(13)	101.0(5)	C(42)-C(43)-O(44)	122(4)
O(7)-Sr(2)-O(13)	110.3(5)	C(43)-O(44)-C(45)	113(4)
O(10)-Sr(2)-O(13)	59.4(4)	O(44)-C(45)-C(46)	117(3)
O(1)-Sr(2)-O(21)	171.1(6)	C(45)-C(46)-O(47)	122(4)
O(4)-Sr(2)-O(21)	129.1(5)	C(46)-O(47)-C(48)	114(3)
O(7)-Sr(2)-O(21)	75.4(7)	O(47)-C(48)-C(49)	112(2)
O(10)-Sr(2)-O(21)	74.1(5)	C(48)-C(49)-O(50)	133(3)
O(13)-Sr(2)-O(21)	119.2(5)	C(49)-O(50)-C(51)	119(3)
O(1)-Sr(2)-O(24)	125.7(4)	O(50)-C(51)-C(52)	127(3)
O(4)-Sr(2)-O(24)	82.3(6)	C(51)-C(52)-O(53)	110(3)
O(7)-Sr(2)-O(24)	74.2(5)	C(52)-O(53)-C(54)	115(2)
O(10)-Sr(2)-O(24)	123.2(4)	O(53)-C(54)-C(55)	117(2)
O(13)-Sr(2)-O(24)	175.3(6)	O(53)-C(54)-C(59)	123(2)
O(21)-Sr(2)-O(24)	60.0(5)	C(55)-C(54)-C(59)	119(2)
O(1)-Sr(2)-O(27)	71.0(5)	O(41)-C(55)-C(54)	114(2)
O(4)-Sr(2)-O(27)	71.3(6)	O(41)-C(55)-C(56)	125(2)
O(7)-Sr(2)-O(27)	117.2(5)	C(54)-C(55)-C(56)	122(3)
O(10)-Sr(2)-O(27)	175.3(6)	C(55)-C(56)-C(57)	118(2)
O(13)-Sr(2)-O(27)	117.4(4)	C(56)-C(57)-C(58)	122(3)

TABLE 41 (Continued)

O(21)-Sr(2)-O(27)	110.6(5)	C(57)-C(58)-C(59)	123(3)
O(24)-Sr(2)-O(27)	60.2(4)	C(54)-C(59)-C(58)	116(3)
O(1)-Sr(2)-O(30)	76.9(7)		

Symmetry operations:

[i] = 0.5-x, 1.5-y, 2-z

[ii] = -x, y, 0.5-z

TABLE 42

ANISOTROPIC THERMAL PARAMETERS FOR

$[Sr(Benzo\text{-}15\text{-}crown\text{-}5)_2]_3(Cu_2I_4)_3$ (**VIII**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	59(1)	53(1)	83(1)	-13(1)	53(1)	-13(1)
I(2)	96(1)	54(1)	87(1)	-9(1)	64(1)	6(1)
I(3)	65(1)	56(1)	63(1)	-9(1)	42(1)	-1(1)
I(4)	62(1)	59(1)	68(1)	0(1)	46(1)	0(1)
I(5)	97(1)	58(1)	88(1)	20(1)	72(1)	11(1)
I(6)	66(1)	79(1)	79(1)	32(1)	50(1)	14(1)
Cu(1)	51(2)	56(2)	73(2)	0(2)	42(2)	5(2)
Cu(2)	56(2)	58(2)	77(2)	4(2)	45(2)	13(2)
Cu(3)	57(2)	53(2)	69(2)	10(2)	40(2)	-7(2)
Sr(1)	40(2)	33(2)	46(2)	0	33(2)	0
Sr(2)	33(1)	31(1)	39(1)	-1(1)	25(1)	-2(1)
O(1)	39(10)	48(11)	74(10)	-11(9)	38(9)	17(8)
C(2)	67(19)	40(17)	94(19)	-17(14)	62(17)	-10(14)
C(3)	83(20)	101(23)	80(18)	1(18)	68(17)	31(17)
O(4)	55(10)	61(12)	75(10)	9(9)	52(9)	-8(9)
C(5)	57(18)	109(25)	86(19)	29(18)	56(17)	33(19)
C(6)	88(23)	76(22)	124(23)	60(19)	85(21)	21(18)
O(7)	64(12)	38(10)	70(11)	3(9)	47(10)	-6(8)
C(8)	64(18)	51(17)	73(18)	-17(15)	52(16)	-19(14)
C(9)	96(23)	65(20)	65(17)	-41(18)	58(18)	-32(15)
O(10)	52(10)	53(11)	39(9)	2(9)	25(8)	-10(8)
C(11)	21(13)	65(18)	35(13)	6(13)	7(11)	7(14)
C(12)	35(14)	36(15)	46(13)	-16(13)	18(12)	-12(12)
O(13)	36(10)	40(11)	46(8)	-16(9)	14(8)	-3(8)
C(14)	42(15)	25(15)	39(13)	1(13)	30(13)	17(11)
C(15)	36(16)	42(17)	44(14)	6(14)	24(13)	0(12)
C(16)	76(19)	29(16)	64(16)	-37(16)	48(15)	-26(14)
C(17)	89(22)	40(19)	79(18)	-17(18)	62(18)	-34(16)
C(18)	85(21)	22(16)	65(16)	30(16)	46(17)	29(13)
C(19)	61(17)	25(15)	100(18)	17(15)	61(16)	24(14)
O(21)	50(11)	19(9)	74(10)	8(9)	39(9)	11(8)
C(22)	41(16)	43(17)	85(18)	-3(15)	37(15)	5(15)
C(23)	110(24)	55(19)	62(17)	3(18)	63(19)	14(14)
O(24)	36(10)	69(13)	47(9)	8(10)	9(9)	19(9)
C(25)	51(21)	136(31)	116(26)	-2(21)	45(21)	61(23)
C(26)	51(19)	117(29)	81(20)	-22(21)	28(17)	3(20)
O(27)	58(11)	53(11)	51(10)	-19(10)	32(10)	-7(9)

TABLE 42 (Continued)

C(28)	122(27)	134(30)	99(22)	-78(25)	98(23)	-70(24)
C(29)	74(21)	73(22)	67(18)	-7(19)	46(18)	-22(17)
O(30)	76(12)	72(13)	87(11)	-42(11)	60(11)	-57(10)
C(31)	66(19)	95(24)	85(18)	19(18)	61(17)	-9(16)
C(32)	44(15)	62(17)	66(15)	-10(14)	47(14)	2(13)
O(33)	54(10)	50(10)	47(8)	-8(9)	39(8)	-7(8)
C(34)	52(17)	39(17)	41(13)	-25(15)	33(14)	-13(12)
C(35)	25(14)	51(19)	52(15)	7(14)	26(13)	26(13)
C(36)	84(22)	17(15)	93(19)	-38(16)	61(19)	-11(14)
C(37)	46(18)	55(20)	83(19)	-33(17)	44(17)	-32(16)
C(38)	27(15)	104(25)	51(15)	20(18)	23(13)	-6(17)
C(39)	23(15)	63(19)	62(16)	2(14)	26(14)	-17(14)
O(41)	39(10)	39(11)	107(12)	4(9)	53(10)	0(9)
C(42)	71(24)	90(26)	111(25)	-55(22)	44(21)	-11(20)
C(43)	112(34)	101(30)	131(30)	-30(27)	50(28)	46(23)
O(44)	63(13)	68(14)	102(14)	2(12)	56(13)	12(12)
C(45)	129(38)	83(29)	210(44)	-5(28)	109(36)	71(32)
C(46)	96(32)	94(30)	170(39)	-12(23)	75(30)	72(27)
O(47)	102(14)	73(13)	55(10)	-26(11)	54(11)	-4(10)
C(48)	113(27)	123(30)	55(20)	85(25)	40(21)	57(22)
C(49)	194(45)	219(49)	45(22)	-75(41)	-22(25)	72(30)
O(50)	78(12)	52(11)	61(10)	-7(10)	49(10)	-1(9)
C(51)	97(30)	281(53)	150(32)	-18(33)	62(27)	-174(35)
C(52)	56(19)	64(20)	102(22)	-5(17)	48(18)	-16(18)
O(53)	45(11)	62(12)	52(10)	6(10)	27(9)	-23(9)
C(54)	35(18)	50(18)	60(17)	28(16)	29(15)	6(15)
C(55)	28(16)	78(22)	44(15)	9(17)	21(14)	2(15)
C(56)	72(21)	64(21)	79(18)	3(17)	64(18)	-11(16)
C(57)	61(20)	91(23)	70(19)	20(20)	51(17)	17(18)
C(58)	110(28)	50(20)	88(22)	47(20)	77(23)	12(17)
C(59)	63(21)	111(30)	93(21)	-16(21)	52(19)	-35(20)

The anisotropic displacement exponent takes the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$$

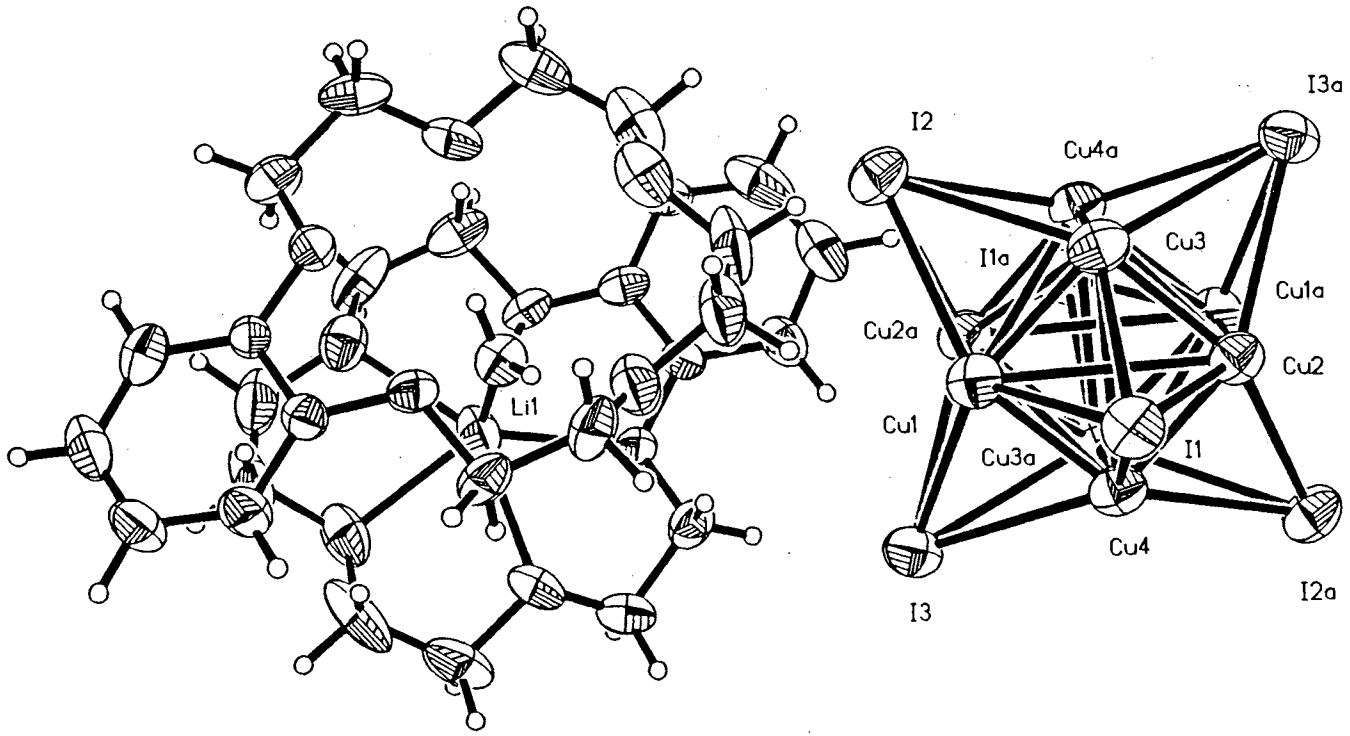


Figure 28. Projection View of $[Li(H_2O)(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_4I_6$ (**IX**)

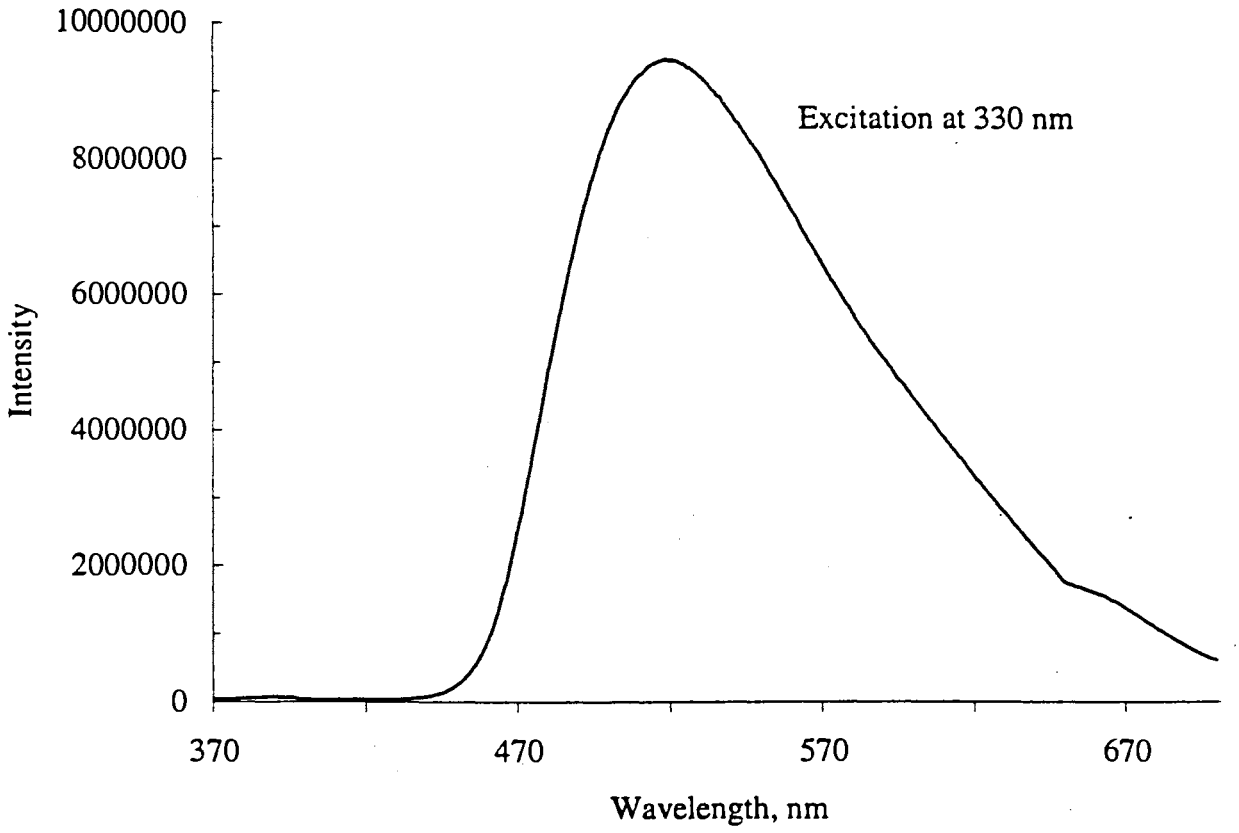


Figure 29. Emission spectrum of $[Li(H_2O)(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_4I_6$ (**IX**)

TABLE 43

CRYSTAL DATA FOR

$[Li(H_2O)(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_3$ (**IX**)

Formula	$C_{28}H_{42}Cu_2I_3LiO_{11}$
Space group	$P2_1/c$
A	11.081(8) Å
B	16.103(10) Å
C	22.211(14) Å
β	90.38(3)°
V	3976(5) $Å^3$
Z	4
Mw	1069.3 g $mole^{-1}$
Density (calc.)	1.787 Mg m^{-3}
$\mu(MoK_\alpha)$	3.447 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	2072
Collected Reflections	14963
Independent Reflections	11569
Observed Reflections ($F > 4.0\sigma$)	4000
Number of parameters	425
Final R indices	R=6.05 %, R_w=6.23 %
R indices (all data)	R=18.07 %, R_w= 9.48 %
GOF	1.20

TABLE 44

POSITIONAL PARAMETERS FOR

$[Li(H_2O)(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_3$ (**IX**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
Cu(1)	0.3752(3)	0.4478(2)	0.4688(1)
Cu(2)	0.5973(3)	0.5404(2)	0.4472(1)
Cu(3)	0.5538(3)	0.4175(2)	0.4582(1)
Cu(4)	0.4230(3)	0.5728(2)	0.4582(1)
I(1)	0.4592(1)	0.4841(1)	0.3618(1)
I(2)	0.4272(1)	0.3066(1)	0.5197(1)
I(3)	0.2189(1)	0.5473(1)	0.5144(1)
Li(1)	-0.108(2)	0.4312(12)	0.8773(9)
O(99)	-0.250(7)	0.3680(4)	0.8160(3)
H(99A)	0.0008	0.2998	0.8185
H(99B)	0.0011	0.3812	0.7696
O(1)	0.0309(6)	0.5345(4)	0.8919(3)
C(2)	0.0284(12)	0.5954(7)	0.8433(5)
H(2A)	0.0590	0.5699	0.8075
H(2B)	0.0772	0.6429	0.8529
C(3)	-0.1014(12)	0.6176(8)	0.8334(6)
H(3A)	-0.1095	0.6574	0.8014
H(3B)	-0.1319	0.6419	0.8697
O(4)	-0.1644(8)	0.5432(6)	0.8186(4)
C(5)	-0.2934(14)	0.5516(11)	0.8142(7)
H(5A)	-0.3128	0.5818	0.7781
H(5B)	-0.3229	0.5823	0.8481
C(6)	-0.3490(13)	0.4673(12)	0.8148(8)
H(6A)	-0.3218	0.4370	0.7803
H(6B)	-0.4354	0.4712	0.8132
O(7)	-0.3123(8)	0.4293(6)	0.8695(4)
C(8)	-0.3575(14)	0.3452(11)	0.8753(9)
H(8A)	-0.3338	0.3097	0.8427
H(8B)	-0.4439	0.3458	0.8775
C(9)	-0.3045(15)	0.3151(10)	0.9309(10)
H(9A)	-0.3291	0.2589	0.9385
H(9B)	-0.3328	0.3491	0.9633
O(10)	-0.1756(9)	0.3191(5)	0.9315(4)
C(11)	-0.117(2)	0.3042(8)	0.9883(6)
H(11A)	-0.1281	0.2469	0.9989
H(11B)	-0.1515	0.3379	1.0194

TABLE 44 (Continued)

C(12)	0.0145(14)	0.3224(7)	0.9828(5)
H(12A)	0.0521	0.2846	0.9552
H(12B)	0.0534	0.3172	0.10214
O(13)	0.0241(8)	0.4065(4)	0.9611(3)
C(14)	0.1398(12)	0.4386(6)	0.9509(5)
C(15)	0.1423(10)	0.5075(6)	0.9122(5)
C(16)	0.2550(12)	0.5429(8)	0.8972(6)
H(16A)	0.2568	0.5900	0.8707
C(17)	0.3605(14)	0.5102(10)	0.9228(8)
H(17A)	0.4369	0.5335	0.9116
C(18)	0.3555(15)	0.4443(12)	0.9618(9)
H(18A)	0.4292	0.4254	0.9802
C(19)	0.2495(14)	0.4062(8)	0.9762(6)
H(19A)	0.2487	0.3578	1.0014
O(21)	-0.1092(7)	0.2915(4)	0.6860(3)
C(22)	-0.1042(12)	0.3650(7)	0.6491(5)
H(22A)	-0.1345	0.4126	0.6701
H(22B)	-0.1518	0.3568	0.6133
C(23)	0.0263(13)	0.3801(8)	0.6366(6)
H(23A)	0.0361	0.4245	0.6082
H(23B)	0.0600	0.3302	0.6201
O(24)	0.0893(8)	0.3986(5)	0.6923(4)
C(25)	0.2193(14)	0.3917(10)	0.6873(8)
H(25A)	0.2493	0.4421	0.6698
H(25B)	0.2399	0.3462	0.6614
C(26)	0.2714(14)	0.3798(11)	0.7464(9)
H(26A)	0.2422	0.4221	0.7731
H(26B)	0.3575	0.3849	0.7442
O(27)	0.2428(8)	0.2977(6)	0.7686(4)
C(28)	0.2713(14)	0.2842(12)	0.8300(8)
H(28A)	0.2383	0.3290	0.8531
H(28B)	0.3573	0.2846	0.8354
C(29)	0.2198(13)	0.2038(10)	0.8501(6)
H(29A)	0.2458	0.1943	0.8909
H(29B)	0.2487	0.1590	0.8257
O(30)	0.0894(8)	0.2085(5)	0.8495(3)
C(31)	0.0347(14)	0.1294(8)	0.8470(5)
H(31A)	0.0419	0.1032	0.8857
H(31B)	0.0703	0.0936	0.8175
C(32)	-0.1003(12)	0.1404(7)	0.8317(5)
H(32A)	-0.1379	0.1739	0.8621
H(32B)	-0.1428	0.0886	0.8287
O(33)	-0.1073(6)	0.1846(4)	0.7745(3)
C(34)	-0.2221(9)	0.2034(6)	0.7514(4)
C(35)	-0.2218(10)	0.2625(6)	0.7031(5)

TABLE 44 (Continued)

C(36)	-0.3337(13)	0.2827(8)	0.6763(6)
H(36A)	-0.3370	0.3187	0.6420
C(37)	-0.4398(13)	0.2479(9)	0.6962(8)
H(37A)	-0.5164	0.2643	0.6796
C(38)	-0.4406(13)	0.1928(10)	0.7444(8)
H(38A)	-0.5133	0.1693	0.7604
C(39)	-0.3303(14)	0.1698(7)	0.7704(5)
H(39A)	-0.3268	0.1289	0.8018

TABLE 45

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[Li(H_2O)(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_3$ (**IX**)

Cu(1)...Cu(2)	2.920(5)	O(1)-C(2)	1.459(13)
Cu(1)...Cu(3)	2.053(5)	O(1)-C(15)	1.382(13)
Cu(1)...Cu(4)	2.096(4)	C(2)-C(3)	1.50(2)
Cu(1)-I(1)	2.626(4)	C(3)-O(4)	1.42(2)
Cu(1)-I(2)	2.602(3)	O(4)-C(5)	1.439(2)
Cu(1)-I(3)	2.572(4)	C(5)-C(6)	1.49(2)
Cu(1)...Cu(2^i)	1.898(4)	C(6)-O(7)	1.42(2)
Cu(1)...Cu(3^i)	2.817(4)	O(7)-C(8)	1.45(2)
Cu(1)...Cu(4^i)	2.773(5)	C(8)-C(9)	1.45(3)
Cu(2)...Cu(3)	2.051(4)	C(9)-O(10)	1.43(2)
Cu(2)...Cu(4)	2.018(4)	O(10)-C(11)	1.44(2)
Cu(2)-I(1)	2.593(3)	C(11)-C(12)	1.49(2)
Cu(2)...Cu(1^i)	1.898(4)	C(12)-O(13)	1.443(13)
Cu(2)...Cu(3^i)	2.781(5)	O(13)-C(14)	1.40(2)
Cu(2)...Cu(4^i)	2.793(4)	C(14)-C(15)	1.403(15)
Cu(2)-I(2^i)	2.587(3)	C(14)-C(19)	1.44(2)
Cu(2)-I(3^i)	2.616(4)	C(15)-C(16)	1.42(2)
Cu(3)...Cu(4)	2.890(4)	C(16)-C(17)	1.40(2)
Cu(3)-I(1)	2.609(4)	C(17)-C(18)	1.37(3)
Cu(3)-I(2)	2.656(4)	C(18)-C(19)	1.36(2)
Cu(3)...Cu(1^i)	2.817(4)	O(21)-C(22)	1.441(13)
Cu(3)...Cu(2^i)	2.781(5)	O(21)-C(35)	1.397(13)
Cu(3)...Cu(4^i)	1.881(4)	C(22)-C(23)	1.50(2)
Cu(3)-I(3^i)	2.648(4)	C(23)-O(24)	1.45(2)
Cu(4)-I(1)	2.607(3)	O(24)-C(25)	1.45(2)
Cu(4)-I(3)	2.623(4)	C(25)-C(26)	1.44(2)
Cu(4)...Cu(1^i)	2.773(5)	C(26)-O(27)	1.45(2)
Cu(4)...Cu(2^i)	2.793(4)	O(27)-C(28)	1.41(2)
Cu(4)...Cu(3^i)	1.881(4)	C(28)-C(29)	1.48(2)
Cu(4)-I(2^i)	2.599(3)	C(29)-O(30)	1.45(2)
I(2)-Cu(2^i)	2.587(3)	O(30)-C(31)	1.41(2)
I(2)-Cu(4^i)	2.599(3)	C(31)-C(32)	1.54(2)
I(3)-Cu(2^i)	2.616(4)	C(32)O(33)	1.458(13)
I(3)-Cu(3^i)	2.648(4)	O(33)-C(34)	1.402(12)
Li(1)-O(99)	1.94(2)	C(34)-C(35)	1.433(14)
Li(1)-O(1)	2.29(2)	C(34)-C(39)	1.38(2)
Li(1)-O(7)	2.27(2)	C(36)-C(37)	1.38(2)
Li(1)-O(10)	2.30(2)	C(37)-C(38)	1.39(2)
Li(1)-O(13)	2.39(2)	C(38)-C(39)	1.40(2)

TABLE 45 (Continued)

Cu(1)-I(1)-Cu(2)	68.0(1)	C(9)-O(10)-C(11)	116.6(13)
Cu(1)-I(1)-Cu(3)	46.2(1)	O(10)-C(11)-C(12)	109.4(11)
Cu(2)-I(1)-Cu(3)	46.4(1)	C(11)-C(12)-O(13)	106.7(11)
Cu(1)-I(1)-Cu(4)	47.2(1)	C(12)-O(13)-C(14)	118.0(9)
Cu(2)-I(1)-Cu(4)	45.7(1)	O(13)-C(14)-C(15)	114.3(10)
Cu(3)-I(1)-Cu(4)	67.3(1)	O(13)-C(14)-C(19)	125.1(10)
Cu(1)-I(2)-Cu(3)	46.0(1)	C(15)-C(14)-C(19)	120.6(12)
Cu(1)-I(2)-Cu(2^{i})	42.9(1)	O(1)-C(15)-C(14)	115.3(10)
Cu(3)-I(2)-Cu(2^{i})	64.0(1)	O(1)-C(15)-C(16)	125.8(10)
Cu(1)-I(2)-Cu(4^{i})	64.4(1)	C(14)-C(15)-C(16)	118.9(11)
Cu(3)-I(2)-Cu(4^{i})	41.9(1)	C(15)-C(16)-C(17)	119.3(12)
Cu(2^{i})-I(2)-Cu(4^{i})	45.8(1)	C(16)-C(17)-C(18)	120.7(14)
Cu(1)-I(3)-Cu(4)	47.6(1)	C(17)-C(18)-C(19)	122(2)
Cu(1)-I(3)-Cu(2i)	42.9(1)	C(14)-C(19)-C(18)	118.2(13)
Cu(4)-I(3)-Cu(2i)	64.4(1)	C(22)-O(21)-C(35)	118.0(8)
Cu(1)-I(3)-Cu(3^{i})	65.3(1)	O(21)-C(22)-C(23)	106.3(10)
Cu(4)-I(3)-Cu(3^{i})	41.8(1)	C(22)-C(23)-O(24)	109.7(11)
Cu(2^{i})-I(3)-Cu(3^{i})	45.8(1)	C(23)-O(24)-C(25)	113.2(11)
O(1)-Li(1)-O(4)	72.0(6)	O(24)-C(25)-C(26)	109.4(13)
O(1)-Li(1)-O(7)	133.6(9)	C(25)-C(26)-O(27)	110.2(13)
O(4)-Li(1)-O(7)	72.6(7)	C(26)-O(27)-C(28)	114.9(12)
O(1)-Li(1)-O(10)	135.9(10)	O(27)-C(28)-C(29)	109.9(13)
O(4)-Li(1)-O(10)	145.2(9)	C(28)-C(29)-O(30)	109.7(12)
O(7)-Li(1)-O(10)	72.7(7)	C(29)-O(30)-C(31)	112.5(10)
O(1)-Li(1)-O(13)	66.6(6)	O(30)-C(31)-C(32)	108.7(10)
O(4)-Li(1)-O(13)	136.9(9)	C(31)-C(32)-O(33)	107.1(9)
O(7)-Li(1)-O(13)	131.5(10)	C(32)-O(33)-C(34)	117.9(8)
O(10)-Li(1)-O(13)	70.3(6)	O(33)-C(34)-C(35)	114.3(9)
C(2)-O(1)-C(15)	117.7(8)	O(33)-C(34)-C(39)	126.2(9)
O(1)-C(2)-C(3)	106.4(10)	C(35)-C(34)-C(39)	119.6(10)
C(2)-C(3)-O(4)	107.6(10)	O(21)-C(35)-C(34)	115.7(9)
C(3)-O(4)-C(5)	115.0(11)	O(21)-C(35)-C(36)	126.6(10)
O(4)-C(5)-C(6)	108.9(13)	C(34)-C(35)-C(36)	117.6(10)
C(5)-C(6)-O(7)	106.6(13)	C(35)-C(36)-C(37)	121.4(12)
C(6)-O(7)-C(8)	112.5(12)	C(36)-C(37)-C(38)	121.0(14)
O(7)-C(8)-C(9)	104.5(13)	C(37)-C(38)-C(39)	118.5(13)
C(8)-C(9)-O(10)	113.1(15)	C(34)-C(39)-C(38)	121.9(12)
C(9)-O(10)-C(11)	116.6(13)		

Symmetry operation:

^{i} = 1-x, 1-y, 1-z

TABLE 46

ANISOTROPIC THERMAL PARAMETERS FOR

$[Li(H_2O)(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_2I_3$ (**IX**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	71(2)	61(2)	62(2)	-2(2)	-6(2)	-8(1)
Cu(2)	70(2)	56(2)	54(2)	-2(1)	-5(1)	22(1)
Cu(3)	82(2)	54(2)	66(2)	6(2)	-4(2)	-8(1)
Cu(4)	74(2)	54(2)	57(2)	2(1)	-10(2)	-2(1)
I(1)	75(1)	67(1)	49(1)	-5(1)	-7(1)	-10(1)
I(2)	95(1)	46(1)	78(1)	-10(1)	-9(1)	-4(1)
I(3)	65(1)	78(1)	64(1)	15(1)	1(1)	7(1)
Li(1)	42(11)	78(13)	83(14)	-14(10)	-9(11)	-14(11)
O(99)	78(6)	62(4)	58(5)	0(4)	8(4)	-12(4)
O(1)	48(5)	60(4)	-1(4)	-1(4)	-12(4)	14(3)
C(2)	95(11)	66(7)	62(8)	-15(7)	1(8)	19(6)
C(3)	73(10)	90(10)	79(9)	28(8)	-18(8)	9(7)
O(4)	54(6)	99(6)	86(6)	18(5)	-27(5)	-2(5)
C(5)	85(13)	163(16)	84(11)	36(12)	-25(9)	20(11)
C(6)	43(9)	212(21)	119(15)	5(11)	-32(9)	-61(15)
O(7)	58(6)	117(7)	96(7)	-16(5)	-12(5)	-39(6)
C(8)	45(10)	129(15)	214(22)	-32(10)	-7(12)	-91(15)
C(9)	81(14)	79(10)	207(23)	-28(10)	50(14)	-25(12)
O(10)	89(7)	66(5)	83(7)	-15(5)	13(6)	-13(5)
C(11)	177(18)	60(8)	73(10)	-27(10)	30(12)	5(7)
C(12)	136(13)	59(8)	50(8)	14(8)	-10(8)	3(6)
O(13)	96 (7)	37(4)	64(5)	3(4)	-7(5)	11(3)
C(14)	84(10)	45(6)	51(7)	12(7)	-4(7)	-12(5)
C(15)	43(7)	49(6)	69(7)	4(5)	-12(6)	-18(6)
C(16)	55(9)	73(8)	97(10)	2(7)	-12(8)	-29(7)
C(17)	62(11)	115(13)	122(14)	-7(10)	5(10)	-36(11)
C(18)	59(12)	149(17)	146(17)	28(12)	-37(11)	-56(14)
C(19)	91(12)	73(8)	89(10)	37(9)	-38(9)	-6(7)
O(21)	66(5)	54(4)	63(5)	2(4)	-12(4)	17(4)
C(22)	94(10)	59(7)	64(8)	-8(7)	-10(7)	24(6)
C(23)	99(12)	79(9)	86(10)	-23(8)	17(10)	23(8)
O(24)	59(6)	95(6)	104(7)	-12(5)	13(6)	-4(5)
C(25)	86(13)	107(12)	118(14)	-33(9)	31(11)	-21(10)
C(26)	58(10)	137(15)	170(19)	-55(10)	25(12)	-69(14)
O(27)	71(6)	118(8)	79(7)	-6(6)	-4(5)	-26(6)
C(28)	68(11)	168(18)	128(16)	-2(11)	-4(11)	-44(14)
C(29)	79(11)	139(14)	69(9)	38(10)	-33(8)	-12(9)

TABLE 46 (Continued)

O(30)	72(6)	78(6)	79(6)	25(5)	-18(5)	-6(5)
C(31)	129(14)	81(9)	56(8)	51(10)	-8(8)	9(7)
C(32)	102(11)	57(7)	51(7)	1(7)	-6(7)	16(6)
O(33)	57(5)	60(4)	49(4)	-4(4)	2(4)	14(3)
C(34)	38(7)	43(5)	53(7)	0(5)	0(6)	-6(5)
C(35)	51(8)	48(6)	57(7)	-1(6)	-4(6)	-6(5
C(36)	70(10)	76(8)	94(10)	5(8)	-32(9)	0(7)
C(37)	59(10)	105(11)	122(14)	4(9)	-25(9)	-7(10)
C(38)	55(10)	110(12)	120(13)	-26(9)	-2(9)	-17(10)
C(39)	98(11)	61(7)	69(8)	-22(8)	16(9)	-2(6)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

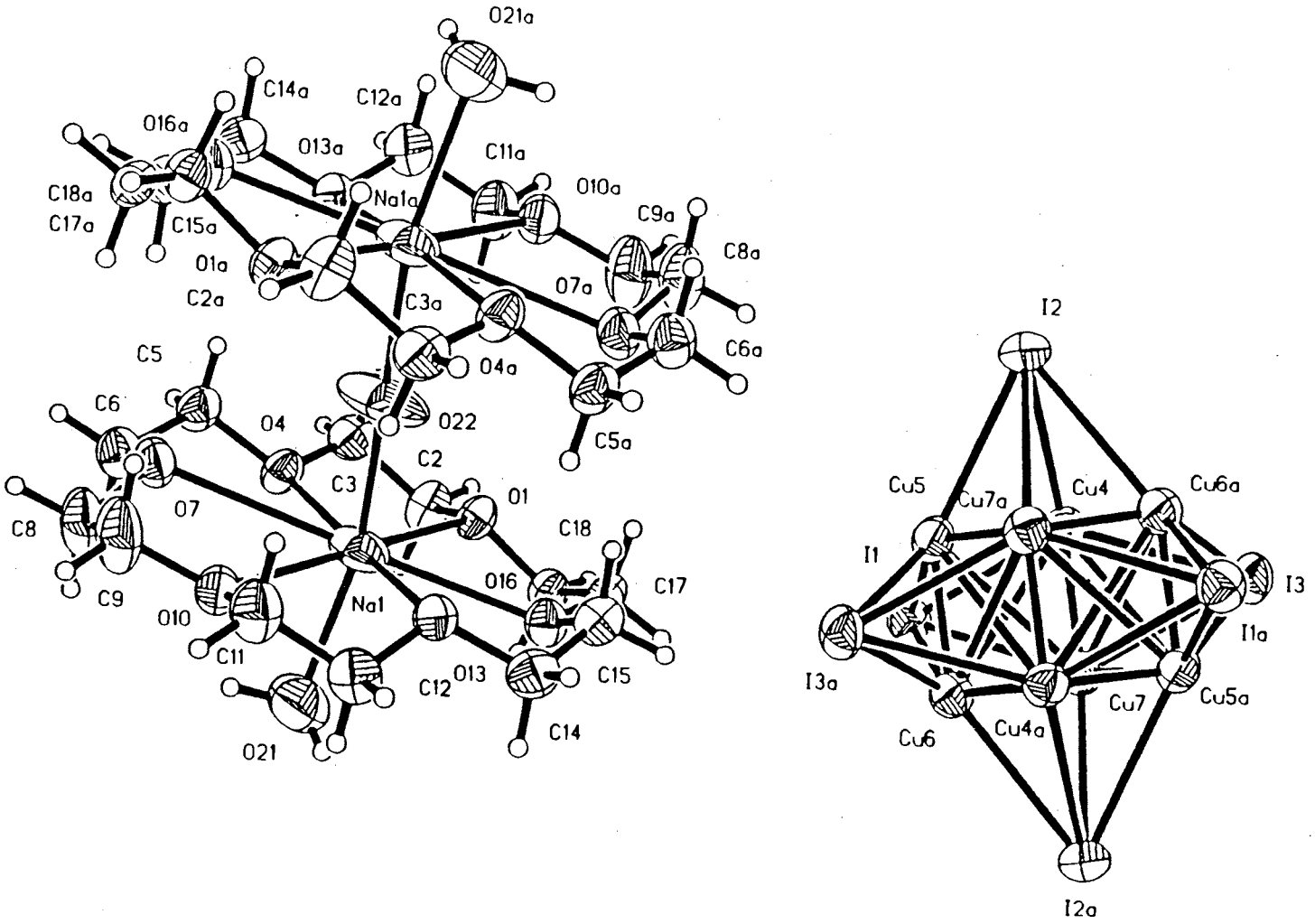


Figure 30. Projection View of $[Na_2(H_2O)_3(18\text{-Crown-}6)_2]Cu_4I_6$ (**X**)

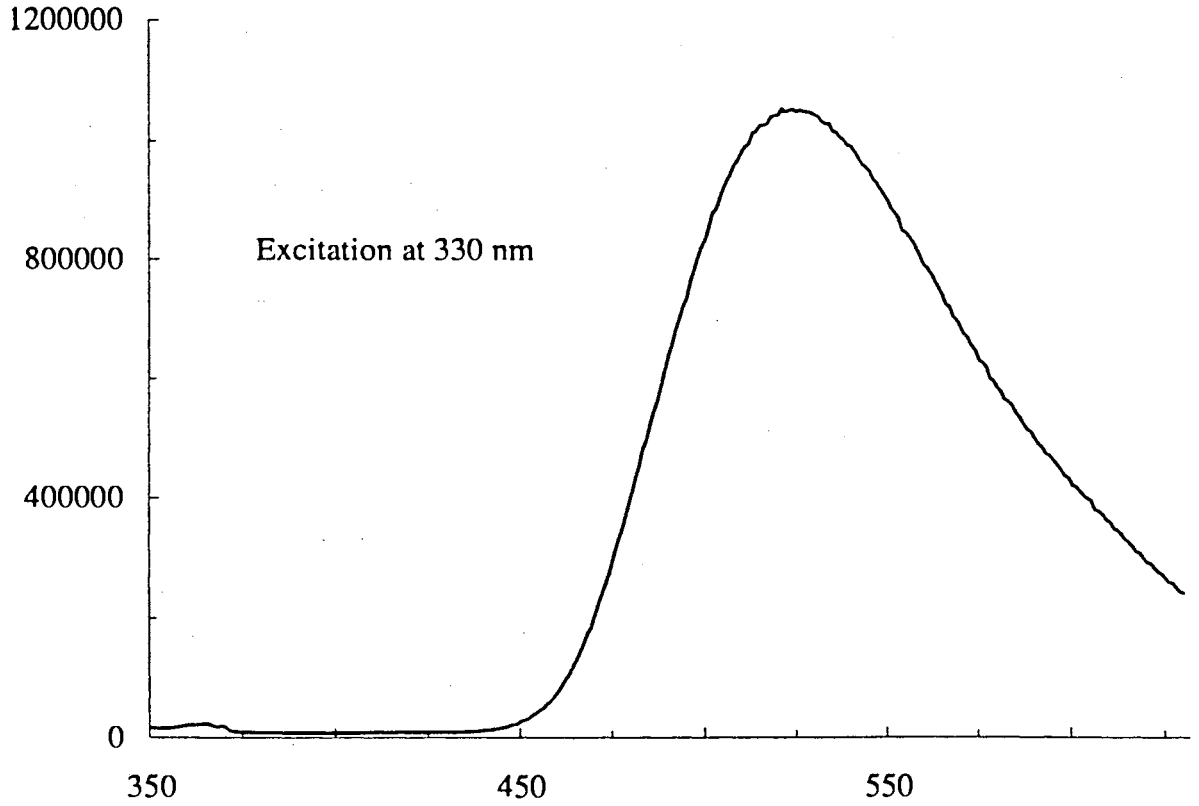


Figure 31. Emission spectrum of $[Na_2(H_2O)_3(18\text{-Crown-}6)_2]Cu_4I_6$ (**X**)

TABLE 47

CRYSTAL DATA FOR

$[Na_2(H_2O)_3(18\text{-Crown-}6)_2]Cu_4I_6$ (**X**)

Formula	$C_{24}H_{54}Cu_4I_6Na_2O_{15}$
Space group	$P2_1/c$
a	11.303(2) Å
b	13.926(2) Å
c	15.268(3) Å
β	96.950(10)°
V	2385.4(7) $Å^3$
Z	4
Mw	821.1 g $mole^{-1}$
Density (calc.)	2.286 Mg m^{-3}
$\mu(MoK_\alpha)$	5.712 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	1544
Collected Reflections	8518
Independent Reflections	6951
Observed Reflections ($F > 4.0\sigma$)	2371
Number of parameters	251
Final R indices	$R = 4.33$ %, $R_w = 4.55$ %
R indices (all data)	$R = 13.76$ %, $R_w = 7.13$ %
GOF	0.89

TABLE 48

POSITIONAL PARAMETERS FOR

$[Na_2(H_2O)_3(18\text{-Crown-}6)_2]Cu_4I_6$ (**X**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.2754(1)	0.9642(1)	0.0177(1)
I(2)	-0.0325(1)	0.8249(1)	0.1214(1)
I(3)	-0.0340(1)	0.8638(1)	-0.1665(1)
Cu(1)	0.0636(3)	0.8930(2)	-0.113(2)
Cu(2)	0.0862(3)	0.9763(2)	0.0971(2)
Cu(3)	0.1072(3)	1.0862(2)	0.0203(2)
Cu(4)	0.0818(3)	0.9988(2)	-0.0836(2)
Na(1)	0.6383(5)	0.10819(4)	0.4324(4)
O(1)	0.7010(7)	0.9541(6)	0.3265(5)
C(2)	0.8203(12)	0.9233(11)	0.3458(9)
H(2A)	0.8733	0.9740	0.3334
H(2B)	0.8348	0.8685	0.3104
C(3)	0.8403(12)	0.8999(12)	0.4413(9)
H(3A)	0.9182	0.8727	0.4562
H(3B)	0.7823	0.8532	0.4540
O(4)	0.8285(8)	0.9818(6)	0.4904(6)
C(5)	0.8566(12)	0.9654(10)	0.5827(9)
H(5A)	0.9351	0.9385	0.5952
H(5B)	0.8005	0.9211	0.6025
C(6)	0.8479(13)	1.0570(11)	0.6311(10)
H(6A)	0.9000	1.1026	0.6082
H(6B)	0.8730	1.0490	0.6930
O(7)	0.7323(9)	1.0908(7)	0.6167(6)
C(8)	0.725(2)	1.1842(12)	0.6518(11)
H(8A)	0.7756	1.2279	0.6251
H(8B)	0.7497	1.1826	0.7142
C(9)	0.608(2)	1.2199(13)	0.6350(10)
H(9A)	0.5985	1.2806	0.6632
H(9B)	0.5571	1.1741	0.6594
O(10)	0.5662(9)	1.2265(7)	0.5466(6)
C(11)	0.4536(15)	1.2645(12)	0.5313(10)
H(11A)	0.4518	1.3251	0.5612
H(11B)	0.3976	1.2221	0.5538
C(12)	0.4195(13)	1.2770(10)	0.4380(10)
H(12A)	0.4779	1.3167	0.4150
H(12B)	0.3431	1.3076	0.4259

TABLE 48 (Continued)

O(13)	0.4164(8)	1.1868(6)	0.3945(6)
C(14)	0.3751(13)	1.1951(11)	0.3034(9)
H(14A)	0.4188	1.2446	0.2776
H(14B)	0.2921	1.2118	0.2953
C(15)	0.3957(12)	1.1027(10)	0.2598(9)
H(15A)	0.3665	1.1054	0.1982
H(15B)	0.3539	1.0528	0.2867
O(16)	0.5189(8)	1.0835(7)	0.2706(5)
C(17)	0.5487(12)	1..0078(10)	0.2186(8)
H(17A)	0.5268	1.0225	0.1573
H(17B)	0.5057	0.9514	0.2325
C(18)	0.6772(12)	0.9852(10)	0.2367(8)
H(18A)	0.7003	0.9370	0.1971
H(18B)	0.7211	1.0429	0.2287
O(21)	0.7469(11)	1.2100(9)	0.3980(8)
O(22)	0.4631(10)	1.0063(12)	0.4793(9)

TABLE 49

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[Na_2(H_2O)_3(18\text{-Crown-}6)_2]Cu_4I_6$ (**X**)

I(1)-Cu(1)	2.579(3)	Cu(4)-Cu(1^{i})	2.765(5)
I(1)-Cu(2)	2.588(4)	Cu(4)-Cu(2^{i})	1.916(5)
I(1)-Cu(3)	2.553(3)	Cu(4)-Cu(3^{i})	2.720(5)
I(1)-Cu(4)	2.568(3)	Na(1)-O(1)	2.562(11)
I(2)-Cu(1)	2.591(3)	Na(1)-O(4)	2.626(10)
I(2)-Cu(2)	2.550(3)	Na(1)-O(7)	2.888(11)
I(2)-Cu(3^{i})	2.545(3)	Na(1)-O(10)	2.847(11)
I(2)-Cu(4^{i})	2.567(3)	Na(1)-O(13)	2.899(10)
I(3)-Cu(1)	2.523(3)	Na(1)-O(16)	2.667(10)
I(3)-Cu(4)	2.539(3)	Na(1)-O(21)	2.262(14)
I(3)-Cu(2^{i})	2.564(3)	Na(1)-O(22)	2.426(15)
I(3)-Cu(3^{i})	2.569(3)	Na(1)-O(22^{ii})	2.24(2)
Cu(1)-Cu(2)	2.012(4)	O(1)-C(2)	1.41(2)
Cu(1)-Cu(3)	2.767(4)	O(1)-C(18)	1.432(14)
Cu(1)-Cu(4)	1.867(4)	C(2)-C(3)	1.48(2)
Cu(1)-Cu(2^{i})	2.712(4)	C(3)-O(4)	1.38(2)
Cu(1)-Cu(3^{i})	1.940(5)	O(4)-C(5)	1.424(15)
Cu(1)-Cu(4^{i})	2.765(5)	C(5)-C(6)	1.48(2)
Cu(2)-Cu(3)	1.960(4)	C(6)-O(7)	1.38(2)
Cu(2)-Cu(4)	2.771(4)	O(7)-C(8)	1.41(2)
Cu(2)-I(3^{i})	2.564(3)	C(8)-C(9)	1.41(3)
Cu(2)-Cu(1^{i})	2.712(4)	C(9)-O(10)	1.38(2)
Cu(2)-Cu(3^{i})	2.793(4)	O(10)-C(11)	1.37(2)
Cu(2)-Cu(4^{i})	1.916(5)	C(11)-C(12)	1.44(2)
Cu(3)-Cu(4)	1.992(4)	C(12)-O(13)	1.42(2)
Cu(3)-I(2^{i})	2.545(3)	O(13)-C(14)	1.417(15)
Cu(3)-I(3^{i})	2.569(3)	C(14)-C(15)	1.48(2)
Cu(3)-Cu(1^{i})	1.940(5)	C(15)-C(16)	1.41(2)
Cu(3)-Cu(2^{i})	2.793(4)	C(16)-C(17)	1.39(2)
Cu(3)-Cu(4^{i})	2.720(5)	C(17)-C(18)	1.48(2)
Cu(4)-I(2^{i})	2.567(3)	O(22)-Na(1^{ii})	2.24(2)
Cu(1)-I(1)-Cu(2)	45.8(1)	O(10)-Na(1)-O(21)	77.8(4)
Cu(1)-I(1)-Cu(3)	65.2(1)	O(13)-Na(1)-O(21)	92.1(4)
Cu(2)-I(1)-Cu(3)	44.8(1)	O(16)-Na(1)-O(21)	90.4(4)
Cu(1)-I(1)-Cu(4)	42.5(1)	O(1)-Na(1)-O(22)	100.5(5)
Cu(2)-I(1)-Cu(4)	65.0(1)	O(4)-Na(1)-O(22)	109.5(4)
Cu(3)-I(1)-Cu(4)	45.8(1)	O(7)-Na(1)-O(22)	87.0(4)
Cu(1)-I(2)-Cu(2)	46.1(1)	O(10)-Na(1)-O(22)	79.8(5)

TABLE 49 (Continued)

Cu(1)-I(2)-Cu(3^{i})	44.4(1)	O(13)-Na(1)-O(22)	63.9(4)
Cu(2)-I(2)-Cu(3^{i})	66.5(1)	O(16)-Na(1)-O(22)	86.4(4)
Cu(1)-I(2)-Cu(4^{i})	64.8(1)	O(21)-Na(1)-O(22)	153.6(6)
Cu(2)-I(2)-Cu(4^{i})	44.0(1)	O(1)-Na(1)-O(22^{ii})	101.5(5)
Cu(3^{i})-I(2)-Cu(4^{i})	45.9(1)	O(4)-Na(1)-O(22^{ii})	87.9(4)
Cu(1)-I(3)-Cu(4)	43.3(1)	O(7)-Na(1)-O(22^{ii})	65.9(4)
Cu(1)-I(3)-Cu(2^{i})	64.4(1)	O(10)-Na(1)-O(22^{ii})	79.3(5)
Cu(4)-I(3)-Cu(2^{i})	44.1(1)	O(13)-Na(1)-O(22^{ii})	84.5(4)
Cu(1)-I(3)-Cu(3^{i})	44.8(1)	O(16)-Na(1)-O(22^{ii})	108.9(4)
Cu(4)-I(3)-Cu(3^{i})	64.3(1)	O(21)-Na(1)-O(22^{ii})	154.6(6)
Cu(2^{i})-I(3)-Cu(3^{i})	44.9(1)	C(2)-O(1)-C(18)	110.9(10)
O(1)-Na(1)-O(4)	64.3(3)	O(1)-C(2)-C(3)	107.5(11)
O(1)-Na(1)-O(7)	123.2(3)	C(2)-C(3)-O(4)	109.9(12)
O(4)-Na(1)-O(7)	60.2(3)	C(3)-O(4)-C(5)	112.4(10)
O(1)-Na(1)-O(10)	178.7(4)	O(4)-C(5)-C(6)	109.5(11)
O(4)-Na(1)-O(10)	116.9(3)	C(5)-C(6)-O(7)	109.4(11)
O(7)-Na(1)-O(10)	58.1(3)	C(6)-O(7)-C(8)	110.6(11)
O(1)-Na(1)-O(13)	121.5(3)	O(7)-C(8)-C(9)	110.7(14)
O(4)-Na(1)-O(13)	171.2(4)	C(8)-C(9)-O(10)	113.7(15)
O(7)-Na(1)-O(13)	112.4(3)	C(9)-O(10)-C(11)	113.0(12)
O(10)-Na(1)-O(13)	57.4(3)	O(10)-C(11)-C(12)	110.3(13)
O(1)-Na(1)-O(16)	64.5(3)	C(11)-C(12)-O(13)	110.2(12)
O(4)-Na(1)-O(16)	128.2(4)	C(12)-O(13)-C(14)	111.9(10)
O(7)-Na(1)-O(16)	170.8(4)	O(13)-C(14)-C(15)	108.6(11)
O(10)-Na(1)-O(16)	114.3(3)	C(14)-C(15)-O(16)	108.7(11)
O(13)-Na(1)-O(16)	58.8(3)	C(15)-O(16)-C(17)	112.5(10)
O(1)-Na(1)-O(21)	101.7(5)	O(16)-C(17)-C(18)	110.8(10)
O(4)-Na(1)-O(21)	93.0(4)	O(1)-C(18)-C(17)	108.0(10)
O(7)-Na(1)-O(21)	92.6(4)	Na(1)-O(22)-Na(1^{ii})	155.7(6)

Symmetry operation:

^{i} = -x, 2-y, -z

^{ii} = 1-x, 2-y, 1-z

TABLE 50

ANISOTROPIC THERMAL PARAMETERS FOR

$[Na_2(H_2O)_3(18\text{-Crown-}6)_2]Cu_4I_6$ (**X**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	47(1)	60(1)	67(1)	4(1)	3(1)	-1(1)
I(2)	68(1)	48(1)	58(1)	1(1)	14(1)	12(1)
I(3)	78(1)	57(1)	50(1)	5(1)	-3(1)	-18(1)
Cu(1)	56(2)	46(2)	51(2)	4(2)	4(2)	0(1)
Cu(2)	60(2)	51(2)	47(2)	5(2)	-2(2)	-1(1)
Cu(3)	59(2)	53(2)	54(2)	0(2)	3(2)	-3(2)
Cu(4)	58(2)	54(2)	49(2)	1(2)	8(2)	-4(2)
Na(1)	94(5)	72(4)	110(5)	-29(4)	49(4)	-5(4)
O(1)	54(6)	70(6)	42(5)	6(5)	10(4)	-2(4)
C(2)	61(10)	82(11)	61(9)	29(9)	18(8)	-4(8)
C(3)	41(8)	90(12)	81(11)	-8(8)	7(8)	16(10)
O(4)	64(6)	58(6)	53(5)	14(5)	1(5)	1(5)
C(5)	64(9)	64(9)	62(9)	9(8)	-4(7)	15(7)
C(6)	66(11)	71(10)	69(9)	3(9)	-7(8)	-6(8)
O(7)	72(7)	57(6)	66(6)	5(5)	-7(5)	-7(5)
C(8)	116(16)	93(13)	75(11)	8(12)	-11(11)	-36(10)
C(9)	122(16)	95(14)	79(12)	29(13)	-16(12)	-49(11)
O(10)	72(7)	66(6)	56(6)	4(6)	-2(5)	-3(5)
C(11)	90(13)	87(13)	74(11)	12(10)	-5(10)	-14(9)
C(12)	66(10)	63(10)	89(12)	13(8)	5(9)	-7(9)
O(13)	60(6)	59(6)	60(6)	0(5)	9(5)	-5(5)
C(14)	63(9)	79(11)	62(10)	-1(9)	18(8)	10(8)
C(15)	55(9)	77(10)	59(9)	9(8)	13(7)	2(8)
O(16)	60(6)	66(6)	55(6)	4(5)	4(5)	-10(5)
C(17)	61(10)	73(10)	38(7)	-1(8)	0(7)	9(7)
C(18)	60(9)	64(9)	50(8)	4(8)	9(7)	-13(7)
O(21)	134(11)	109(9)	120(10)	-37(9)	25(9)	-10(8)
C(22)	42(6)	64(12)	45(8)	-18(7)	-16(6)	10(8)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

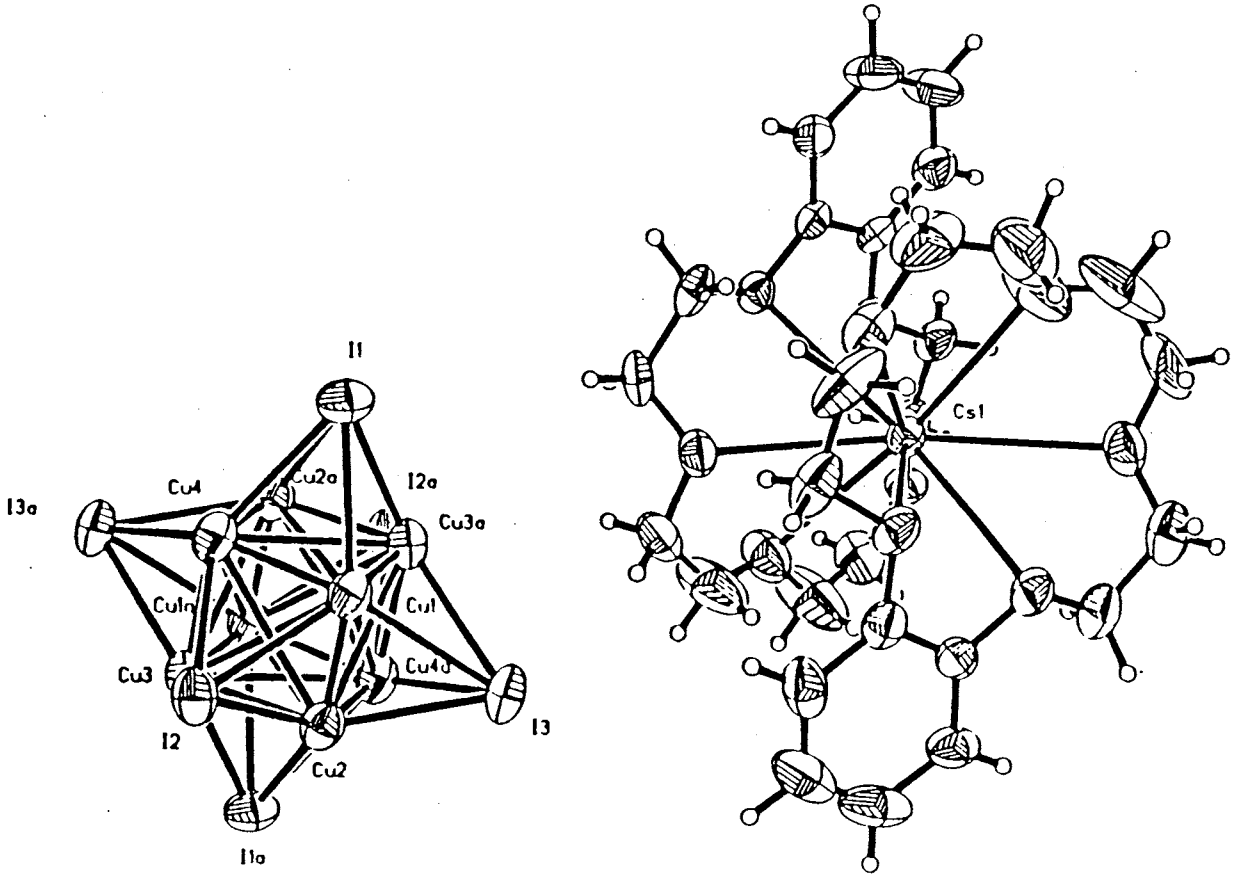


Figure 32. Projection View of $[Cs(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_4I_6$ (**XI**)

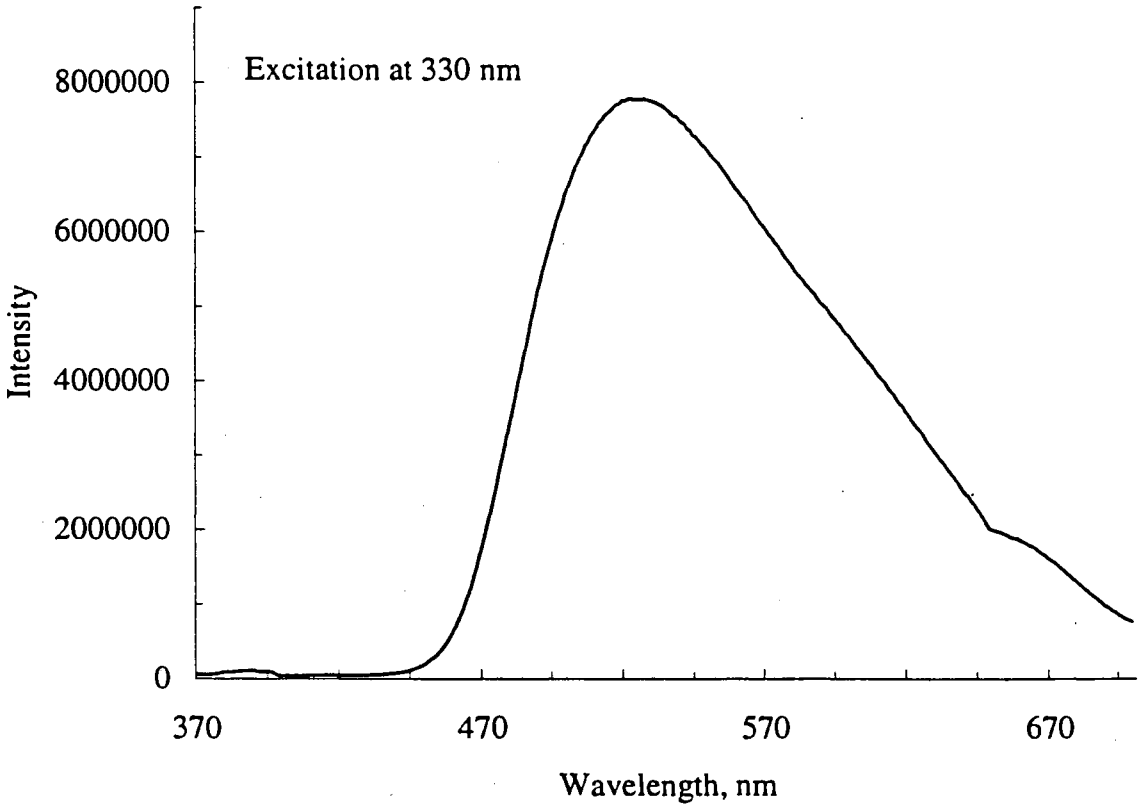


Figure 33. Emission spectrum of $[Cs(Benzo\text{-}15\text{-}crown\text{-}5)_2]_2Cu_4I_6$ (**XI**)

TABLE 51

CRYSTAL DATA FOR

$[Cs(Benzo\text{-}15\text{-}crown\text{-}5)_2]Cu_2I_3$ (**XI**)

Formula	$C_{28}H_{40}CsCu_2I_3O_{10}$
Space group	$P2_1/c$
A	10.896(4) Å
B	16.277(5) Å
C	22.638(7) Å
β	91.37(2)°
V	4011(2) $Å^3$
Z	4
Mw	941.8 g $mole^{-1}$
Density (calc.)	1.950 Mg m^{-3}
$\mu(MoK_\alpha)$	4.309 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	22400
Collected Reflections	14200
Independent Reflections	11679
Observed Reflections ($F > 4.0\sigma$)	4163
Number of parameters	416
Final R indices	$R = 5.52\ \%$, $R_w = 5.82\ \%$
R indices (all data)	$R = 16.61\ \%$, $R_w = 9.11\ \%$
GOF	1.19

TABLE 52

POSITIONAL PARAMETERS FOR

$[Cs(Benzo\text{-}15\text{-}crown\text{-}5)_2]Cu_2I_3$ (**XI**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
Cu(1)	0.9057(3)	0.0388(2)	0.5519(1)
Cu(2)	1.0777(3)	0.0727(2)	0.5411(1)
Cu(3)	1.1326(3)	-0.0505(2)	0.5274(1)
Cu(4)	0.9475(3)	-0.0845(2)	0.5403(1)
I(1)	0.7167(1)	-0.0514(1)	0.5175(1)
I(2)	1.0525(1)	-0.0177(1)	0.6341(1)
I(3)	0.9247(1)	0.1915(1)	0.5232(1)
Cs(1)	0.4662(1)	0.3764(1)	0.3127(1)
O(1)	0.4009(7)	0.2932(4)	0.1859(3)
C(2)	0.3947(12)	0.3612(7)	0.1446(5)
H(2A)	0.3548	0.4076	0.1620
H(2B)	0.3498	0.3452	0.1095
C(3)	0.5260(13)	0.3831(8)	0.1326(5)
H(3A)	0.5297	0.4250	0.1029
H(3B)	0.5668	0.3350	0.1184
O(4)	0.5856(7)	0.4113(5)	0.1857(3)
C(5)	0.7173(14)	0.4111(10)	0.1820(6)
H(5A)	0.7436	0.4626	0.1660
H(5B)	0.7406	0.3686	0.1550
C(6)	0.7786(14)	0.3877(15)	0.2309(9)
H(6A)	0.7662	0.4350	0.2554
H(6B)	0.8649	0.3839	0.2238
O(7)	0.7429(9)	0.3280(7)	0.2672(5)
C(8)	0.7941(15)	0.2978(14)	0.3109(9)
H(8A)	0.7833	0.3425	0.3380
H(8B)	0.8808	0.2933	0.3050
C(9)	0.7553(12)	0.2321(9)	0.3463(7)
H(9A)	0.7901	0.2330	0.3857
H(9B)	0.7873	0.1850	0.3264
O(10)	0.6230(8)	0.2213(5)	0.3498(3)
C(11)	0.5827(12)	0.1393(7)	0.3395(5)
H(11A)	0.6006	0.1057	0.3735
H(11B)	0.6247	0.1167	0.3064
C(12)	0.4440(11)	0.1412(6)	0.3270(4)
H(12A)	0.4021	0.1658	0.3594
H(12B)	0.4143	0.0861	0.3219

TABLE 52 (Continued)

O(13)	0.4237(7)	0.1888(4)	0.2729(3)
C(14)	0.3044(11)	0.1993(6)	0.2504(4)
C(15)	0.2902(11)	0.2572(6)	0.2027(4)
C(16)	0.1742(13)	0.2711(8)	0.1768(6)
H(16A)	0.1640	0.3093	0.1448
C(17)	0.0736(14)	0.2282(10)	0.1982(7)
H(17A)	-0.0072	0.2373	0.1816
C(18)	0.0874(13)	0.1741(9)	0.2449(7)
H(18A)	0.0171	0.1450	0.2587
C(19)	0.1996(12)	0.1593(7)	0.2702(5)
H(19A)	0.2086	0.1225	0.3032
O(21)	0.5152(7)	0.5371(4)	0.3966(3)
C(22)	0.5089(13)	0.6027(7)	0.3551(6)
H(22A)	0.5477	0.5858	0.3195
H(22B)	0.5501	0.6507	0.3703
C(23)	0.3773(15)	0.6191(8)	0.3399(6)
H(23A)	0.3672	0.6672	0.3158
H(23B)	0.3361	0.6278	0.3764
O(24)	0.3207(9)	0.5486(6)	0.3118(4)
C(25)	0.191(2)	0.5375(14)	0.3195(13)
H(25A)	0.1485	0.5779	0.2958
H(25B)	0.1810	0.5521	0.3602
C(26)	0.137(2)	0.467(2)	0.3181(15)
H(26A)	0.1375	0.4569	0.2763
H(26B)	0.0527	0.4716	0.3289
O(27)	0.1888(11)	0.4015(12)	0.3433(7)
C(28)	0.144(2)	0.372(2)	0.3909(11)
H(28A)	0.0564	0.3646	0.3872
H(28B)	0.1586	0.4111	0.4222
C(29)	0.192(2)	0.2963(11)	0.4126(9)
H(29A)	0.1707	0.2560	0.3832
H(29B)	0.1577	0.2788	0.4492
O(30)	0.3256(10)	0.2932(5)	0.4205(4)
C(31)	0.371(2)	0.3000(9)	0.4795(6)
H(31A)	0.3608	0.2483	0.4992
H(31B)	0.3275	0.3416	0.5006
C(32)	0.505(2)	0.3228(8)	0.4805(5)
H(32A)	0.5470	0.2853	0.4551
H(32B)	0.5438	0.3212	0.5190
O(33)	0.5135(8)	0.4034(4)	0.4569(3)
C(34)	0.6271(13)	0.4380(7)	0.4503(5)
C(35)	0.6316(11)	0.5100(7)	0.4168(5)
C(36)	0.7424(12)	0.5513(9)	0.4052(6)
H(36A)	0.7416	0.6012	0.3826
C(37)	0.852(2)	0.5186(14)	0.4297(9)

TABLE 52 (Continued)

H(37A)	0.9300	0.5447	0.4238
C(38)	0.846(2)	0.4471(15)	0.4644(9)
H(38A)	0.9206	0.4250	0.4808
C(39)	0.738(2)	0.4060(9)	0.4747(6)
H(39A)	0.7376	0.3564	0.4977

TABLE 53

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[Cs(Benzo\text{-}15\text{-}crown\text{-}5)_2]Cu_2I_3$ (**XI**)

Cu(1)...Cu(2)	1.975(4)	Cs(1)-O(30)	3.212(9)
Cu(1)...Cu(3)	2.933(4)	Cs(1)-O(33)	3.321(7)
Cu(1)...Cu(4)	2.076(4)	O(1)-C(2)	1.450(13)
Cu(1)-I(1)	2.632(3)	O(1)-C(15)	1.400(13)
Cu(1)-I(2)	2.592(3)	C(2)-C(3)	1.50(2)
Cu(1)-I(3)	2.578(3)	C(3)-O(4)	1.429(15)
Cu(1)...Cu(2^i)	2.789(4)	O(4)-C(5)	1.44(2)
Cu(1)...Cu(3^i)	1.844(4)	C(5)-C(6)	1.33(2)
Cu(1)...Cu(4^i)	2.762(4)	C(6)-O(7)	1.34(2)
Cu(2)...Cu(3)	2.118(4)	O(7)-C(8)	1.23(2)
Cu(2)...Cu(4)	2.925(4)	C(8)-C(9)	1.41(3)
Cu(2)-I(2)	2.589(3)	C(9)-O(10)	1.46(2)
Cu(2)-I(3)	2.579(3)	O(10)-C(11)	1.422(14)
Cu(2)...Cu(1^i)	2.789(4)	C(11)-C(12)	1.53(2)
Cu(2)...Cu(3^i)	2.760(4)	C(12)-O(13)	1.461(12)
Cu(2)...Cu(4^i)	1.866(4)	O(13)-C(14)	1.395(14)
Cu(2)-I(1^i)	2.653(3)	C(14)-C(15)	1.438(14)
Cu(3)...Cu(4)	2.118(4)	C(14)-C(19)	1.40(2)
Cu(3)-I(2)	2.643(3)	C(15)-C(16)	1.40(2)
Cu(3)...Cu(1^i)	1.844(4)	C(16)-C(17)	1.40(2)
Cu(3)...Cu(2^i)	2.760(4)	C(17)-C(18)	1.38(2)
Cu(3)...Cu(4^i)	2.806(4)	C(18)-C(19)	1.36(2)
Cu(3)-I(1^i)	2.561(3)	O(21)-C(22)	1.423(14)
Cu(3)-I(3^i)	2.633(3)	O(21)-C(35)	1.407(14)
Cu(4)-I(1)	2.611(3)	C(22)-C(23)	1.49(2)
Cu(4)-I(2)	2.623(3)	C(23)-O(24)	1.44(2)
Cu(4)...Cu(1^i)	2.762(4)	O(24)-C(25)	1.44(2)
Cu(4)...Cu(2^i)	1.866(4)	C(25)-C(26)	1.29(4)
Cu(4)...Cu(3^i)	2.806(4)	C(26)-O(27)	1.33(4)
Cu(4)-I(3^i)	22.671(3)	O(27)-C(28)	1.29(3)
I(1)-Cu(2^i)	2.653(3)	C(28)-C(29)	1.42(3)
I(1)-Cu(3^i)	2.561(3)	C(29)-O(30)	1.46(2)
I(3)-Cu(3^i)	2.633(3)	O(30)-C(31)	1.42(2)
I(3)-Cu(4^i)	2.671(3)	C(31)-C(32)	1.51(3)
Cs(1)-O(1)	3.238(7)	C(32)O(33)	1.420(15)
Cs(1)-O(4)	3.235(8)	O(33)-C(34)	1.37(2)
Cs(1)-O(7)	3.305(10)	C(34)-C(35)	1.40(2)
Cs(1)-O(10)	3.152(8)	C(34)-C(39)	1.42(2)
Cs(1)-O(13)	3.214(7)	C(36)-C(37)	1.41(2)

TABLE 53 (Continued)

Cs(1)-O(24)	3.220(10)	C(37)-C(38)	1.41(3)
Cs(1)-O(27)	3.143(13)	C(38)-C(39)	1.38(3)
Cu(1)-I(1)-Cu(4)	46.7(1)	O(4)-Cs(1)-O(33)	142.6(2)
Cu(1)-I(1)-Cu(2^{i})	63.7(1)	O(7)-Cs(1)-O(33)	102.5(2)
Cu(4)-I(1)-Cu(2^{i})	41.5(1)	O(10)-Cs(1)-O(33)	76.9(2)
Cu(1)-I(1)-Cu(3^{i})	41.6(1)	O(13)-Cs(1)-O(33)	114.8(2)
Cu(4)-I(1)-Cu(3^{i})	65.7(1)	O(21)-Cs(1)-O(33)	45.9(2)
Cu(2^{i})-I(1)-Cu(3^{i})	47.9(1)	O(24)-Cs(1)-O(33)	87.5(2)
Cu(1)-I(2)-Cu(2)	44.8(1)	O(27)-Cs(1)-O(33)	83.9(3)
Cu(1)-I(2)-Cu(3)	68.1(1)	O(30)-Cs(1)-O(33)	51.3(2)
Cu(2)-I(2)-Cu(3)	47.7(1)	C(2)-O(1)-C(15)	117.8(8)
Cu(1)-I(2)-Cu(4)	46.9(1)	O(1)-C(2)-C(3)	105.6(10)
Cu(2)-I(2)-Cu(4)	68.3(1)	C(2)-C(3)-O(4)	109.8(10)
Cu(3)-I(2)-Cu(4)	47.4(1)	C(3)-O(4)-C(5)	112.6(10)
Cu(1)-I(3)-Cu(2)	45.0(1)	O(4)-C(5)-C(6)	115.6(13)
Cu(1)-I(3)-Cu(3^{i})	41.4(1)	C(5)-C(6)-O(7)	124.8(15)
Cu(2)-I(3)-Cu(3^{i})	63.9(1)	C(6)-O(7)-C(8)	130.8(14)
Cu(1)-I(3)-Cu(4^{i})	63.5(1)	O(7)-C(8)-C(9)	129(2)
Cu(2)-I(3)-Cu(4^{i})	41.6(1)	C(8)-C(9)-O(10)	115.8(12)
Cu(3^{i})-I(3)-Cu(4^{i})	47.1(1)	C(9)-O(10)-C(11)	114.0(10)
O(1)-Cs(1)-O(4)	50.9(2)	O(10)-C(11)-C(12)	108.1(9)
O(1)-Cs(1)-O(7)	78.8(2)	C(11)-C(12)-O(13)	107.1(9)
O(4)-Cs(1)-O(7)	51.3(2)	C(12)-O(13)-C(14)	119.5(8)
O(1)-Cs(1)-O(10)	90.4(2)	O(13)-C(14)-C(15)	115.9(9)
O(4)-Cs(1)-O(10)	98.7(2)	O(13)-C(14)-C(19)	125.8(9)
O(7)-Cs(1)-O(10)	53.1(2)	C(15)-C(14)-C(19)	118.2(11)
O(1)-Cs(1)-O(13)	47.7(2)	O(1)-C(15)-C(14)	113.5(9)
O(4)-Cs(1)-O(13)	88.6(2)	O(1)-C(15)-C(16)	126.4(9)
O(7)-Cs(1)-O(13)	79.2(2)	C(14)-C(15)-C(16)	120.0(11)
O(10)-Cs(1)-O(13)	52.2(2)	C(15)-C(16)-C(17)	118.8(12)
O(1)-Cs(1)-O(21)	151.6(2)	C(16)-C(17)-C(18)	120.8(13)
O(4)-Cs(1)-O(21)	108.2(2)	C(17)-C(18)-C(19)	121.2(13)
O(7)-Cs(1)-O(21)	103.6(2)	C(14)-C(19)-C(18)	120.9(12)
O(10)-Cs(1)-O(21)	114.0(2)	C(22)-O(21)-C(35)	118.6(9)
O(13)-Cs(1)-O(21)	160.7(2)	O(21)-C(22)-C(23)	108.5(10)
O(1)-Cs(1)-O(24)	105.1(2)	C(22)-C(23)-O(24)	111.0(11)
O(4)-Cs(1)-O(24)	92.9(2)	C(23)-O(24)-C(25)	117.3(14)
O(7)-Cs(1)-O(24)	131.2(3)	O(24)-C(25)-C(26)	124(2)
O(10)-Cs(1)-O(24)	164.3(2)	C(25)-C(26)-O(27)	121(2)
O(13)-Cs(1)-O(24)	139.2(2)	C(26)-O(27)-C(28)	119(2)
O(21)-Cs(1)-O(24)	51.7(2)	O(27)-C(28)-C(29)	118(2)
O(1)-Cs(1)-O(27)	93.3(3)	C(28)-C(29)-O(30)	116(2)
O(4)-Cs(1)-O(27)	125.6(3)	C(29)-O(30)-C(31)	116.9(13)
O(7)-Cs(1)-O(27)	171.4(4)	O(30)-C(31)-C(32)	110.5(12)

TABLE 53 (Continued)

O(10)-Cs(1)-O(27)	124.3(4)	C(31)-C(32)-O(33)	107.0(12)
O(13)-Cs(1)-O(27)	93.0(4)	C(32)-O(33)-C(34)	119.0(11)
O(21)-Cs(1)-O(27)	85.0(3)	O(33)-C(34)-C(35)	116.5(11)
O(24)-Cs(1)-O(27)	54.0(4)	O(33)-C(34)-C(39)	124.8(11)
O(1)-Cs(1)-O(30)	113.5(2)	C(35)-C(34)-C(39)	118.7(12)
O(4)-Cs(1)-O(30)	163.5(2)	O(21)-C(35)-C(34)	113.3(10)
O(7)-Cs(1)-O(30)	126.3(3)	O(21)-C(35)-C(36)	124.0(10)
O(10)-Cs(1)-O(30)	74.0(2)	C(34)-C(35)-C(36)	122.7(12)
O(13)-Cs(1)-O(30)	75.2(2)	C(35)-C(36)-C(37)	117.9(14)
O(21)-Cs(1)-O(30)	88.3(2)	C(36)-C(37)-C(38)	118(2)
O(24)-Cs(1)-O(30)	97.4(2)	C(37)-C(38)-C(39)	124(2)
O(27)-Cs(1)-O(30)	53.7(4)	C(34)-C(39)-C(38)	118.5(15)
O(1)-Cs(1)-O(33)	162.2(2)		

Symmetry operation:

^{i} = 2-x, -y, 1-z

TABLE 54

ANISOTROPIC THERMAL PARAMETERS FOR

[Cs(Benzo-15-crown-5)$_2$]Cu_2I_3 (**XI**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	72(2)	59(2)	63(2)	3(1)	9(1)	9(1)
Cu(2)	79(2)	61(2)	68(2)	2(2)	2(2)	-5(1)
Cu(3)	77(2)	67(2)	70(2)	14(2)	0(2)	6(1)
Cu(4)	86(2)	58(2)	73(2)	1(2)	13(2)	9(1)
I(1)	73(1)	89(1)	83(1)	-16(1)	14(1)	-18(1)
I(2)	91(1)	76(1)	58(1)	15(1	1(1)	8(1)
I(3)	114(1)	51(1)	86(1)	17(1)	8(1)	2(1)
Cs(1)	69(1)	57(1)	62(1)	3(1)	11(1)	-6(1)
O(1)	80(5)	46(4)	62(4)	-3(4)	-9(4)	15(3)
C(2)	100(11)	59(7)	78(8)	-12(7)	-12(7)	22(6)
C(3)	125(12)	66(8)	84(9)	-8(8)	11(9)	25(7)
O(4)	62(5)	78(5)	81(6)	-11(4)	10(4)	12(4)
C(5)	102(12)	125(13)	106(12)	-4(10)	26(10)	42(10)
C(6)	69(11)	317(32)	180(19)	-23(15)	21(12)	140(22)
O(7)	82(7)	133(8)	113(7)	4(6)	-7(6)	46(6)
C(8)	61(12)	264(27)	214(23)	-34(14)	-6(13)	94(21)
C(9)	65(10)	113(12)	122(12)	16(9)	-17(9)	15(10)
O(10)	77(6)	72(5)	90(6)	15(5)	-1(4)	17(5)
C(11)	91(10)	66(8)	85(8)	42(7)	-4(7)	4(6)
C(12)	125(11)	45(7)	60(7)	3(7)	-6(7)	11(5)
O(13)	76(5)	56(4)	54(4)	0(4)	-6(4)	9(3)
C(14)	67(8)	41(6)	62(6)	-2(6)	6(6)	-2(5)
C(15)	71(8)	42(6)	63(6)	-12(6)	4(6)	-1(5)
C(16)	103(11)	73(9)	93(9)	-6(8)	-26(9)	13(7)
C(17)	71(10)	148(14)	131(13)	-37(10)	-27(9)	32(11)
C(18)	77(11)	119(12)	125(12)	-48(9)	-14(9)	27(10)
C(19)	77(9)	69(8)	83(9)	3(7)	-12(8)	-6(7)
O(21)	85(6)	58(5)	71(5)	-4(4)	2(4)	14(4)
C(22)	116(11)	64(8)	79(9)	7(8)	-1(8)	5(7)
C(23)	153(15)	82(10)	72(8)	28(10)	-8(9)	14(8)
O(24)	102(7)	95(7)	96(6)	32(6)	-23(6)	2(5)
C(25)	120(25)	190(24)	324(32)	80(19)	-144(23)	-57(23)
C(26)	56(15)	382(51)	273(39)	16(23)	-4(20)	-27(37)
O(27)	77(9)	244(17)	183(13)	17(10)	15(8)	81(12)
C(28)	101(15)	199(26)	219(25)	20(17)	15(16)	9(21)
C(29)	144(19)	125(16)	189(19)	-50(14)	86(15)	-2(14)
O(30)	116(8)	73(6)	98(7)	-9(5)	41(6)	-7(5)

TABLE 54 (Continued)

C(31)	256(23)	74(10)	64(9)	-59(13)	55(12)	-7(7)
C(32)	189(18)	66(9)	55(8)	1(11)	-7(10)	10(7)
O(33)	97(7)	59(5)	75(5)	-10(5)	1(5)	15(4)
C(34)	94(10)	64(8)	54(7)	1(8)	-12(7)	-8(6)
C(35)	66(8)	66(8)	73(7)	5(7)	-9(6)	-24(6)
C(36)	62(9)	96(10)	113(11)	-16(8)	20(8)	-31(8)
C(37)	66(12)	196(21)	150(17)	-31(14)	25(12)	-92(15)
C(38)	74(13)	191(22)	127(16)	19(15)	-24(11)	-55(15)
C(39)	121(13)	100(11)	76(9)	41(11)	-31(9)	-20(8)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

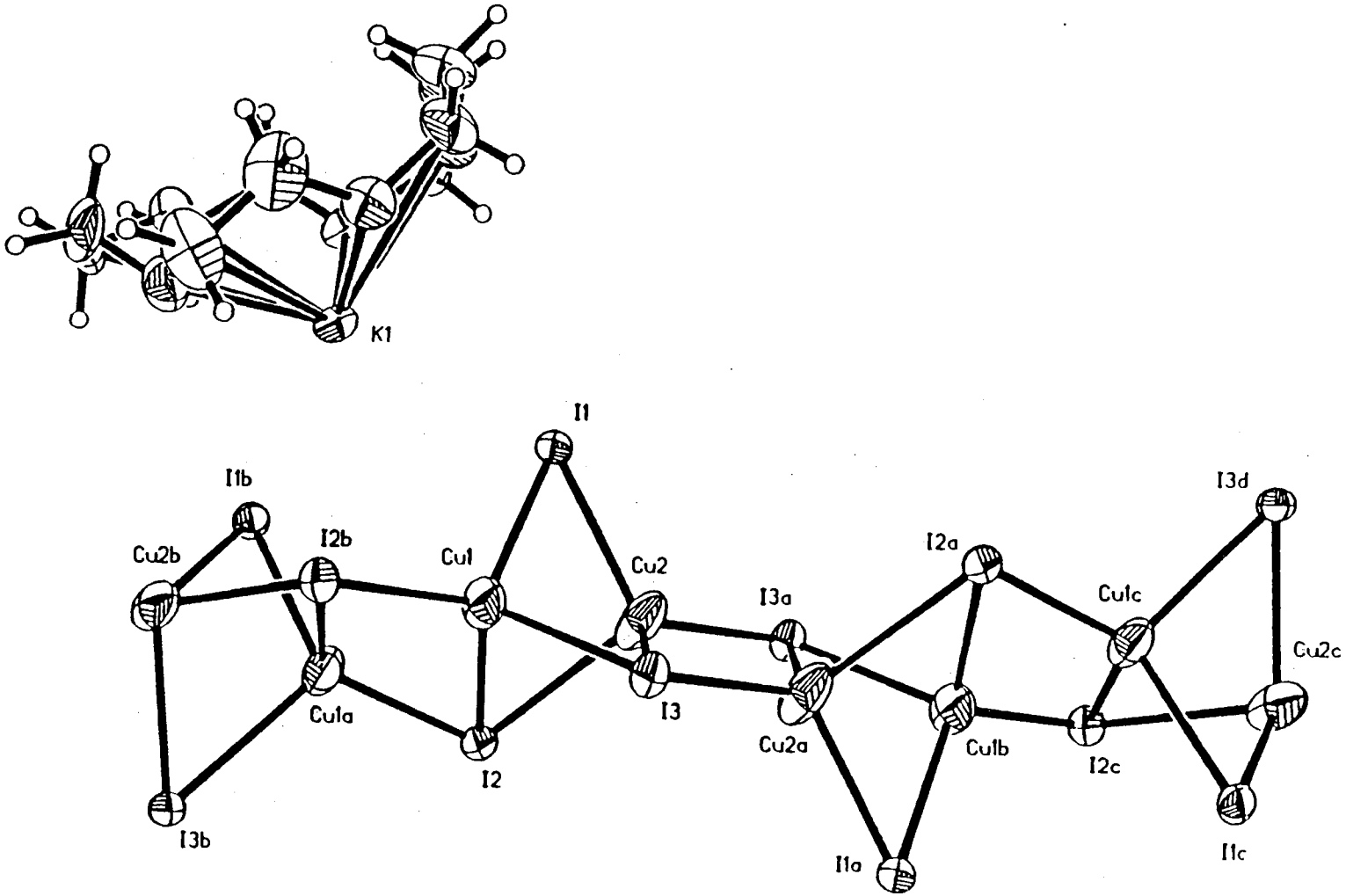


Figure 34. Projection View of $[K(15\text{-Crown-5})]Cu_2I_3$ **(XII)**

TABLE 55

CRYSTAL DATA FOR

[K(15-Crown-5)]Cu_2I_3 (**XII**)

Formula	$C_{10}H_{20}Cu_2I_3KO_5$
Space group	C2/c
A	23.818(14) Å
B	10.956(6) Å
C	17.071(10) Å
β	119.75(2)°
V	3874(4) $Å^3$
Z	8
Mw	767.1 g $mole^{-1}$
Density (calc.)	2.631 Mg m^{-3}
$\mu(MoK_\alpha)$	7.206 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	2848
Collected Reflections	6605
Independent Reflections	5650
Observed Reflections ($F > 5.5\ \sigma$)	2175
Number of parameters	191
Final R indices	$R = 5.86\ \%$, $R_w = 6.94\ \%$
R indices (all data)	$R = 12.87\ \%$, $R_w = 9.14\ \%$
GOF	1.36

TABLE 56

POSITIONAL PARAMETERS FOR

[K(15-Crown-5)]Cu_2I_3 (**XII**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.4610(1)	-0.2610(1)	0.1009(1)
I(2)	0.5984(1)	-0.0010(1)	0.2570(1)
I(3)	0.4267(1)	0.1067(1)	0.0154(1)
Cu(1)	0.4629(1)	-0.0395(3)	0.1612(2)
Cu(2)	0.5160(2)	-0.0729(3)	0.0715(2)
K(1)	0.3815(2)	-0.3435(4)	0.2192(3)
O(1)	0.2519(6)	-0.3271(14)	0.1026(9)
C(2)	0.2137(10)	-0.313(3)	0.142(2)
H(2A)	0.2062	-0.3919	0.1594
H(2B)	0.1728	-0.2787	0.0988
C(3)	0.2424(12)	-0.248(3)	0.221(2)
H(3A)	0.2510	-0.1710	0.2031
H(3B)	0.2143	-0.2347	0.2457
O(4)	0.3030(8)	-0.291(2)	0.2880(10)
C(5)	0.3003(13)	-0.370(2)	0.349(2)
H(5A)	0.2677	-0.4287	0.3136
H(5B)	0.2875	-0.3279	0.3871
C(6)	0.3611(15)	-0.434(2)	0.3985(15)
H(6A)	0.3950	-0.3751	0.4275
H(6B)	0.3604	-0.4852	0.4437
O(7)	0.3697(7)	-0.5057(14)	0.3405(9)
C(8)	0.4288(12)	-0.567(2)	0.3792(12)
H(8A)	0.4357	-0.6126	0.4312
H(8B	0.4633	-0.5089	0.3970
C(9)	0.4280(10)	-0.649(2)	0.3100(13)
H(9A)	0.4629	-0.7066	0.3340
H(9B)	0.3878	-0.6927	0.2831
O(10)	0.4303(6)	-0.5736(12)	0.2477(9)
C(11)	0.4116(10)	-0.634(2)	0.1656(14)
H(11A)	0.4308	-0.7132	0.1773
H(11B)	0.4277	-0.5876	0.1331
C(12)	0.3410(12)	-0.645(2)	0.1085(15)
H(12A)	0.3291	-0.6923	0.0552
H(12B)	0.3233	-0.6826	0.1422
O(13)	0.3195(7)	-0.5238(14)	0.0862(9)
C(14)	0.2514(12)	-0.529(2)	0.045(2)

TABLE 56 (Continued)

H(14A)	0.2402	-0.5608	0.0881
H(14B)	0.2323	-0.5776	-0.0083
C(15)	0.2295(11)	-0.402(2)	0.0277(14)
H(15A)	0.2469	-0.3731	-0.0091
H(15B)	0.1833	-0.3951	-0.0077

TABLE 57

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

[K(15-Crown-5)]Cu_2I_3 (**XII**)

I(1)-Cu(1)	2.628(4)	K(1)-O(13)	2.813 (15)
I(1)-Cu(2)	2.620(4)	O(1)-C(2)	1.38(4)
I(2)-Cu(1)	2.832(4)	O(1)-C(15)	1.38(3)
I(2)-Cu(2)	2.887(4)	C(2)-C(3)	1.38(4)
I(2)-Cu(1^{i})	2.508(5)	C(3)-O(4)	1.40(3)
I(3)-Cu(1)	2.714(4)	O(4)-C(5)	1.38(4)
I(3)-Cu(2)	2.699(4)	C(5)-C(6)	1.45(4)
I(3)-Cu(2^{ii})	2.492(5)	C(6)-O(7)	1.36(4)
Cu(1)-Cu(2)	2.448(7)	O(7)-C(8)	1.39(3)
Cu(1)-I(2^{i})	2.508(5)	C(8)-C(9)	1.48(4)
Cu(1)-Cu(1^{i})	2.646(5)	C(9)-O(10)	1.37(3)
Cu(2)-Cu(2^{ii})	2.691(8)	O(10)-C(11)	1.40(3)
K(1)-O(1)	2.724(12)	C(11)-C(12)	1.47(3)
K(1)-O(4)	2.72(2)	C(12)-O(13)	1.40(3)
K(1)-O(7)	2.85(2)	O(13)-C(14)	1.41(3)
K(1)-O(10)	2.718(13)	C(14)-C(15)	1.46(4)
Cu(1)-I(1)-Cu(2)	55.6(1)	O(10)-K(1)-O(13)	60.0(4)
Cu(1)-I(2)-Cu(2)	50.7(1)	C(2)-O(1)-C(15)	118(2)
Cu(1)-I(2)-Cu(1^{i})	59.0(1)	O(1)-C(2)-C(3)	114(2)
Cu(2)-I(2)-Cu(1^{i})	107.3(1)	C(2)-C(3)-O(4)	116(3)
Cu(1)-I(3)-Cu(2)	53.8(1)	C(3)-O(4)-C(5)	114(2)
Cu(1)-I(3)-Cu(2^{ii})	116.0(1)	O(4)-C(5)-C(6)	110(3)
Cu(2)-I(3)-Cu(2^{ii})	62.3(2)	C(5)-C(6)-O(7)	109(2)
O(1)-K(1)-O(4)	61.9(5)	C(6)-O(7)-C(8)	114(2)
O(1)-K(1)-O(7)	95.0(5)	O(7)-C(8)-C(9)	107.6(14)
O(4)-K(1)-O(7)	58.7(5)	C(8)-C(9)-O(10)	105(2)
O(1)-K(1)-O(10)	114.9(4)	C(9)-O(10)-C(11)	112.3(15)
O(4)-K(1)-O(10)	116.4(6)	O(10)-C(11)-C(12)	113(2)
O(7)-K(1)-O(10)	58.6(5)	C(11)-C(12)-O(13)	104(2)
O(1)-K(1)-O(13)	60.4(5)	C(12)-O(13)-C(14)	106(2)
O(4)-K(1)-O(13)	107.4(5)	O(13)-C(14)-C(15)	106(2)
O(7)-K(1)-O(13)	86.9(5)	O(1)-C(15)-C(14)	115(2)

Symmetry operations:

^{i} = 1-x, y, 0.5-z

^{ii} = 1-x, -y, -z

TABLE 58

ANISOTROPIC THERMAL PARAMETERS FOR

[K(15-Crown-5)]Cu_2I_3 (**XII**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	50(1)	36(1)	44(1)	-3(1)	24(1)	-4(1)
I(2)	45(1)	48(1)	46(1)	-7(1)	24(1)	-2(1)
I(3)	52(1)	45(1)	50(1)	12(1)	30(1)	10(1)
Cu(1)	110(2)	63(2)	90(2)	4(2)	75(2)	-7(1)
Cu(2)	142(3)	69(2)	149(3)	20(2)	124(3)	23(2)
K(1)	45(2)	47(2)	57(2)	-1(2)	23(2)	8(2)
O(1)	52(8)	76(10)	76(9)	8(8)	27(8)	0(8)
C(2)	42(13)	189(33)	91(18)	30(17)	20(13)	24(21)
C(3)	80(17)	131(26)	86(18)	63(19)	22(15)	0(18)
O(4)	90(12)	102(13)	76(10)	-3(10)	49(10)	-19(9)
C(5)	137(23)	84(18)	116(20)	11(18)	109(20)	-3(16)
C(6)	161(25)	52(14)	60(13)	-16(16)	67(16)	-13(11)
O(7)	76(10)	78(11)	57(8)	-9(9)	30(8)	-1(8)
C(8)	90(17)	107(20)	33(10)	-24(16)	-2(11)	32(12)
C(9)	71(14)	64(14)	70(13)	-12(11)	41(11)	7(12)
O(10)	51(8)	48(8)	86(9)	11(6)	38(7)	15(7)
C(11)	79(15)	53(12)	83(14)	19(11)	55(13)	-6(11)
C(12)	103(19)	53(14)	81(14)	-24(13)	58(14)	-30(12)
O(13)	58(9)	72(11)	73(9)	4(8)	25(7)	-9(8)
C(14)	96(20)	72(17)	104(19)	-26(15)	36(16)	-35(15)
C(15)	67(14)	96(20)	54(12)	-1(14)	-2(11)	-1(14)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

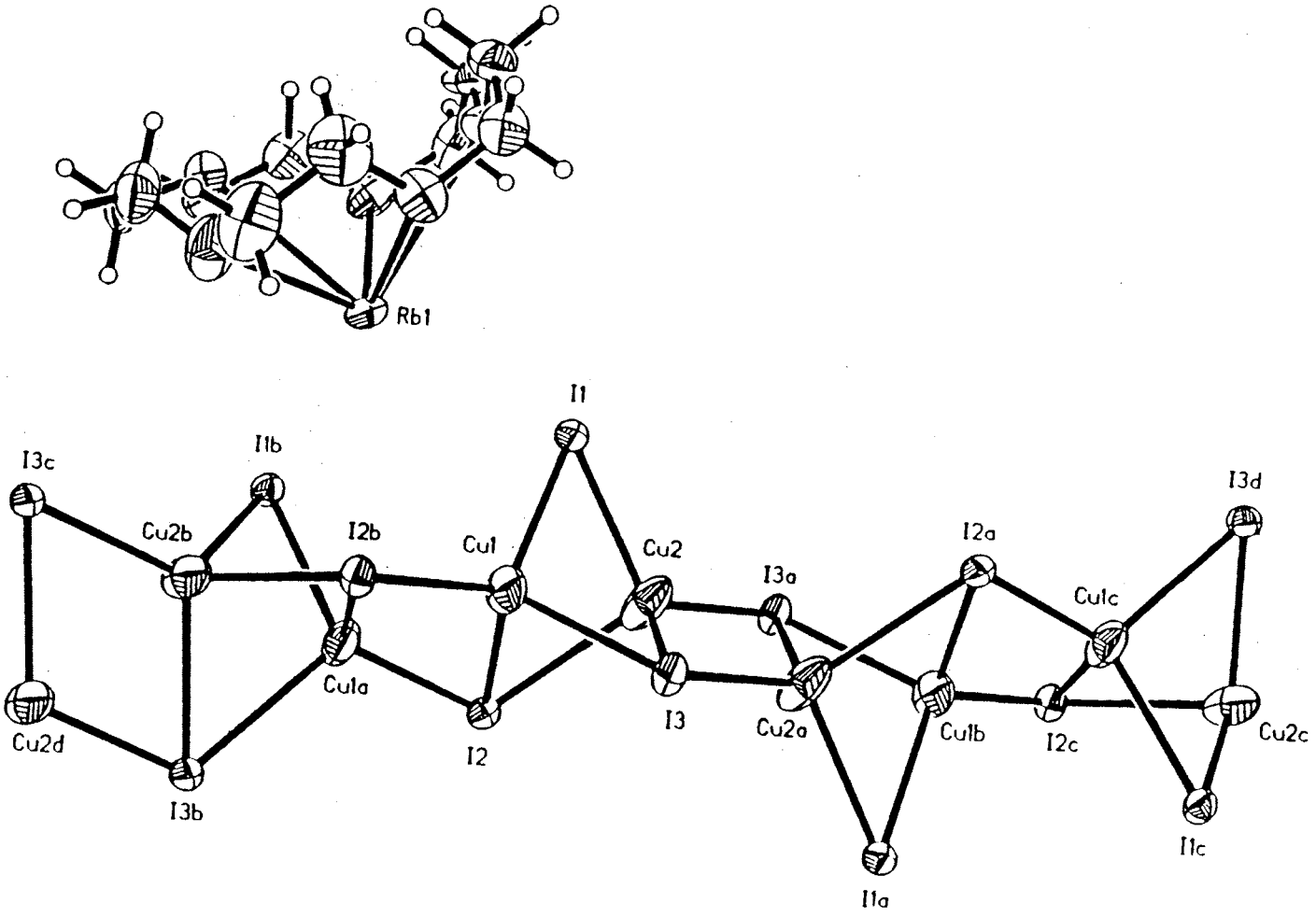


Figure 35. Projection View of $[Rb(15\text{-Crown-5})]Cu_2I_3$ **(XIII)**

TABLE 59

CRYSTAL DATA FOR

[Rb(15-Crown-5)]Cu_2I_3 (**XIII**)

Formula	$C_{10}H_{20}Cu_2I_3RbO_5$
Space group	C2/c
A	24.613(3) Å
B	11.1700(10) Å
C	17.211(3) Å
β	119.900(10)°
V	4101.9(9) $Å^3$
Z	8
Mw	813.5 g $mole^{-1}$
Density (calc.)	2.635 Mg m^{-3}
$\mu(MoK_\alpha)$	8.960 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	2992
Collected Reflections	6963
Independent Reflections	5968
Observed Reflections ($F > 3.5\ \sigma$)	1929
Number of parameters	191
Final R indices	R = 5.84 %, R_w = 5.75 %
R indices (all data)	R = 17.00 %, R_w = 8.21 %
GOF	0.93

TABLE 60

POSITIONAL PARAMETERS FOR

[Rb(15-Crown-5)]Cu_2I_3 (**XIII**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.4595(1)	-0.2525(1)	0.0984(1)
I(2)	0.5955(1)	0.0082(1)	0.2556(1)
I(3)	0.4274(1)	0.1110(1)	0.0136(1)
Cu(1)	0.4627(2)	-0.0337(3)	0.1602(2)
Cu(2)	0.5149(2)	-0.0690(3)	0.0707(3)
Rb(1)	0.3789(1)	-0.3294(2)	0.2200(1)
O(1)	0.2467(6)	-0.330(2)	0.0991(11)
C(2)	0.2095(12)	-0.341(4)	0.138(2)
H(2A)	0.2054	-0.4234	0.1491
H(2B)	0.1685	-0.3098	0.0976
C(3)	0.236(2)	-0.274(3)	0.219(2)
H(3A)	0.2380	-0.1908	0.2057
H(3B)	0.2077	-0.2786	0.2424
O(4)	0.2921(11)	-0.307(2)	0.2849(15)
C(5)	0.294(2)	-0.383(3)	0.343(2)
H(5A)	0.2628	-0.4433	0.3118
H(5B)	0.2829	-0.3419	0.3822
C(6)	0.354(2)	-0.440(3)	0.397(2)
H(6A)	0.3861	-0.3814	0.4281
H(6B)	0.3526	-0.4910	0.4414
O(7)	0.3678(8)	-0.510(2)	0.3411(10)
C(8)	0.4286(11)	-0.554(3)	0.3832(15)
H(8A)	0.4371	-0.5990	0.4355
H(8B	0.4583	-0.4893	0.4010
C(9)	0.4322(9)	-0.630(3)	0.318(2)
H(9A)	0.4706	-0.6748	0.3464
H(9B)	0.3981	-0.6861	0.2943
O(10)	0.4298(6)	-0.5650(15)	0.2468(12)
C(11)	0.4095(13)	-0.629(2)	0.164(2)
H(11A)	0.4271	-0.7076	0.1773
H(11B)	0.4246	-0.5881	0.1296
C(12)	0.3437(13)	-0.637(2)	0.113(2)
H(12A)	0.3322	-0.6864	0.0616
H(12B)	0.3285	-0.6754	0.1488
O(13)	0.3154(7)	-0.527(2)	0.0859(11)
C(14)	0.2483(11)	-0.530(3)	0.042(2)

TABLE 60 (Continued)

H(14A)	0.2347	-0.5671	0.0797
H(14B)	0.2315	-0.5736	-0.0130
C(15)	0.2269(14)	-0.402(3)	0.024(2)
H(15A)	0.2411	-0.3673	-0.0140
H(15B)	0.1819	-0.4019	-0.0094

TABLE 61

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

[Rb(15-Crown-5)]Cu_2I_3 (**XIII**)

I(1)-Cu(1)	2.650(4)	Rb(1)-O(13)	3.01(2)
I(1)-Cu(2)	2.633(5)	O(1)-C(2)	1.38(4)
I(2)-Cu(1)	2.872(4)	O(1)-C(15)	1.39(4)
I(2)-Cu(2)	2.917(4)	C(2)-C(3)	1.43(5)
I(2)-Cu(1^{i})	2.538(5)	C(3)-O(4)	1.33(4)
I(3)-Cu(1)	2.747(4)	O(4)-C(5)	1.29(5)
I(3)-Cu(2)	2.745(4)	C(5)-C(6)	1.45(4)
I(3)-Cu(2^{ii})	2.529(6)	C(6)-O(7)	1.40(4)
Cu(1)-Cu(2)	2.480(7)	O(7)-C(8)	1.39(3)
Cu(1)-I(2^{i})	2.538(5)	C(8)-C(9)	1.46(4)
Cu(1)-Cu(1^{i})	2.697(6)	C(9)-O(10)	1.39(4)
Cu(2)-I(3^{ii})	2.529(6)	O(10)-C(11)	1.44(4)
Cu(2)-Cu(2^{ii})	2.657(8)	C(11)-C(12)	1.41(4)
Rb(1)-O(1)	2.86(13)	C(12)-O(13)	1.37(3)
Rb(1)-O(4)	2.87(3)	O(13)-C(14)	1.43(3)
Rb(1)-O(7)	3.01(2)	C(14)-C(15)	1.49(4)
Rb(1)-O(10)	2.85(2)		
Cu(1)-I(1)-Cu(2)	56.0(1)	O(10)-Rb(1)-O(13)	57.6(4)
Cu(1)-I(2)-Cu(2)	50.7(1)	C(2)-O(1)-C(15)	113(2)
Cu(1)-I(2)-Cu(1^{i})	59.4(1)	O(1)-C(2)-C(3)	110(3)
Cu(2)-I(2)-Cu(1^{i})	107.3(1)	C(2)-C(3)-O(4)	117(3)
Cu(1)-I(3)-Cu(2)	53.7(1)	C(3)-O(4)-C(5)	118(3)
Cu(1)-I(3)-Cu(2^{ii})	114.0(1)	O(4)-C(5)-C(6)	115(4)
Cu(2)-I(3)-Cu(2^{ii})	60.3(2)	C(5)-C(6)-O(7)	108(2)
O(1)-Rb(1)-O(4)	59.1(6)	C(6)-O(7)-C(8)	114(2)
O(1)-Rb(1)-O(7)	92.2(5)	O(7)-C(8)-C(9)	106(2)
O(4)-Rb(1)-O(7)	56.3(6)	C(8)-C(9)-O(10)	112(2)
O(1)-Rb(1)-O(10)	111.2(5)	C(9)-O(10)-C(11)	117(2)
O(4)-Rb(1)-O(10)	111.6(6)	O(10)-C(11)-C(12)	112(3)
O(7)-Rb(1)-O(10)	56.9(6)	C(11)-C(12)-O(13)	112(2)
O(1)-Rb(1)-O(13)	58.1(5)	C(12)-O(13)-C(14)	115(2)
O(4)-Rb(1)-O(13)	99.1(6)	O(13)-C(14)-C(15)	107(2)
O(7)-Rb(1)-O(13)	81.2(5)	O(1)-C(15)-C(14)	115(2)

Symmetry operations:

^{i} = 1-x, y, 0.5-z

^{ii} = 1-x, -y, -z

TABLE 62

ANISOTROPIC THERMAL PARAMETERS FOR

[Rb(15-Crown-5)]Cu_2I_3 (**XIII**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	52(1)	35(1)	45(1)	-4(1)	27(1)	-4(1)
I(2)	50(1)	42(1)	47(1)	-9(1)	29(1)	-4(1)
I(3)	56(1)	44(1)	50(1)	14(1)	35(1)	11(1)
Cu(1)	115(2)	64(2)	85(2)	1(2)	77(2)	-9(2)
Cu(2)	139(3)	64(2)	147(3)	25(2)	123(3)	28(2)
Rb(1)	49(1)	41(1)	61(1)	-7(1)	26(1)	7(1)
O(1)	39(9)	88(14)	68(11)	16(9)	14(9)	-2(10)
C(2)	51(18)	176(41)	93(24)	11(22)	12(18)	5(26)
C(3)	111(28)	132(34)	129(31)	51(28)	76(26)	31(30)
O(4)	132(18)	86(16)	91(15)	30(14)	68(14)	20(13)
C(5)	145(31)	107(29)	75(21)	-2(25)	66(22)	9(22)
C(6)	182(34)	91(24)	45(16)	-31(25)	63(21)	0(18)
O(7)	88(12)	76(13)	62(11)	-11(11)	39(10)	-5(11)
C(8)	69(18)	95(23)	43(14)	-21(17)	12(14)	10(16)
C(9)	29(12)	101(23)	71(18)	12(14)	11(12)	25(18)
O(10)	57(10)	67(12)	91(12)	9(9)	43(10)	22(11)
C(11)	110(23)	70(21)	104(22)	38(19)	82(20)	29(18)
C(12)	93(22)	65(21)	137(26)	-44(18)	88(21)	-43(20)
O(13)	69(11)	57(12)	78(11)	-8(10)	37(10)	-14(10)
C(14)	70(18)	80(23)	63(16)	-29(16)	17(14)	-7(16)
C(15)	119(24)	89(26)	82(22)	-13(22)	53(19)	-3(21)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}Rb^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hRba^*b^*+2U_{13}hla^*c^*+2U_{23}Rblb^*c^*)] \times 10^3$

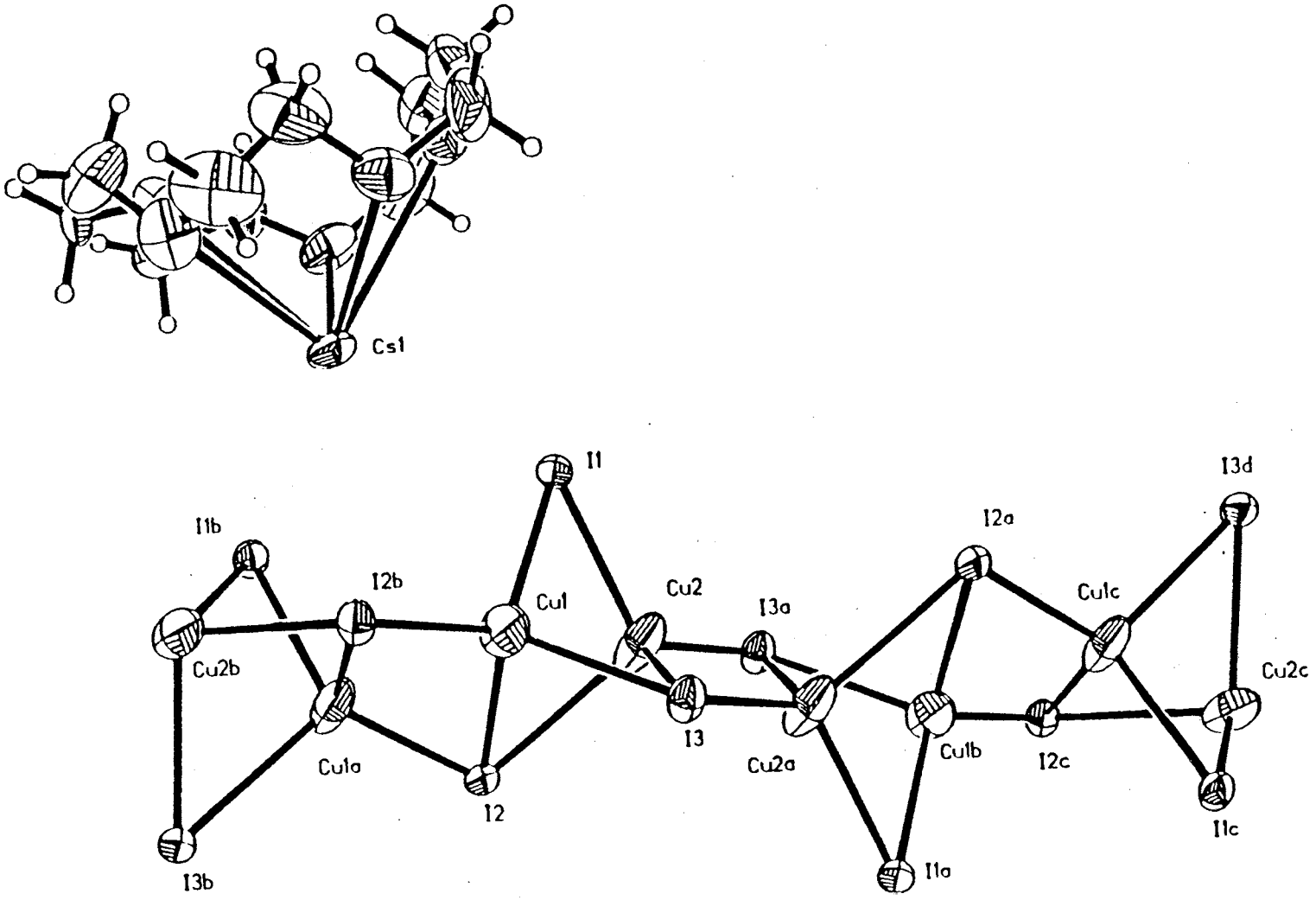


Figure 36. Projection View of $[Cs(15\text{-Crown-5})]Cu_2I_3$ **(XIV)**

TABLE 63

CRYSTAL DATA FOR

[Cs(15-Crown-5)]Cu_2I_3 (**XIV**)

Formula	$C_{10}H_{20}CsCu_2I_3O_5$
Space group	C2/c
A	25.19(3) Å
B	11.177(12) Å
C	16.86(3) Å
β	120.36(7)°
V	4088(11) $Å^3$
Z	8
Mw	861.0 g $mole^{-1}$
Density (calc.)	2.798 Mg m^{-3}
$\mu(MoK_\alpha)$	8.380 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	3136
Collected Reflections	6938
Independent Reflections	5956
Observed Reflections ($F > 6.0\ \sigma$)	1978
Number of parameters	191
Final R indices	$R = 5.95\ \%$, $R_w = 6.85\ \%$
R indices (all data)	$R = 13.99\ \%$, $R_w = 9.16\ \%$
GOF	1.36

TABLE 64

POSITIONAL PARAMETERS FOR

[Cs(15-Crown-5)]Cu_2I_3 (**XIV**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.4568(1)	-0.2400(1)	0.0980(1)
I(2)	0.5903(1)	0.0277(1)	0.2544(1)
I(3)	0.4285(1)	0.1191(1)	0.0070(1)
Cu(1)	0.4622(2)	-0.0231(3)	0.1583(3)
Cu(2)	0.5129(2)	-0.0641(3)	0.0711(3)
Cs(1)	0.3742(1)	-0.3082(1)	0.2259(1)
O(1)	0.2374(8)	-0.342(2)	0.0994(14)
C(2)	0.2014(12)	-0.365(4)	0.144(3)
H(2A)	0.1591	-0.3441	0.1037
H(2B)	0.2035	-0.4484	0.1592
C(3)	0.226(2)	-0.300(4)	0.216(4)
H(3A)	0.1976	-0.3025	0.2388
H(3B)	0.2270	-0.2192	0.1988
O(4)	0.2804(11)	-0.327(2)	0.287(2)
C(5)	0.286(2)	-0.419(4)	0.343(3)
H(5A)	0.2690	-0.3948	0.3808
H(5B)	0.2619	-0.4857	0.3066
C(6)	0.344(2)	-0.455(4)	0.398(2)
H(6A)	0.3458	-0.5057	0.4458
H(6B)	0.3695	-0.3864	0.4275
O(7)	0.3654(10)	-0.518(2)	0.3473(13)
C(8)	0.4271(12)	-0.542(3)	0.390(2)
H(8A)	0.4500	-0.4687	0.4006
H(8B	0.4408	-0.5809	0.4473
C(9)	0.4359(12)	-0.624(3)	0.323(2)
H(9A)	0.4062	-0.6874	0.3012
H(9B)	0.4764	-0.6584	0.3542
O(10)	0.4280(8)	-0.552(2)	0.2505(2)
C(11)	0.410(2)	-0.623(3)	0.171(3)
H(11A)	0.4247	-0.5869	0.1343
H(11B)	0.4281	-0.7002	0.1898
C(12)	0.3437(15)	-0.637(2)	0.116(2)
H(12A)	0.3288	-0.6782	0.1510
H(12B)	0.3344	-0.6858	0.0636
O(13)	0.3129(9)	-0.527(2)	0.0855(12)
C(14)	0.2507(12)	-0.533(3)	0.045(2)

TABLE 64 (Continued)

H(14A)	0.2347	-0.5802	-0.0097
H(14B)	0.2400	-0.5720	0.0859
C(15)	0.2237(14)	-0.420(4)	0.022(2)
H(15A)	0.1799	-0.4309	-0.0131
H(15B)	0.2359	-0.3802	-0.0166

TABLE 65

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

[Cs(15-Crown-5)]Cu_2I_3 (**XIV**)

I(1)-Cu(1)	2.607(6)	Cs(1)-O(13)	3.21(2)
I(1)-Cu(2)	2.590(6)	O(1)-C(2)	1.46(5)
I(2)-Cu(1)	2.843(6)	O(1)-C(15)	1.46(4)
I(2)-Cu(2)	2.882(6)	C(2)-C(3)	1.28(6)
I(2)-Cu(1^{i})	2.491(7)	C(3)-O(4)	1.32(4)
I(3)-Cu(1)	2.751(6)	O(4)-C(5)	1.36(6)
I(3)-Cu(2)	2.750(6)	C(5)-C(6)	1.33(6)
I(3)-Cu(2^{ii})	2.502(7)	C(6)-O(7)	1.42(6)
Cu(1)...Cu(2)	2.430(9)	O(7)-C(8)	1.37(4)
Cu(1)-I(2^{i})	2.491(7)	C(8)-C(9)	1.55(5)
Cu(1)...Cu(1^{i})	2.690(8)	C(9)-O(10)	1.40(4)
Cu(2)-I(3^{ii})	2.502(7)	O(10)-C(11)	1.42(5)
Cu(2)...Cu(2^{ii})	2.579(10)	C(11)-C(12)	1.44(5)
Cs(1)-O(1)	3.02(2)	C(12)-O(13)	1.40(3)
Cs(1)-O(4)	3.03(3)	O(13)-C(14)	1.36(4)
Cs(1)-O(7)	3.19(2)	C(14)-C(15)	1.39(5)
Cs(1)-O(10)	2.98(2)		
Cu(1)-I(1)-Cu(2)	55.8(2)	O(10)-Cs(1)-O(13)	54.5(5)
Cu(1)-I(2)-Cu(2)	50.2(2)	C(2)-O(1)-C(15)	115(2)
Cu(1)-I(2)-Cu(1^{i})	60.1(2)	O(1)-C(2)-C(3)	105(4)
Cu(2)-I(2)-Cu(1^{i})	106.2(2)	C(2)-C(3)-O(4)	121(4)
Cu(1)-I(3)-Cu(2)	52.4(2)	C(3)-O(4)-C(5)	120(4)
Cu(1)-I(3)-Cu(2^{ii})	111.0(2)	O(4)-C(5)-C(6)	114(4)
Cu(2)-I(3)-Cu(2^{ii})	58.6(2)	C(5)-C(6)-O(7)	110(3)
O(1)-Cs(1)-O(4)	54.8(6)	C(6)-O(7)-C(8)	118(2)
O(1)-Cs(1)-O(7)	86.4(5)	O(7)-C(8)-C(9)	106(2)
O(4)-Cs(1)-O(7)	53.9(6)	C(8)-C(9)-O(10)	106(2)
O(1)-Cs(1)-O(10)	105.2(5)	C(9)-O(10)-C(11)	110(2)
O(4)-Cs(1)-O(10)	105.5(7)	O(10)-C(11)-C(12)	113(4)
O(7)-Cs(1)-O(10)	54.1(7)	C(11)-C(12)-O(13)	112(2)
O(1)-Cs(1)-O(13)	55.5(6)	C(12)-O(13)-C(14)	115(2)
O(4)-Cs(1)-O(13)	91.8(6)	O(13)-C(14)-C(15)	112(3)
O(7)-Cs(1)-O(13)	75.5(5)	O(1)-C(15)-C(14)	116(2)

Symmetry operations:

^{i} = 1-x, y, 0.5-z

^{ii} = 1-x, -y, -z

TABLE 66

ANISOTROPIC THERMAL PARAMETERS FOR

[Cs(15-Crown-5)]Cu_2I_3 (**XIV**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	65(1)	33(1)	46(1)	-5(1)	30(1)	-5(1)
I(2)	62(1)	37(1)	46(1)	-10(1)	31(1)	-2(1)
I(3)	72(1)	42(1)	52(1)	15(1)	38(1)	10(1)
Cu(1)	148(3)	64(2)	109(3)	-10(2)	100(2)	-22(2)
Cu(2)	160(3)	63(2)	140(3)	23(2)	125(3)	125(3)
Cs(1)	62(1)	41(1)	74(1)	-9(1)	33(1)	12(1)
O(1)	64(11)	88(14)	92(14)	-2(10)	23(10)	2(11)
C(2)	43(15)	157(38)	155(33)	-9(20)	35(19)	-25(29)
C(3)	102(30)	116(34)	228(54)	28(27)	86(36)	-30(37)
O(4)	119(17)	97(18)	103(15)	32(15)	54(14)	9(14)
C(5)	157(38)	114(34)	156(38)	5(30)	103(32)	42(32)
C(6)	241(46)	104(29)	61(19)	-83(32)	97(28)	-31(21)
O(7)	111(15)	92(15)	77(12)	-23(12)	41(12)	-20(12)
C(8)	73(19)	133(30)	53(16)	-29(20)	-12(14)	48(20)
C(9)	82(18)	95(22)	62(17)	30(16)	27(14)	26(17)
O(10)	92(13)	57(12)	115(15)	16(10)	53(12)	53(12)
C(11)	126(28)	90(26)	147(33)	48(23)	90(26)	31(25)
C(12)	141(28)	57(19)	103(22)	16(18)	91(22)	-4(17)
O(13)	106(14)	59(12)	82(12)	-5(11)	57(11)	2(10)
C(14)	71(18)	115(28)	56(16)	0(19)	26(13)	-4(17)
C(15)	98(23)	167(38)	45(15)	8(26)	15(15)	29(22)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}Cs^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hCsa^*b^*+2U_{13}hla^*c^*+2U_{23}Cslb^*c^*)] \times 10^3$

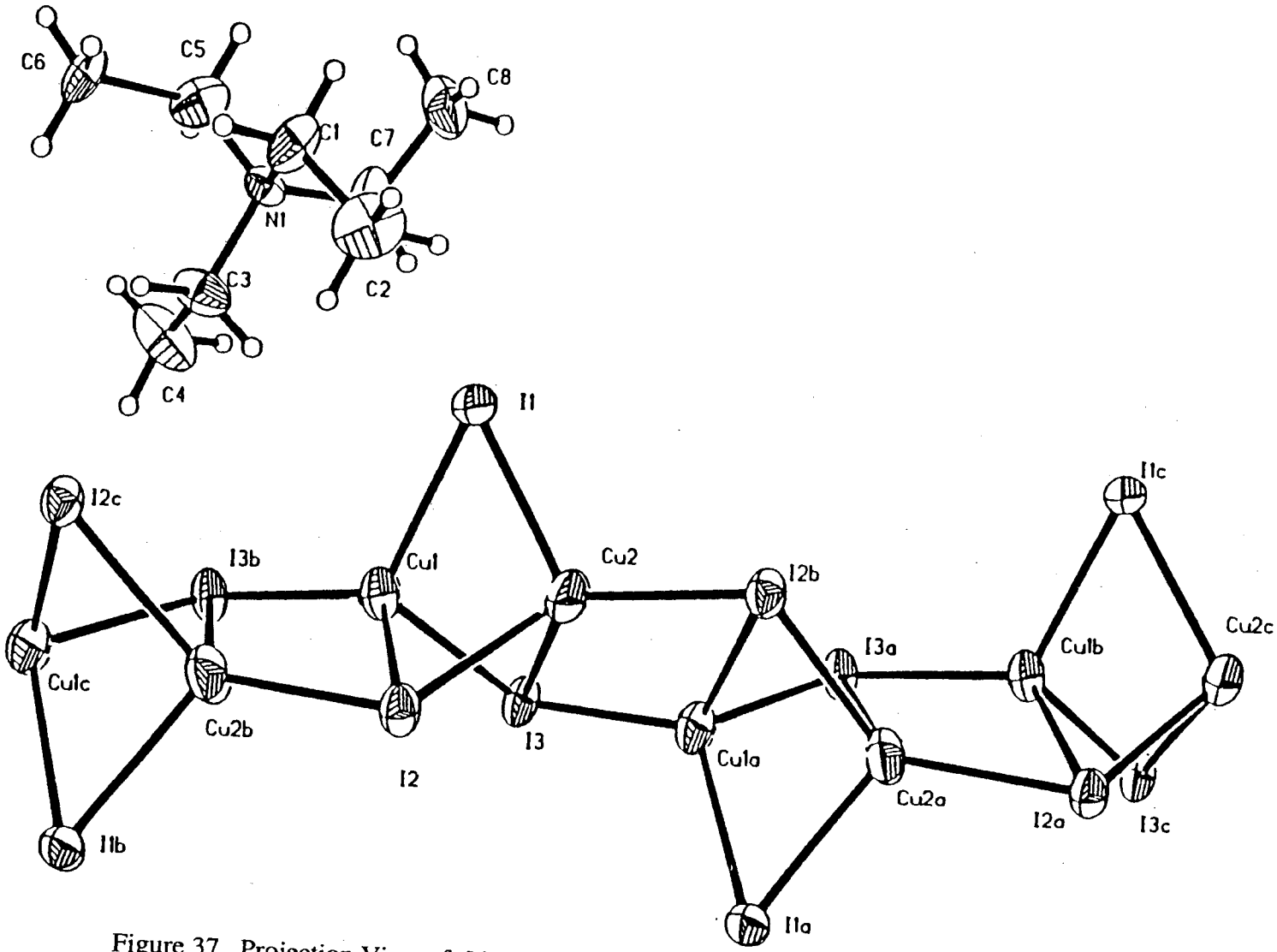


Figure 37. Projection View of $[C_8H_{20}N]Cu_2I_3$ (**XV**)

TABLE 67

CRYSTAL DATA FOR

$[C_8H_{20}N]Cu_2I_3$ (**XV**)

Formula	$C_8H_{20}Cu_2I_3N$
Space group	$Pna2_1$
a	8.313(5) Å
b	17.486(7) Å
c	10.566(5) Å
V	1536.8(13) $Å^3$
Z	4
Mw	638.0 g $mole^{-1}$
Density (calc.)	2.758 g cm^{-3}
$\mu(MoK_\alpha)$	87.65 cm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	1168
Collected Reflections	3055
Independent Reflections	2577
Observed Reflections ($F > 4.0\sigma$)	1302
Number of parameters	127
Final R indices	$R = 4.67$ %, $R_w = 5.27$%
R indices (all data)	$R = 10.18$ %, $R_w = 6.73$%
GOF	1.11

TABLE 68

POSITIONAL PARAMETERS FOR

$[C_8H_{20}N]Cu_2I_3$ (**XV**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	-0.2334(2)	0.4148(1)	0.1250(2)
I(2)	-0.1672(2)	0.1970(1)	-0.0099(2)
I(3)	-0.3910(2)	0.2258(1)	0.3437
Cu(1)	-0.1391(4)	0.2827(2)	0.2091(4)
Cu(2)	-0.4002(4)	0.2909(2)	0.0984(5)
N(1)	0.262(2)	0.5723(8)	0.1649(15)
C(1)	0.227(3)	0.5838(15)	0.030(2)
H(1A)	0.3256	0.5819	-0.0171
H(1B)	0.1829	0.6342	0.0217
C(2)	0.108(4)	0.5280(15)	-0.0271(25)
H(2A)	0.0849	0.5365	-0.1142
H(2B)	0.1500	0.4749	-0.0194
H(2C)	0.0060	0.5277	0.0198
C(3)	0.331(3)	0.4931(12)	0.183(2)
H(3A)	0.4174	0.4845	0.1250
H(3B)	0.2474	0.4568	0.1648
C(4)	0.383(4)	0.472(2)	0.318(2)
H(4A)	0.4227	0.4211	0.3251
H(4B)	0.4678	0.5079	0.3359
H(4C)	0.2961	0.4799	0.3761
C(5)	0.375(3)	0.6295(14)	0.209(3)
H(5A)	0.3891	0.3267	0.2991
H(5B)	0.3267	0.6784	0.1925
C(6)	0.542(2)	0.6261(12)	0.149(3)
H(6A)	0.6093	0.6665	0.1785
H(6B)	0.5907	0.5776	0.1655
H(6C)	0.5276	0.6316	0.0579
C(7)	0.104(3)	0.582(2)	0.240(3)
H(7A)	0.1299	0.5806	0.3282
H(7B)	0.0372	0.5387	0.2209
C(8)	0.011(3)	0.6522(14)	0.216(3)
H(8A)	-0.0852	0.6539	0.2653
H(8B)	0.0774	0.6955	0.2356
H(8C)	-0.0160	0.6533	0.1273

TABLE 69

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[C_8H_{20}N]Cu_2I_3$ (**XV**)

I(1)-Cu(1)	2.596(4)	Cu(2)-I(2^{ii})	2.505(4)
I(1)-Cu(2)	2.588(4)	Cu(2)-Cu(1^{ii})	2.649(5)
I(2)-Cu(1)	2.766(5)	N(1)-C(1)	1.46(3)
I(2)-Cu(2)	2.785(4)	N(1)-C(3)	1.51(3)
I(2)-Cu(2^{i})	2.505(4)	N(1)-C(5)	1.44(3)
I(3)-Cu(1)	2.720(4)	N(1)-C(7)	1.54(3)
I(3)-Cu(2)	2.831(5)	C(1)-C(2)	1.52(4)
I(3)-Cu(1^{ii})	2.510(4)	C(3)-C(4)	1.52(4)
Cu(1)-Cu(2)	2.470(5)	C(5)-C(6)	1.53(3)
Cu(1)-I(3^{i})	2.510(4)	C(7)-C(8)	1.47(4)
Cu(1)-Cu(2^{i})	2.639(5)		
Cu(1)-I(1)-Cu(2)	56.9(1)	C(3)-N(1)-C(5)	110(2)
Cu(1)-I(2)-Cu(2)	52.8(1)	C(1)-N(1)-C(7)	108(2)
Cu(1)-I(2)-Cu(2^{i})	59.8(1)	C(3)-N(1)-C(7)	111(2)
Cu(2)-I(2)-Cu(2^{i})	112.3(2)	C(5)-N(1)-C(7)	108(2)
Cu(1)-I(3)-Cu(2)	52.8(1)	N(1)-C(1)-C(2)	116(2)
Cu(1)-I(3)-Cu(1^{ii})	111.0(1)	N(1)-C(3)-C(4)	116(2)
Cu(2)-I(3)-Cu(1^{ii})	58.9(1)	N(1)-C(5)-C(6)	115(2)
C(1)-N(1)-C(3)	109(2)	N(1)-C(7)-C(8)	117(2)
C(1)-N(1)-C(5)	110(2)		

Symmetry operations:

^{i} = 0.5+x, 0.5-y, z

^{ii} = x-0.5, 0.5-y, z

TABLE 70

ANISOTROPIC THERMAL PARAMETERS FOR

$[C_8H_{20}N]Cu_2I_3$ (**XV**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	54(1)	44(1)	69(1)	-6(1)	-9(1)	10(1)
I(2)	41(1)	64(1)	48(1)	4(1)	-7(1)	-11(1)
I(3)	39(1)	79(1)	41(1)	-10(1)	-5(1)	12(1)
Cu(1)	51(2)	77(2)	82(2)	4(1)	-25(2)	8(2)
Cu(2)	57(2)	77(2)	119(4)	-16(1)	-38(2)	16(2)
N(1)	46(9)	40(8)	33(10)	7(7)	-14(8)	-1(7)
C(1)	61(14)	84(17)	41(13)	-30(13)	-19(12)	4(12)
C(2)	126(24)	111(20)	31(13)	-16(19)	-15(17)	-2(15)
C(3)	95(18)	57(12)	50(14)	24(13)	17(15)	1(11)
C(4)	129(27)	112(22)	48(19)	62(20)	7(18)	6(15)
C(5)	93(19)	72(14)	49(14)	-21(14)	-1(15)	4(13)
C(6)	43(11)	79(13)	80(18)	-32(11)	-7(14)	-6(15)
C(7)	51(13)	139(23)	46(15)	2(16)	17(13)	-17(16)
C(8)	61(15)	100(18)	93(21)	28(17)	11(17)	6(17)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

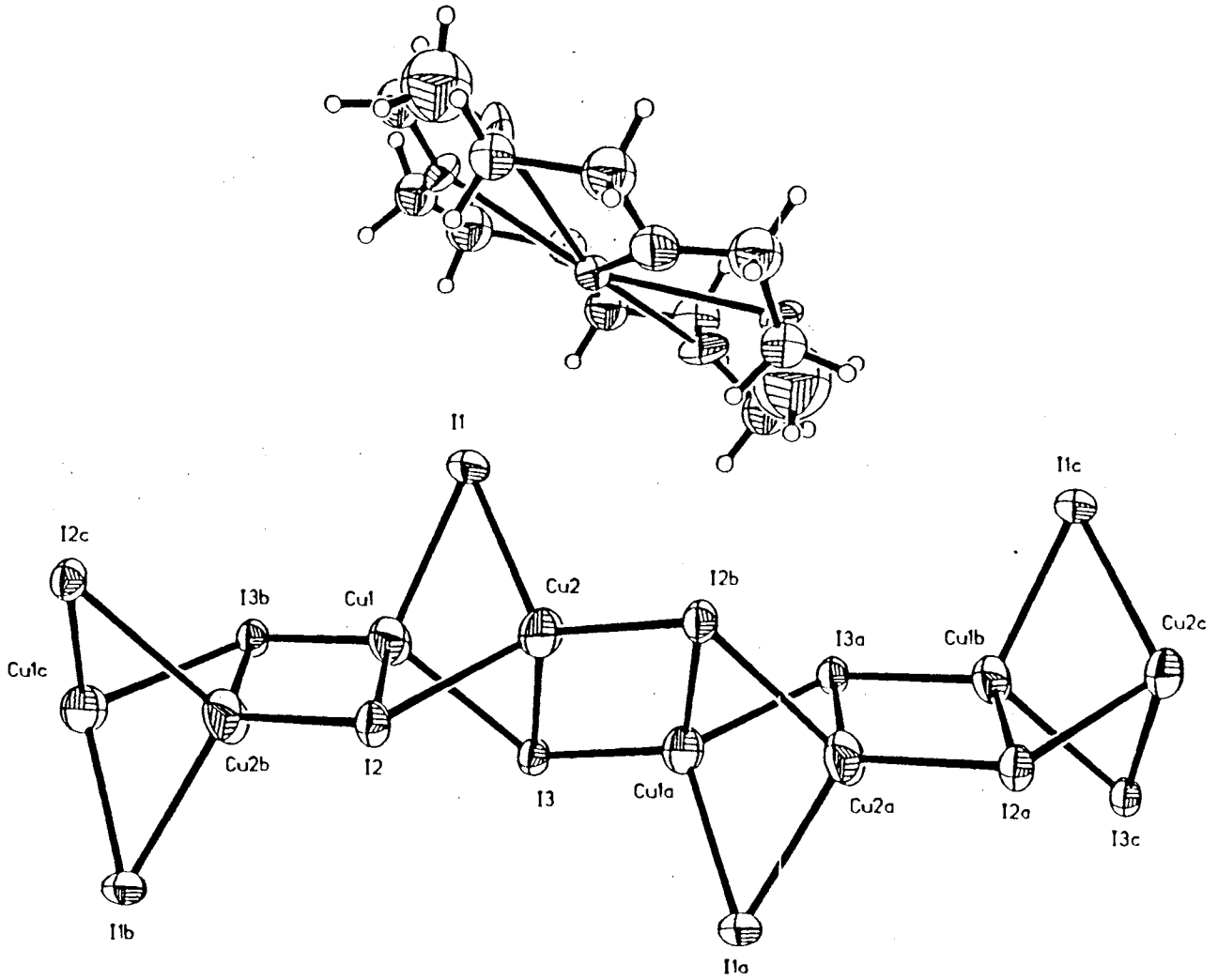


Figure 38. Projection View of $[K(18\text{-Crown-6})]Cu_2I_3$ (**XVI**)

TABLE 71

CRYSTAL DATA FOR

[K(18-Crown-6)]Cu_2I_3 (**XVI**)

Formula	$C_{12}H_{24}Cu_2I_3KO_6$
Space group	$P2_1/c$
A	15.440(7) Å
B	17.635(6) Å
C	8.422(3) Å
β	97.14(4)°
V	1761.8(7) $Å^3$
Z	4
Mw	811.19 g $mole^{-1}$
Density (calc.)	2.368 g cm^{-3}
$\mu(MoK_\alpha)$	61.44 cm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	1520
Collected Reflections	8310
Independent Reflections	6620
Observed Reflections ($F > 2.0\sigma$)	6611
Number of parameters	363
Final R indices	R = 8.61 %, R_w = 21.75 %
R indices (all data)	R = 18.20 %, R_w = 27.15 %
GOF	0.893

TABLE 72

POSITIONAL PARAMETERS FOR

[K(18-Crown-6)]Cu_2I_3 (**XVI**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.7296(1)	0.5801(1)	1.0741(1)
I(2)	0.6168(1)	0.7960(1)	1.1440(1)
I(3)	0.8588(1)	0.7901(1)	0.9745(1)
Cu(1)	0.7730(2)	0.7152(1)	1.1988(3)
Cu(2)	0.6993(2)	0.7101(1)	0.9217(3)
K(1)	0.7631(2)	0.4078(2)	0.9071(4)
O(1)	0.9242(13)	0.3482(11)	1.012(3)
C(2)	0.932(3)	0.336(3)	1.196(5)
H(2A)	0.972(3)	0.295(3)	1.219(5)
H(2B)	0.960(3)	0.381(3)	1.240(5)
C(3)	0.871(3)	0.324(2)	1.271(5)
H(3A)	0.882(3)	0.276(2)	1.320(5)
H(3B)	0.876(3)	0.361(2)	1.356(5)
O(4)	0.797(2)	0.3237(13)	1.196(3)
C(5)	0.718(3)	0.291(2)	1.242(6)
H(5A)	0.730(3)	0.239(2)	1.220(6)
H(5B)	0.718(3)	0.295(2)	1.356(6)
C(6)	0.648(6)	0.296(5)	1.150(10)
H(6A)	0.617(6)	0.248(5)	1.130(10)
H(6B)	0.618(6)	0.324(5)	1.223(10)
O(7)	0.623(3)	0.336(2)	1.035(4)
C(8)	0.551(2)	0.374(2)	1.010(4)
H(8A)	0.506(2)	0.345(2)	1.050(4)
H(8B	0.559(2)	0.422(2)	1.066(4)
C(9)	0.5318(15)	0.3875(12)	0.817(2)
H(9A)	0.5207(15)	0.3391(12)	0.766(2)
H(9B)	0.4804(15)	0.4181(12)	0.793(2)
O(10)	0.597(2)	0.4246(13)	0.756(4)
C(11)	0.576(4)	0.430(2)	0.589(6)
H(11A)	0.572(4)	0.3842)	0.530(6)
H(11B)	0.521(4)	0.456(2)	0.579(6)
C(12)	0.648(2)	0.484(2)	0.551(5)
H(12A)	0.638(2)	0.504(2)	0.445(5)
H(12B)	0.652(2)	0.525(2)	0.625(5)
O(13)	0.728(2)	0.4420(12)	0.575(3)
C(14)	0.791(7)	0.483(6)	0.563(14)

TABLE 72 (Continued)

H(14A)	0.797(7)	0.463(6)	0.458(14)
H(14B)	0.761(7)	0.531(6)	0.551(14)
C(15)	0.894(3)	0.489(2)	0.628(5)
H(15A)	0.940(3)	0.493(2)	0.560(5)
H(15B)	0.896(3)	0.535(2)	0.691(5)
O(16)	0.898(2)	0.4361(12)	0.746(4)
C(17)	0.970(3)	0.395(3)	0.782(5)
H(17A)	0.969(3)	0.345(3)	0.735(5)
H(17B)	1.019(3)	0.420(3)	0.743(5)
C(18)	0.9956(14)	0.3852(11)	0.955(2)
H(18A)	1.0093(14)	0.4315(11)	1.013(2)
H(18B)	1.0455(14)	0.3523(11)	0.968(2)
O(1')	0.903(2)	0.3354(13)	1.120(2)
C(2')	0.856(3)	0.282(3)	1.226(6)
H(2'A)	0.863(3)	0.232(3)	1.182(6)
H(2'B)	0.891(3)	0.282(3)	1.328(6)
C(3')	0.785(3)	0.285(2)	1.252(5)
H(3'A)	0.763(3)	0.234(2)	1.245(5)
H(3'B)	0.787(3)	0.300(2)	1.362(5)
O(4')	0.728(2)	0.3272(15)	1.176(3)
C(5')	0.643(4)	0.321(3)	1.206(7)
H(5'A)	0.633(4)	0.268(3)	1.218(7)
H(5'B)	0.632(4)	0.345(3)	1.304(7)
C(6')	0.592(3)	0.338(3)	1.100(5)
H(6'A)	0.544(3)	0.303(3)	1.099(5)
H(6'B)	0.572(3)	0.385(3)	1.140(5)
O(7')	0.599(2)	0.3497(15)	0.918(4)
C(9')	0.569(4)	0.393(4)	0.625(7)
H(9'A)	0.527(4)	0.425(4)	0.563(7)
H(9'B)	0.571(4)	0.345(4)	0.573(7)
O(10')	0.640(2)	0.4346(15)	0.645(3)
C(11')	0.677(3)	0.456(2)	0.498(5)
H(11C)	0.688(3)	0.410(2)	0.440(5)
H(11D)	0.634(3)	0.485(2)	0.433(5)
C(12')	0.764(3)	0.498(3)	0.539(7)
H(12C)	0.781(3)	0.516(3)	0.440(7)
H(12D)	0.756(3)	0.540(3)	0.607(7)
O(13')	0.822(2)	0.4517(15)	0.604(3)
C(14')	0.899(6)	0.461(5)	0.577(10)
H(14C)	0.908(6)	0.438(5)	0.478(10)
H(14D)	0.908(6)	0.515(5)	0.566(10)
C(15')	0.955(3)	0.434(2)	0.707(4)
H(15C)	0.967(3)	0.3832)	0.677(4)
H(15D)	1.008(3)	0.462(2)	0.705(4)
O(16')	0.9366(15)	0.4294(11)	0.883(3)

TABLE 72 (Continued)

C(18')	0.970(3)	0.376(2)	1.126(5)
H(18C)	1.016(3)	0.346(2)	1.181(5)
H(18D)	0.968(3)	0.424(2)	1.181(5)

TABLE 73

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

[K(18-Crown-6)]Cu_2I_3 (**XVI**)

I(3)-Cu(1^{i})	2.528(3)	C(5)-C(6)	1.26(9)
I(3)-Cu(1)	2.773(3)	C(6)-O(7)	1.23(8)
I(3)-Cu(2)	2.824(3)	O(7)-C(8)	1.29(5)
I(2)-Cu(2^{ii})	2.523(3)	C(8)-C(9)	1.63(4)
I(2)-Cu(1)	2.789(3)	C(9)-O(10)	1.36(3)
I(2)-Cu(2)	2.831(3)	C(9)-O(7')	1.43(3)
I(1)-Cu(2)	2.641(3)	C(9)-C(9')	1.79(6)
I(1)-Cu(1)	2.657(3)	O(10)-C(11)	1.41(5)
I(1)-K(1)	3.414(3)	C(11)-C(12)	1.53(6)
Cu(1)-Cu(2)	2.467(3)	C(12)-O(13)	1.44(4)
Cu(1)-I(3^{ii})	2.528(3)	O(13)-C(14)	1.22(11)
Cu(1)-Cu(2^{ii})	2.661(4)	C(14)-C(15)	1.63(11)
Cu(2)-I(2^{i})	2.523(3)	C(15)-O(16)	1.36(5)
Cu(2)-Cu(1^{i})	2.661(4)	O(16)-C(17)	1.33(5)
K(1)-O(16)	2.68(3)	C(17)-C(18)	1.47(5)
K(1)-O(10)	2.73(3)	C(18)-O(16')	1.29(3)
K(1)-O(16')	2.74(2)	C(18)-C(18')	1.55(4)
K(1)-O(7')	2.74(2)	O(1')-C(18')	1.25(5)
K(1)-O(1)	2.74(2)	O(1')-C(2')	1.55(5)
K(1)-O(10')	2.77(3)	C(2')-C(3')	1.15(5)
K(1)-O(4')	2.78(3)	C(3')-O(4')	1.27(5)
K(1)-O(7)	2.82(4)	O(4')-C(5')	1.37(7)
K(1)-O(4)	2.84(2)	C(5')-C(6')	1.15(7)
K(1)-O(13)	2.84(2)	C(6')-O(7')	1.56(5)
K(1)-O(13')	2.92(3)	C(9')-O(10')	1.31(6)
K(1)-O(1')	2.93(3)	O(10')-C(11')	1.47(4)
O(1)-C(18)	1.42(3)	C(11')-C(12')	1.54(6)
O(1)-C(2)	1.55(5)	C(12')-O(13')	1.27(4)
C(2)-C(3)	1.21(5)	O(13')-C(14')	1.24(9)
C(3)-O(4)	1.24(5)	C(14')-C(15')	1.40(8)
O(4)-C(5)	1.44(5)	C(15')-O(16')	1.54(4)
Cu(1^{i})-I(3)-Cu(1)	111.59(10)	O(13')-K(1)-O(1')	111.3(8)
Cu(1^{i})-I(3)-Cu(2)	59.33(9)	C(18)-O(1)-C(2)	116(2)
Cu(1)-I(3)-Cu(2)	52.30(7)	C(3)-C(2)-O(1)	125(4)
Cu(2^{ii})-I(2)-Cu(1)	59.89(9)	C(2)-C(3)-O(4)	118(4)
Cu(2^{ii})-I(2)-Cu(2)	111.93(11)	C(3)-O(4)-C(5)	129(3)
Cu(1)-I(2)-Cu(2)	52.08(7)	C(6)-C(5)-O(4)	120(6)
Cu(2)-I(1)-Cu(1)	55.50(8)	O(7)-C(6)-C(5)	133(9)

TABLE 73 (Continued)

O(16)-K(1)-O(10)	119.3(9)	C(6)-O(7)-C(8)	127(6)
O(16')-K(1)-O(7')	165.9(7)	O(7)-C(8)-C(9)	107(3)
O(16)-K(1)-O(1)	60.1(7)	O(10)-C(9)-C(8)	113(2)
O(10)-K(1)-O(1)	162.3(7)	O(7')-C(9)-C(9')	106(3)
O(16')-K(1)-O(10')	119.7(8)	C(9)-O(10)-C(11)	109(3)
O(7')-K(1)-O(10')	63.2(9)	O(10)-C(11)-C(12)	100(4)
O(16')-K(1)-O(4')	115.1(9)	O(13)-C(12)-C(11)	107(3)
O(7')-K(1)-O(4')	60.4(10)	C(14)-O(13)-C(12)	112(5)
O(10')-K(1)-O(4')	123.6(9)	O(13)-C(14)-C(15)	140(8)
O(16)-K(1)-O(7)	163.4(8)	O(16)-C(15)-C(14)	99(5)
O(10)-K(1)-O(7)	60.6(11)	C(17)-O(16)-C(15)	120(4)
O(1)-K(1)-O(7)	114.3(11)	O(16)-C(17)-C(18)	114(4)
O(16)-K(1)-O(4)	117.4(8)	O(1)-C(18)-C(17)	106(3)
O(10)-K(1)-O(4)	121.1(9)	O(16')-C(18)-C(18')	105(2)
O(1)-K(1)-O(4)	57.4(7)	C(18')-O(1')-C(2')	141(4)
O(7)-K(1)-O(4)	60.6(11)	C(3')-C(2')-O(1')	128(4)
O(16)-K(1)-O(13)	61.6(8)	C(2')-C(3')-O(4')	124(5)
O(10)-K(1)-O(13)	57.9(9)	C(3')-O(4')-C(5')	119(4)
O(1)-K(1)-O(13)	116.8(8)	C(6')-C(5')-O(4')	115(5)
O(7)-K(1)-O(13)	114.2(10)	C(5')-C(6')-O(7')	132(5)
O(4)-K(1)-O(13)	160.7(7)	C(9)-O(7')-C(6')	121(2)
O(16')-K(1)-O(13')	58.9(9)	O(10')-C(9')-C(9)	106(4)
O(7')-K(1)-O(13')	121.3(10)	C(9')-O(10')-C(11')	116(4)
O(10')-K(1)-O(13')	60.9(9)	O(10')-C(11')-C(12')	111(4)
O(4')-K(1)-O(13')	163.8(7)	O(13')-C(12')-C(11')	110(4)
O(16')-K(1)-O(1')	56.7(8)	C(14')-O(13')-C(12')	118(5)
O(7')-K(1)-O(1')	115.6(10)	O(13')-C(14')-C(15')	109(7)
O(10')-K(1)-O(1')	160.9(7)	C(14')-C(15')-O(16')	127(5)
O(4')-K(1)-O(1')	58.9(9)	O(1')-C(18')-C(18)	109(3)

Symmetry operations:

[i] = x,-y+3/2,z-1/2

[ii] = x,-y+3/2,z+1/2

TABLE 74

ANISOTROPIC THERMAL PARAMETERS FOR

[K(18-Crown-6)]Cu_2I_3 (**XVI**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	98.4(10)	34.9(5)	58.9(7)	-1.9(5)	4.0(6)	-0.9(5)
I(2)	52.5(6)	59.5(6)	36.9(5)	0.1(4)	3.3(4)	10.1(5)
I(3)	52.4(6)	51.0(5)	35.0(5)	0.8(4)	2.4(4)	-4.4(5)
Cu(1)	117(2)	77.1(15)	49.2(12)	-4.1(11)	-19.4(13)	6.4(14)
Cu(2)	129(3)	85(2)	48.5(13)	8.9(11)	-22.8(14)	-15(2)
K(1)	60(2)	44(2)	47(2)	0.1(13)	12(2)	-1(15)
O(1)	38(12)	61(13)	58(13)	-5(11)	0(11)	-5(10)
C(2)	85(30)	85(30)	85(40)	0(30)	11(30)	0(30)
C(3)	71(30)	71(20)	71(30)	0(200	9(20)	0(20)
O(4)	84(20)	60(15)	60(20)	10(12)	38(20)	-16(20)
C(5)	78(30)	78(30)	78(30)	0(20)	10(30)	0(30)
C(6)	170(10)	170(8)	170(8)	0(60)	21(70)	0(60)
O(7)	234(6)	100(30)	54(20)	-17(20)	64(30)	5(30)
C(8)	64(20)	64(20)	64(20)	0(20)	8(20)	0(20)
C(9)	88(20)	88(14)	88(20)	0(12)	11(13)	0(13)
O(10)	136(30)	51(14)	76(20)	0(14)	10(20)	15(20)
C(11)	89(40)	89(30)	89(40)	0(30)	11(30)	0(30)
C(12)	68(30)	68(20)	68(30)	0(20)	8(20)	0(20)
O(13)	87(20)	53(13)	58(15)	19(11)	-13(14)	-42(14)
C(14)	212(10)	212(11)	212(11)	0(9)	26(9)	0(10)
C(15)	77(30)	77(30)	77(30)	0(20)	10(30)	0(20)
O(16)	68(20)	50(13)	104(20)	13(14)	23(17)	-19(13)
C(17)	93(40)	93(30)	93(40)	0(30)	12(30)	0(30)
C(18)	77(14)	77(12)	77(14)	0(10)	10(11)	0(11)
O(1')	168(30)	56(14)	23(12)	-1(10)	18(20)	32(20)
C(2')	91(40)	91(30)	91(40)	0(30)	11(30)	0(30)
C(3')	70(3)	70(30)	70(30)	0(20)	9(20)	0(20)
O(4')	97(20)	70(20)	67(20)	-15(14)	44(20)	-34(20)
C(5')	99(50)	99(40)	99(40)	0(30)	12(30)	0(30)
C(6')	80(30)	80(30)	80(30)	0(30)	10(30)	0(30)
O(7')	58(17)	84(20)	98(20)	-26(20)	(20)	-4(14)
C(9')	129(60	129(50	129(50	0(40)	16(50)	0(40)
O(10')	84(20)	75(20)	75(20)	-6(15)	28(20)	2(20)
C(11')	71(30)	71(30)	71(30)	0(20)	9(20)	0(20)
C(12')	78(30)	78(30)	78(30)	0(30)	10(30)	0(30)
O(13')	112(30)	72(20)	67(20)	15(15)	22(20)	54(20)
C(15')	67(30)	67(20)	67(200	0(20)	8(20)	0(20)

TABLE 74 (Continued)

O(16')	64(20)	47(12)	86(20)	-1(12)	6(14)	25(11)
C(18')	75(30)	75(20)	75(30)	0(20)	9(20)	0(20)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

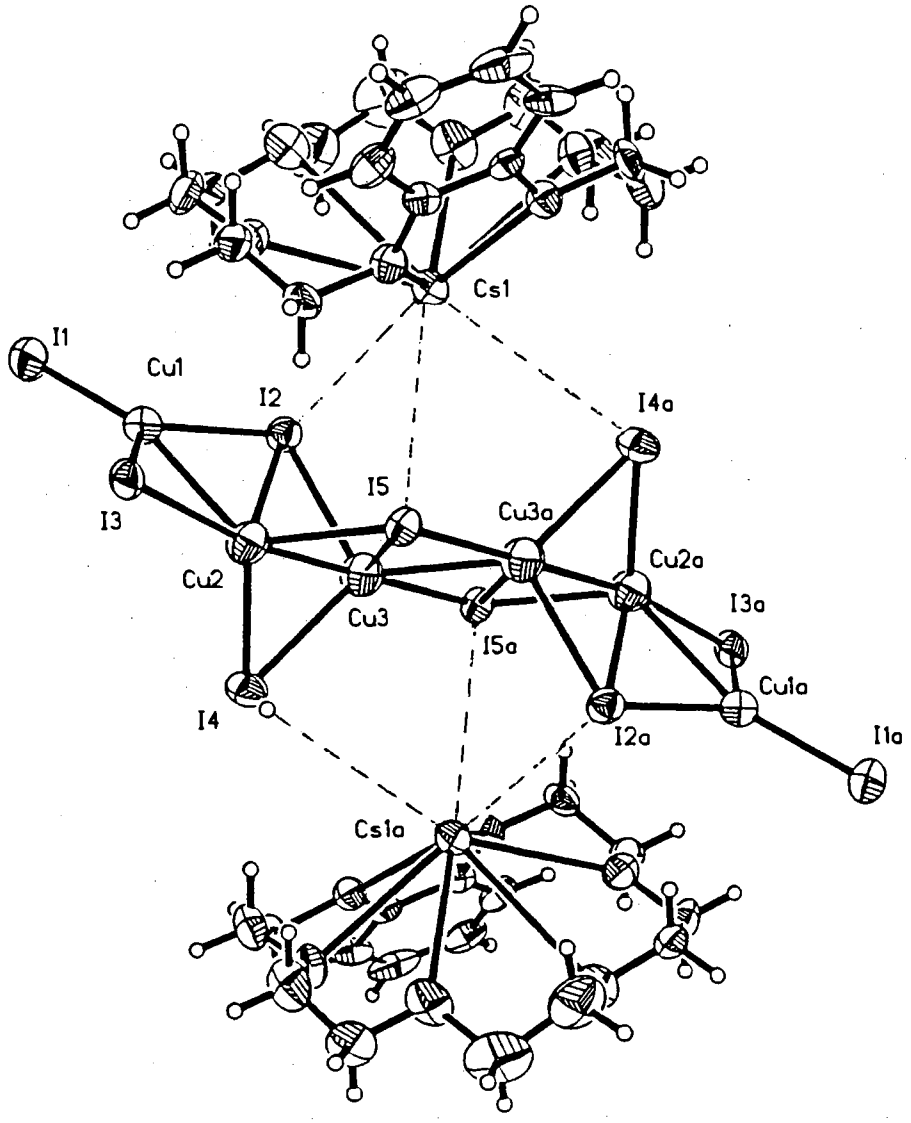


Figure 39. Projection View of $[Cs_4(Benzo\text{-}18\text{-}crown\text{-}6)_5]Cu_6I_{10}$ **(XVII)**

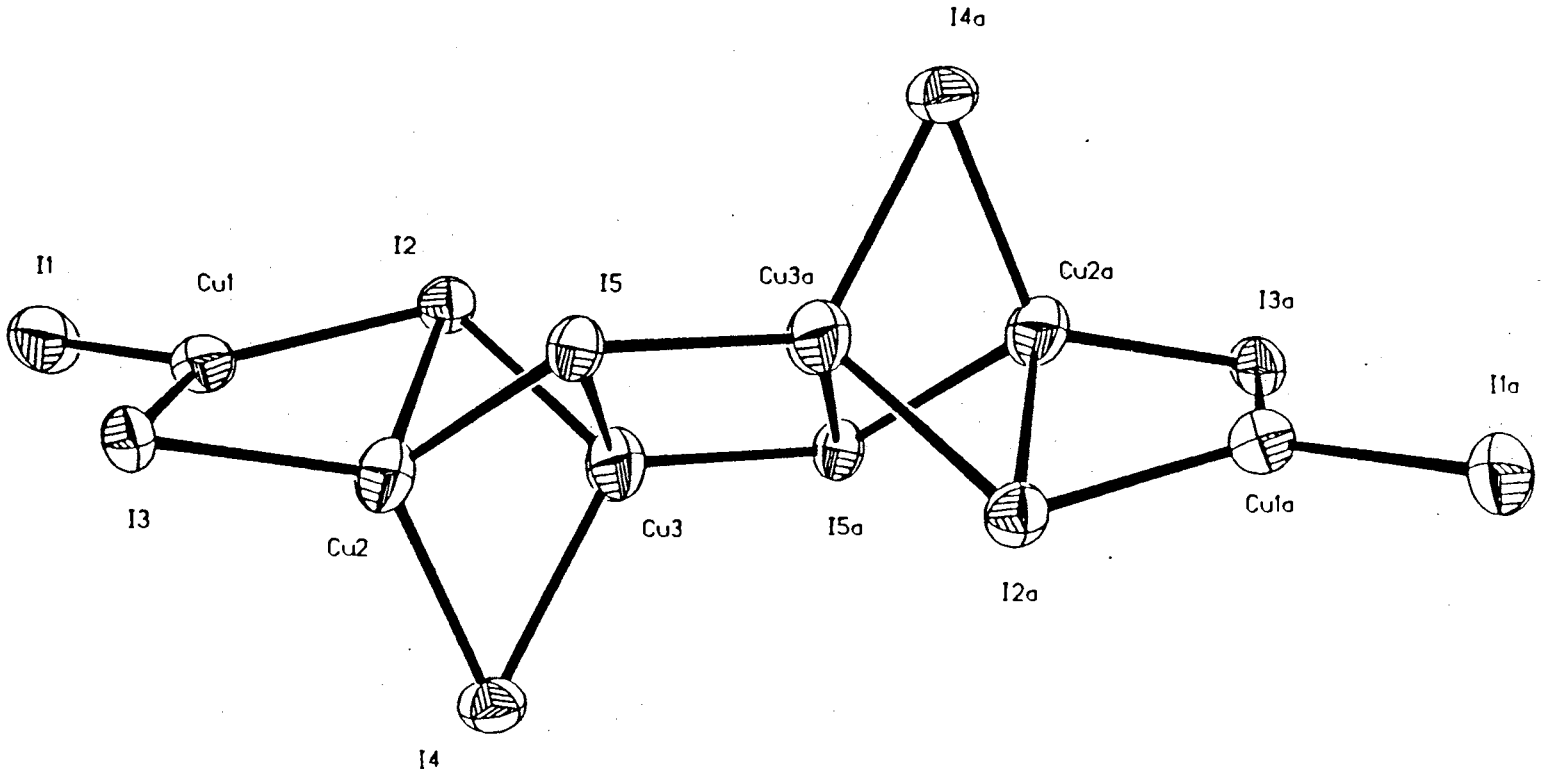


Figure 40. Projection View of $Cu_6I_{10}^{4-}$ Cluster in Compound (**XVII**)

TABLE 75

CRYSTAL DATA FOR

$[Cs_4(Benzo\text{-}18\text{-}crown\text{-}6)_5]Cu_6I_{10}$ (**XVII**)

Formula	$C_{80}H_{120}Cs_4Cu_6I_{10}O_{30}$
Space group	P1bar
a	12.825(4) Å
B	15.594(6) Å
C	16.048(5) Å
α	109.80(3)°
β	100.06(3)°
γ	102.09(3)°
V	2846.2(17) $Å^3$
Z	1
Mw	1871.8 g mol^{-1}
Density (calc.)	2.184 g cm^{-3}
$\mu(MoK_\alpha)$	51.39 cm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	1764
Collected Reflections	18145
Independent Reflections	16150
Observed Reflections ($F > 5.0\sigma$)	5327
Number of parameters	605
Final R indices	R = 6.90 %, R_w = 7.56 %
R indices (all data)	R = 17.97 %, R_w = 10.50 %
GOF	1.51

TABLE 76

POSITIONAL PARAMETERS FOR

$[Cs_4(Benzo\text{-}18\text{-}crown\text{-}6)_5]Cu_6I_{10}$ (**XVII**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
Cu(1)	1.1016(2)	0.6786(2)	-0.1338(2)
Cu(2)	1.1306(2)	0.8449(2)	0.0077(2)
Cu(3)	1.0762(3)	0.9623(2)	-0.0464(2)
I(1)	1.1341(1)	0.5488(1)	-0.2578(1)
I(2)	0.9976(1)	0.7871(1)	-0.1816(1)
I(3)	1.1558(1)	0.7014(1)	0.0356(1)
I(4)	1.2891(1)	0.9890(1)	0.0233(1)
I(5)	0.9840(1)	0.9161(1)	0.0964(1)
Cs(1)	0.7241(1)	0.7288(1)	-0.1032(1)
Cs(1)	1.3379(1)	0.9627(1)	0.5318(1)
O(1)	0.5548(9)	0.7049(7)	0.218(8)
C(2)	0.4498(14)	0.7239(13)	-0.0026(14)
H(2A)	0.4342	0.7645	0.0509
H(2B)	0.3912	0.6651	-0.304
C(3)	0.453(2)	0.7669(15)	-0.076(2)
H(3A)	0.5144	0.8234	-0.0494
H(3B)	0.3865	0.7843	-0.0908
O(4)	0.4728(10)	0.7026(9)	-0.1505(9)
C(5)	0.452(2)	0.721(2)	-0.231(2)
H(5A)	0.5086	0.7758	-0.2252
H(5B)	0.3820	0.7350	-0.2397
C(6)	0.450(2)	0.639(2)	-0.3064(14)
H(6A)	0.4303	0.6479	-0.3626
H(6B)	0.3966	0.5835	-0.3100
O(7)	0.5549(13)	0.6264(11)	-0.2961(10)
C(8)	0.561(3)	0.543(2)	-0.365(2)
H(8A)	0.5379	0.5451	-0.4245
H(8B)	0.5136	0.4865	-0.3648
C(9)	0.679(3)	0.541(2)	-0.344(2)
H(9A)	0.7279	0.6019	-0.3323
H(9B)	0.6905	0.4940	-0.3960
O(10)	0.6993(12)	0.5168(10)	-0.2685(10)
C(11)	0.806(2)	0.5067(13)	-0.248(2)
H(11A)	0.8592	0.5636	-0.2415
H(11B)	0.8126	0.4545	-0.2981
C(12)	0.829(2)	0.4893(12)	-0.160(2)

TABLE 76 (Continued)

H(12A)	0.9012	0.4796	-0.1486
H(12B)	0.7752	0.4332	-0.1665
O(13)	0.8237(10)	0.5674(8)	-0.0918(9)
C(14)	0.840(2)	0.5547(12)	-0.0084(14)
H(14A)	0.9099	0.5424	0.0034
H(14B)	0.7831	0.5012	-0.0124
C(15)	0.8402(14)	0.6432(12)	0.0669(14)
H(15A)	0.8976	0.6960	0.0707
H(15B)	0.8550	0.6361	0.1246
O(16)	0.7386(10)	0.6637(7)	0.0540(8)
C(17)	0.6557(14)	0.6232(10)	0.0852(11)
C(18)	0.5571(14)	0.6456(10)	0.0688(11)
C(19)	0.4714(15)	0.6136(11)	0.1009(11)
H(19A)	0.4046	0.6319	0.0925
C(20)	0.483(2)	0.5517(14)	0.1442(15)
H(20A)	0.4223	0.5258	0.1643
C(21)	0.579(2)	0.5268(12)	0.1602(12)
H(21A)	0.5859	0.4857	0.1926
C(22)	0.665(2)	0.5620(12)	0.1269(12)
H(22A)	0.7320	0.5437	0.1358
O(31)	1.1338(10)	1.0382(10)	0.4603(9)
C(32)	1.059(2)	0.980(2)	0.3710(14)
H(32A)	1.0942	0.9855	0.3242
H(32B)	0.9926	0.9993	0.3627
C(33)	1.034(2)	0.881(2)	0.360(2)
H(33A)	0.9747	0.8403	0.3067
H(33B)	1.0107	0.8791	0.4134
O(34)	1.1308(15)	0.8480(11)	0.3598(10)
C(35)	1.104(3)	0.748(2)	0.337(2)
H(35A)	1.1636	0.7276	0.3159
H(35B)	1.0378	0.7161	0.2873
C(36)	1.094(2)	0.717(2)	0.408(2)
H(36A)	1.0598	0.6492	0.3862
H(36B)	1.0452	0.7483	0.4377
O(37)	1.192(2)	0.745(2)	0.470(2)
C(38)	1.188(4)	0.716(4)	0.552(4)
H(38A)	1.2598	0.7076	0.5694
H(38B)	1.1344	0.6549	0.5279
C(39)	1.202(5)	0.779(4)	0.633(3)
H(39A)	1.1959	0.7482	0.6757
H(39B)	1.1355	0.7950	0.6176
O(40)	1.279(2)	0.857(2)	0.664(2)
C(41)	1.278(3)	0.906(3)	0.752(3)
H(41A)	1.2934	0.8732	0.7917
H(41B)	1.2087	0.9191	0.7545

TABLE 76 (Continued)

C(42)	1.354(3)	0.999(3)	0.782(2)
H(42A)	1.4198	0.9833	0.7700
H(42B)	1.3690	1.0336	0.8467
O(43)	1.342(2)	1.0618(15)	0.7403(11)
C(44)	1.267(2)	1.112(2)	0.766(2)
H(44A)	1.2834	1.1423	0.8313
H(44B)	1.1937	1.0683	0.7435
C(45)	1.274(2)	1.179(2)	0.7286(14)
H(45A)	1.3474	1.2211	0.7478
H(45B)	1.2254	1.2167	0.7493
O(46)	1.2354(12)	1.1334(12)	0.6275(10)
C(47)	1.212(2)	1.188(2)	0.576(2)
C(48)	1.158(2)	1.134(2)	0.489(2)
C(49)	1.124(2)	1.183(2)	0.433(2)
H(49A)	1.0848	1.1449	0.3699
C(50)	1.152(2)	1.277(2)	0.470(2)
H(50A)	1.1288	1.3065	0.4295
C(51)	1.203(3)	1.329(2)	0.559(3)
H(51A)	1.2143	1.3964	0.5821
C(52)	1.238(2)	1.288(2)	0.612(2)
H(52A)	1.2807	1.3275	0.6738
O(63)	1.406(2)	0.820(2)	0.3608(13)
C(64)	1.420(3)	0.830(2)	0.291(3)
H(64A)	1.3917	0.7692	0.2406
H(64B)	1.4957	0.8565	0.2935
C(65)	1.355(2)	0.900(2)	0.268(2)
H(65A)	1.2815	0.8784	0.2729
H(65B)	1.3513	0.9016	0.2087
O(66)	1.4086(13)	0.9906(12)	0.3385(12)
C(67)	1.366(2)	1.063(2)	0.332(2)
C(68)	1.411(2)	1.154(2)	0.396(2)
H(68A)	1.4004	1.2810	0.4561
C(69)	1.376(5)	1.223(3)	0.402(4)
H(69A)	1.4004	1.2810	0.4561
C(70)	1.298(5)	1.205(4)	0.322(4)
H(70A)	1.2780	1.2591	0.3160
C(71)	1.262(4)	1.124(3)	0.258(3)
H(71A)	1.2024	1.1145	0.2063
C(72)	1.298(4)	1.048(3)	0.262(4)
H(72A)	1.2684	0.9847	0.2151
O(73)	1.472(2)	1.1570(12)	0.476(2)
C(74)	1.525(4)	1.2482(26)	0.540(3)
C(74)	1.551(5)	1.2507(32)	0.627(3)
H(74A)	1.4848	1.2916	0.5330
H(74B)	1.5974	1.2691	0.5325

TABLE 76 (Continued)

C(75)	1.2727(7)	1.3517(9)	0.5692(10)
H(75A)	1.4780	1.2381	0.6363
H(75B)	1.5928	1.3131	0.6712

TABLE 77

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[Cs_4(Benzo\text{-}18\text{-}crown\text{-}6)_5]Cu_6I_{10}$ (**XVII**)

Cu(1)-Cu(2)	2.707(3)	C(19)-C(20)	1.38(3)
Cu(1)-I(1)	2.479(3)	C(20)-C(21)	1.38(4)
Cu(1)-I(2)	2.589(3)	O(21)-C(22)	1.40(4)
Cu(1)-I(3)	2.565(4)	O(31)-C(32)	1.44(2)
Cu(2)-Cu(3)	2.448(5)	O(31)-C(48)	1.35(3)
Cu(2)-I(2)	2.940(3)	C(32)-C(33)	1.46(4)
Cu(2)-I(3)	2.498(4)	C(33)-O(34)	1.44(3)
Cu(2)-I(4)	2.602(3)	O(34)-C(35)	1.42(3)
Cu(2)-I(5)	2.745(4)	C(35)-C(36)	1.41 (5)
Cu(3)-I(2)	2.694(3)	C(36)-O(37)	1.33(3)
Cu(3)-I(4)	2.649(3)	O(37)-C(38)	1.55(8)
Cu(3)-I(5)	2.980(4)	C(38)-C(39)	1.28(7)
Cu(3)-Cu(3^{i})	2.866(7)	C(39)-O(40)	1.27(6)
Cu(3)-I(5^{i})	2.503(4)	O(40)-C(41)	1.36(5)
I(5)-Cu(3^{i})	2.503(4)	C(41)-C(42)	1.44(5)
Cs(1)-O(1)	3.252(13)	C(42)-O(43)	1.37(5)
Cs(1)-O(4)	3.085(13)	O(43)-C(44)	1.40(4)
Cs(1)-O(7)	3.113(13)	C(44)-C(45)	1.37(5)
Cs(1)-O10)	3.374(13)	C(45)-O(46)	1.48(2)
Cs(1)-O(13)	3.094(14)	O(46)-C(47)	1.41(4)
Cs(1)-O(16)	3.012(14)	C(47)-C(48)	1.33(3)
O(1)-C(2)	1.46(2)	C(47)-C(52)	1.40(4)
O(1)-C(18)	1.38(2)	C(48)-C(49)	1.43(5)
C(2)-C(3)	1.54(4)	C(49)-C(50)	1.32(4)
C(3)-O(4)	1.39(3)	C(50)-C(51)	1.34(5)
O(4)-C(5)	1.41(3)	C(51)-C(52)	1.30(6)
C(5)-C(6)	1.43(3)	O(63)-C(64)	1.22(6)
C(6)-O(7)	1.38(3)	O(63)-C(75^{ii})	1.39(7)
O(7)-C(8)	1.43(3)	C(64)-C(65)	1.60(5)
C(8)-C(9)	1.50(5)	C(65)-O(66)	1.41(3)
C(9)-O(10)	1.38(4)	O(66)-C(67)	1.37(4)
O(10)-C(11)	1.40(3)	C(67)-C(68)	1.36(4)
C(11)-C(12)	1.52(4)	C(67)-C(72)	1.23(6)
C(12)-O(13)	1.36(2)	C(68)-C(69)	1.23(7)
O(13)-C(14)	1.40(3)	C(68)-O(73)	1.37(4)
C(14)-C(15)	1.49(2)	C(69)-C(70)	1.38(8)
C(15)-O(16)	1.40(2)	C(70)-C(71)	1.26(6)
O(16)-C(17)	1.38(2)	C(71)-C(72)	1.38(7)
C(17)-C(18)	1.39(3)	O(73)-C(74)	1.38(4)
C(17)-C(22)	1.35(3)	C(74)-C(75)	1.35(8)

TABLE 77 (Continued)

C(18)-C(19)	1.36(3)	C(75)-O(63^{ii})	1.39(7)
Cu(1)-I(2)-Cu(3)	107.7(1)	C(20)-C(21)-C(22)	118(2)
Cu(2)-I(2)-Cu(3)	51.3(1)	C(17)-C(22)-C(21)	120(2)
Cu(1)-I(3)-Cu(2)	64.6(1)	C(32)-O(31)-C(48)	118(2)
Cu(2)-I(4)-Cu(3)	55.6(1)	O(31)-C(32)-C(33)	109(2)
Cu(2)-I(5)-Cu(3)	50.4(1)	C(32)-C(33)-O(34)	112(2)
Cu(2)-I(5)-Cu(3^{i})	112.7(1)	C(33)-O(34)-C(35)	112(2)
Cu(3)-I(5)-Cu(3^{i})	62.3(1)	O(34)-C(35)-C(36)	117(2)
O(1)-Cs(1)-O(4)	51.7(4)	C(35)-C(36)-O(37)	110(3)
O(1)-Cs(1)-O(7)	98.6(4)	C(36)-O(37)-C(38)	114(3)
O(4)-Cs(1)-O(7)	52.4(4)	O(37)-C(38)-C(39)	121(5)
O(1)-Cs(1)-O(10)	110.9(3)	C(38)-C(39)-O(40)	120(6)
O(4)-Cs(1)-O(10)	93.4(3)	C(39)-O(40)-C(41)	108(4)
O(7)-Cs(1)-O(10)	51.8(4)	O(40)-C(41)-C(42)	107(4)
O(1)-Cs(1)-O(13)	96.6(4)	C(41)-C(42)-O(43)	124(3)
O(4)-Cs(1)-O(13)	122.8(3)	C(42)-O(43)-C(44)	115(2)
O(7)-Cs(1)-O(13)	100.9(4)	O(43)-C(44)-C(45)	108(2)
O(10)-Cs(1)-O(13)	50.2(4)	C(44)-C(45)-O(46)	110(2)
O(1)-Cs(1)-O(16)	48.5(3)	C(45)-O(46)-C(47)	120(2)
O(4)-Cs(1)-O(16)	97.7(4)	O(46)-C(47)-C(48)	112(2)
O(7)-Cs(1)-O(16)	126.9(4)	O(46)-C(47)-C(52)	125(2)
O(10)-Cs(1)-O(16)	96.8(4)	C(48)-C(47)-C(52)	123(3)
O(13)-Cs(1)-O(16)	55.6(4)	O(31)-C(48)-C(47)	119(3)
C(2)-O(1)-C(18)	116.4(15)	O(31)-C(48)-C(49)	125(2)
O(1)-C(2)-C(3)	109(2)	C(47)-C(48)-C(49)	116(3)
C(2)-C(3)-O(4)	108(2)	C(48)-C(49)-C(50)	119(3)
C(3)-O(4)-C(5)	114(2)	C(49)-C(50)-C(51)	124(4)
O(4)-C(5)-C(6)	108(2)	C(50)-C(51)-C(52)	120(3)
C(5)-C(6)-O(7)	110(2)	C(47)-C(52)-C(51)	119(3)
C(6)-O(7)-C(8)	114(2)	C(64)-O(63)-C(75^{ii})	111(4)
O(7)-C(8)-C(9)	107(2)	O(63)-C(64)-C(65)	111(3)
C(8)-C(9)-O(10)	108(3)	C(64)-C(65)-O(66)	106(2)
C(9)-O(10)-C(11)	112(2)	C(65)-O(66)-C(67)	116(2)
O(10)-C(11)-C(12)	111(2)	O(66)-C(67)-C(68)	122(3)
C(11)-C(12)-O(13)	107(2)	O(66)-C(67)-C(72)	119(3)
C(12)-O(13)-C(14)	110(2)	C(68)-C(67)-C(72)	118(4
O(13)-C(14)-C(15)	109(2)	C(67)-C(68)-C(69)	128(3)
C(14)-C(15)-O(16)	112.5(13)	C(67)-C(68)-O(73)	112(3)
C(15)-O(16)-C(17)	120(2)	C(69)-C(68)-O(73)	115(3)
O(16)-C(17)-C(18)	116(2)	C(68)-C(69)-C(70)	111(4)
O(16)-C(17)-C(22)	124(2)	C(69)-C(70)-C(71)	122(6)
C(18)-C(17)-C(22)	120(2)	C(70)-C(71)-C(72)	122(5)
O(1)-C(18)-C(17)	115(2)	C(67)-C(72)-C(71)	117(4)
O(1)-C(18)-C(19)	123(2)	C(68)-O(73)-C(74)	114(3)

TABLE 77 (Continued)

C(17)-C(18)-C(19)	122(2)	O(73)-C(74)-C(75)	112(4)
C(18)-C(19)-C(20)	117(2)	C(74)-C(75)-O(63^{ii})	117(4)
C(19)-C(20)-C(21)	122(2)		

Symmetry operations:

^{i} = 2-x, 2-y, -z

^{ii} = 3-x, 2-y, 1-z

TABLE 78

ANISOTROPIC THERMAL PARAMETERS FOR

$[Cs_4(Benzo\text{-}18\text{-}crown\text{-}6)_5]Cu_6I_{10}$ (**XVII**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	63(2)	65(1)	87(2)	15(1)	12(1)	18(1)
Cu(2)	91(2)	62(1)	111(2)	22(1)	17(2)	48(1)
Cu(3)	92(2)	72(2)	134(3)	28(2)	-3(2)	53(2)
I(1)	83(1)	85(1)	117(1)	37(1)	20(1)	-1(1)
I(2)	63(1)	57(1)	50(1)	16(1)	10(1)	16(1)
I(3)	59(1)	62(1)	90(1)	25(1)	15(1)	43(1)
I(4)	54(1)	70(1)	78(1)	4(1)	12(1)	37(1)
I(5)	67(1)	50(1)	50(1)	21(1)	20(1)	25(1)
Cs(1)	50(1)	61(1)	55(1)	14(1)	14(1)	24(1)
Cs(2)	57(1)	101(1)	45(1)	13(1)	18(1)	7(1)
O(1)	50(7)	56(7)	58(8)	14(6)	18(6)	21(6)
C(2)	35(10)	83(13)	80(15)	24(10)	26(10)	9(12)
C(3)	57(13)	89(15)	115(20)	34(11)	36(13)	65(15)
O(4)	67(9)	81(8)	64(9)	38(7)	18(7)	46(7)
C(5)	91(17)	106(18)	119(22)	38(14)	26(16)	83(18)
C(6)	112(21)	109(18)	42(13)	36(16)	-23(13)	23(13)
O(7)	83(11)	125(12)	46(9)	34(9)	1(8)	33(9)
C(8)	175(33)	164(28)	30(14)	23(25)	-20(18)	19(16)
C(9)	157(30)	121(22)	62(18)	39(21)	23(20)	11(16)
O(10)	76(10)	101(10)	59(10)	22(8)	22(8)	32(8)
C(11)	59(14)	50(11)	96(18)	11(9)	28(13)	-3(11)
C(12)	88(16)	46(11)	106(19)	31(10)	50(14)	29(12)
O(13)	70(9)	57(7)	67(9)	19(6)	14(7)	18(7)
C(14)	61(13)	49(11)	84(16)	17(9)	0(11)	26(11)
C(15)	44(11)	60(11)	92(16)	11(9)	1(11)	43(11)
O(16)	60(8)	52(6)	68(8)	20(6)	9(7)	39(6)
C(17)	47(11)	45(9)	34(10)	5(8)	20(8)	11(8)
C(18)	54(11)	31(8)	40(10)	5(8)	5(9)	1(7)
C(19)	65(12)	53(10)	41(11)	-16(9)	16(9)	19(9)
C(20)	122(22)	55(13)	60(15)	-28(14)	46(16)	-7(11)
O(21)	114(19)	47(10)	30(11)	6(12)	14(13)	10(8)
C(22)	97(16)	50(10)	45(11)	20(11)	19(11)	13(9)
O(31)	58(9)	98(11)	50(8)	19(8)	-12(7)	0(8)
C(32)	54(13)	110(19)	60(14)	6(13)	-19(11)	-10(13)
C(33)	54(14)	99(18)	84(18)	5(13)	19(13)	-9(14)
O(34)	106(14)	89(11)	68(11)	-7(10)	-8(10)	-4(9)
C(35)	145(28)	81(19)	126(28)	0(18)	-80(24)	-19(18)

TABLE 78 (Continued)

C(36)	98(21)	106(20)	109(23)	-8(16)	-10(19)	44(18)
O(37)	101(16)	182(20)	126(17)	-8(14)	16(14)	64(15)
C(38)	169(42)	297(77)	313(80)	-17(45)	28(51)	233(70)
C(39)	410(88)	274(64)	187(58)	252(66)	217(65)	195(57)
O(40)	171(22)	153(21)	109(18)	32(17)	55(16)	62(17)
C(41)	183(39)	237(48)	152(42)	103(35)	105(34)	97(37)
C(42)	114(26)	213(40)	74(22)	-13(28)	47(20)	-1(25)
O(43)	116(15)	154(16)	51(11)	24(12)	37(10)	50(11)
C(44)	77(18)	182(29)	34(14)	-2(18)	37(13)	26(16)
C(45)	68(16)	144(23)	32(13)	-1(15)	8(12)	-29(14)
O(46)	68(10)	111(12)	49(9)	17(9)	8(8)	-16(9)
C(47)	35(11)	98(18)	92(20)	31(12)	23(12)	-1(16)
C(48)	54(13)	99(18)	60(15)	17(13)	12(12)	-14(14)
C(49)	80(18)	103(20)	106(22)	106(22)	33(16)	17(18)
C(50)	111(23)	130(25)	144(30)	94(20)	56(22)	68(23)
C(51)	126(29)	101(22)	144(35)	43(21)	16(26)	-1(24)
C(52)	53(15)	132(26)	98(23)	29(15)	-11(14)	-10(19)
O(63)	137(19)	153(21)	45(11)	24(15)	10(11)	-7(12)
C(64)	130(29)	66(18)	245(52)	24(17)	90(35)	-15(25)
C(65)	125(24)	146(26)	44(15)	-41(22)	-19(15)	-20(16)
O(66)	86(12)	83(11)	114(15)	27(10)	11(10)	1(10)
C(67)	72(17)	109(21)	109(21)	-18(16)	12(15)	-7(16)
C(68)	73(18)	176(33)	59(18)	36(19)	-2(14)	0(20)
C(69)	131(44)	42(21)	117(46)	48(26)	84(40)	38(25)
C(70)	148(52)	96(38)	112(45)	112(45)	-3(40)	88(37)
C(71)	91(32)	42(20)	52(25)	21(21)	-7(23)	-3(19)
C(72)	62(28)	78(30)	87(35)	6(24)	7(27)	7(27)
O(73)	207(24)	78(12)	123(18)	2(13)	63(18)	-31(12)
C(74)	136(32)	89(24)	328(70)	63(22)	63(22)	6(41)
C(75)	179(52)	109(30)	234(61)	-12(30)	97(49)	-3(39)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

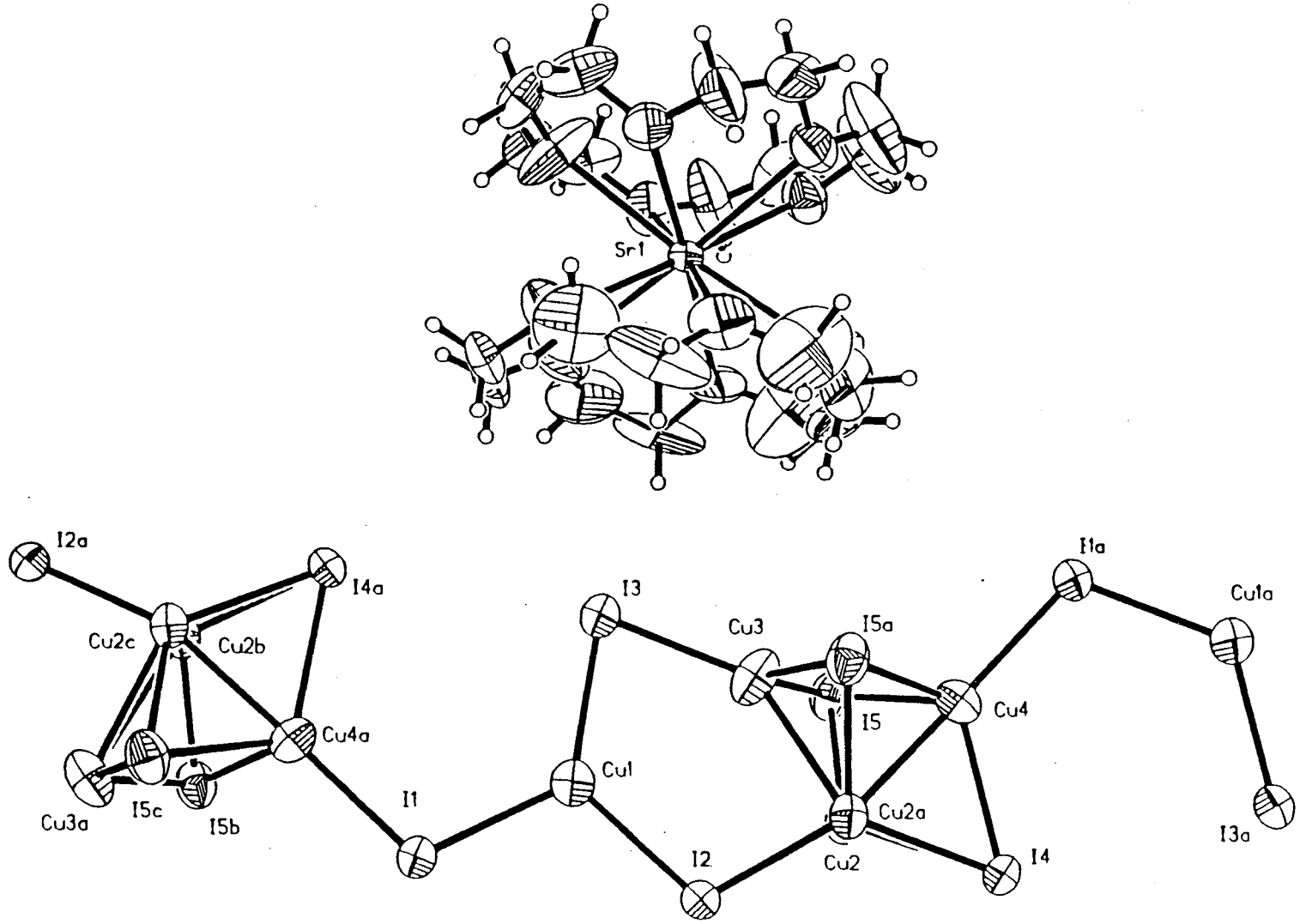


Figure 41. Projection View of $[Sr(15\text{-Crown-}5)_2]Cu_4I_6$ **(XVIII)**

TABLE 79

CRYSTAL DATA FOR

$[Sr(15\text{-Crown-}5)_2]Cu_4I_6$ (**XVIII**)

Formula	$C_{20}H_{40}Cu_4I_6O_{10}Sr$
Space group	Pnma
a	20.516(9) Å
b	13.303(6) Å
c	15.895(7) Å
V	4323(6) $Å^3$
Z	4
Mw	1543.7 g mol^{-1}
Density (Srlc.)	2.372 Mg m^{-3}
$\mu(MoK_\alpha)$	7.483 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	2848
Collected Reflections	7839
Independent Reflections	6528
Observed Reflections ($F > 4.1\ \sigma$)	1928
Number of parameters	206
Final R indices	R = 5.99 %, R_w = 6.69 %
R indices (all data)	R = 20.10 %, R_w = 11.05 %
GOF	1.42

TABLE 80

POSITIONAL PARAMETERS FOR

$[Sr(15\text{-Crown-}5)_2]Cu_4I_6$ (**XVIII**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.1129(1)	0.2500	0.3722(1)
I(2)	0.3233(1)	0.2500	0.4223(1)
I(3)	0.2538(1)	0.2500	0.1476(1)
I(4)	0.5480(1)	0.2500	0.4083(1)
I(5)	0.4327(1)	0.758(1)	0.2155(1)
Cu(1)	0.2304(2)	0.2500	0.3078(2)
Cu(2)	0.4339(2)	0.2041(4)	0.3503(3)
Cu(3)	0.3701(2)	0.2500	0.2116(3)
Cu(4)	0.5221(2)	0.2500	0.2421(2)
Sr(1)	0.3285(1)	0.2500	-0.2138(1)
O(1)	0.4396(13)	0.2500	-0.1064(15)
C(2)	0.443(2)	0.3555(43)	-0.057(2)
H(2A)	0.4886	0.3725	-0.0575
H(2B)	0.4318	0.3380	-0.0006
C(3)	0.411(3)	0.414(4)	-0.081(4)
H(3A)	0.4380	0.4520	-0.1189
H(3B)	0.4072	0.4536	-0.0306
O(4)	0.3510(11)	0.4153(14)	-0.1112(10)
C(5)	0.304(2)	0.464(2)	-0.068(2)
H(5A)	0.3124	0.5352	-0.0655
H(5B)	0.3017	0.4390	-0.0118
C(6)	0.244(2)	0.445(3)	-0.107(2)
H(6A)	0.2416	0.4897	-0.1544
H(6B)	0.2098	0.4636	-0.0691
O(7)	0.2257(10)	0.350(2)	-0.1367(13)
C(8)	0.1724(10)	0.305(2)	-0.105(2)
H(8A)	0.1350	0.3275	-0.1357
H(8B)	0.1672	0.3275	-0.0477
O(21)	0.229(2)	0.2500	-0.327(2)
C(22)	0.2049(12)	0.341(2)	-0.360(2)
H(22A)	0.1673	0.3592	-0.3278
H(22B)	0.1904	0.3285	-0.4167
C(23)	0.250(2)	0.424(2)	-0.361(2)
H(23A)	0.2259	0.4839	-0.3473
H(23B)	0.2663	0.4324	-0.4173
O(24)	0.301(2)	0.4203(13)	-0.3057(10)

TABLE 80 (Continued)

C(25)	0.3536(15)	0.479(3)	-0.324(3)
H(25A)	0.3632	0.5121	-0.2716
H(25B)	0.3416	0.5297	-0.3640
C(26)	0.4103(17)	0.440(2)	-0.344(2)
H(26A)	0.4465	0.4859	-0.3439
H(26B)	0.4038	0.4182	-0.4015
O(27)	0.4260(7)	0.3561(14)	-0.2965(10)
C(28)	0.4762(15)	0.300(2)	-0.328(2)
H(28A)	0.5153	0.3208	-0.3002
H(28B)	0.4803	0.3208	-0.3859

TABLE 81

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[Sr(15\text{-Crown-}5)_2]Cu_4I_6$ (**XVIII**)

I(1)-Cu(1)	2.620(4)	Sr(1)-O(24)	2.76(2)
I(1)-Cu(4^{i})	2.601(5)	Sr(1)-O(27)	2.78(2)
I(2)-Cu(1)	2.635(4)	Sr(1)-O(4^{ii})	2.78(2)
I(2)-Cu(2)	2.613(5)	Sr(1)-O(7^{ii})	2.78(2)
I(2)-Cu(2^{ii})	2.613(5)	Sr(1)-O(24^{ii})	2.76(2)
I(3)-Cu(1)	2.591(4)	Sr(1)-O(27^{ii})	2.78(2)
I(3)-Cu(3)	2.594(5)	O(1)-C(2)	1.61(5)
I(4)-Cu(2)	2.588(5)	O(1)-C(2^{ii})	1.61(5)
I(4)-Cu(4)	2.695(4)	C(2)-C(3)	1.09(7)
I(4)-Cu(2^{ii})	2.588(5)	C(3)-O(4)	1.32(6)
I(5)-Cu(2)	2.741(5)	O(4)-C(5)	1.35(4)
I(5)-Cu(3)	2.651(3)	C(5)-C(6)	1.40(6)
I(5)-Cu(4)	2.985(3)	C(6)-O(7)	1.39(5)
Cu(2)-I(3)	2.636(6)	O(7)-C(8)	1.35(3)
Cu(2)-I(4)	2.570(6)	C(8)-C(8^{ii})	1.46(6)
Cu(3)-I(5^{ii})	2.651(3)	O(21)-C(22)	1.41(3)
Cu(3)-Cu(2^{ii})	2.636(6)	O(21)-C(22^{ii})	1.41(3)
Cu(4)-I(1^{iii})	2.601(5)	C(22)-C(23)	1.45(4)
Cu(4)-I(5^{ii})	2.985(3)	C(23)-O(24)	1.36(4)
Cu(4)-Cu(2^{ii})	2.570(6)	O(24)-C(25)	1.37(4)
Sr(1)-O(1)	2.85(3)	C(25)-C(26)	1.31(5)
Sr(1)-O(4)	2.78(2)	C(26)-O(27)	1.39(4)
Sr(1)-O(7)	2.78(2)	O(27)-C(28)	1.37(3)
Sr(1)-O(21)	2.72(3)	C(28)-C(28^{ii})	1.33(5)
Cu(1)-I(1)-Cu(4^{i})	112.7(1)	O(27)-Sr(1)-O(7^{ii})	176.8(6)
Cu(1)-I(2)-Cu(2)	109.0(1)	O(4A)-Sr(1)-O(7^{ii})	59.1(6)
Cu(1)-I(2)-Cu(2^{ii})	109.0(1)	O(1)-Sr(1)-O(24^{ii})	118.9(4)
Cu(1)-I(3)-Cu(3)	77.6(1)	O(4)-Sr(1)-O(24^{ii})	175.6(5)
Cu(2)-I(4)-Cu(4)	58.2(1)	O(7)-Sr(1)-O(24^{ii})	118.2(6)
Cu(4)-I(4)-Cu(2^{ii})	58.2(1)	O(21)-Sr(1)-O(24^{ii})	59.6(4)
Cu(2)-I(5)-Cu(3)	58.5(1)	O(24)-Sr(1)-O(24^{ii})	110.7(7)
Cu(2)-I(5)-Cu(4)	53.1(1)	O(27)-Sr(1)-O(24^{ii})	108.4(5)
Cu(3)-I(5)-Cu(4)	67.8(1)	O(4A)-Sr(1)-O(24^{ii})	72.2(5)
O(1)-Sr(1)-O(4)	61.0(5)	O(7A)-Sr(1)-O(24^{ii})	71.5(6)
O(1)-Sr(1)-O(7)	110.0(6)	O(1)-Sr(1)-O(27^{ii})	73.0(5)
O(4)-Sr(1)-O(7)	59.1(6)	O(4)-Sr(1)-O(27^{ii})	124.1(6)
O(1)-Sr(1)-O(21)	175.3(9)	O(7)-Sr(1)-O(27^{ii})	176.8(6)
O(4)-Sr(1)-O(21)	120.9(5)	O(21)-Sr(1)-O(27^{ii})	103.1(7)

TABLE 81 (Continued)

O(7)-Sr(1)-O(21)	74.0(7)	O(24)-Sr(1)-O(27^{ii})	108.4(5)
O(1)-Sr(1)-O(24)	118.9(4)	O(27)-Sr(1)-O(27^{ii})	61.0(8)
O(4)-Sr(1)-O(24)	72.2(5)	O(4A)-Sr(1)-O(27^{ii})	75.9(5)
O(7)-Sr(1)-O(24)	71.5(6)	O(7A)-Sr(1)-O(27^{ii})	120.7(6)
O(21)-Sr(1)-O(24)	59.6(4)	O(24A)-Sr(1)-O(27^{ii})	58.7(5)
O(1)-Sr(1)-O(27)	73.0(5)	C(2)-O(1)-C(2^{ii})	122(3)
O(4)-Sr(1)-O(27)	75.9(5)	O(1)-C(2)-C(3)	116(4)
O(7)-Sr(1)-O(27)	120.7(6)	C(2)-C(3)-O(4)	134(5)
O(21)-Sr(1)-O(27)	103.1(7)	C(3)-O(4)-C(5)	119(3)
O(24)-Sr(1)-O(27)	58.7(5)	O(4)-C(5)-C(6)	108(3)
O(1)-Sr(1)-O(4^{ii})	61.0(5)	C(5)-C(6)-O(7)	124(4)
O(4)-Sr(1)-O(4^{ii})	104.7(7)	C(6)-O(7)-C(8)	120(3)
O(7)-Sr(1)-O(4^{ii})	104.3(6)	O(7)-C(8)-C(8A)	116.6(15)
O(21)-Sr(1)-O(4^{ii})	120.9(5)	C(22)-O(21)-C(22^{ii})	118(3)
O(24)-Sr(1)-O(4^{ii})	175.6(5)	O(21)-C(22)-C(23)	116(2)
O(27)-Sr(1)-O(4^{ii})	124.1(6)	C(22)-C(23)-O(24)	117(2)
O(1)-Sr(1)-O(7^{ii})	110.0(6)	C(23)-O(24)-C(25)	116(2)
O(4)-Sr(1)-O(7^{ii})	104.3(6)	O(24)-C(25)-C(26)	122(3)
O(7)-Sr(1)-O(7^{ii})	57.4(9)	C(25)-C(26)-O(27)	113(3)
O(21)-Sr(1)-O(7^{ii})	74.0(7)	C(26)-O(27)-C(28)	114(2)
O(24)-Sr(1)-O(7^{ii})	118.2(6)	O(27)-C(28)-C(28^{ii})	123.1(14)

Symmetry operations:

^{i} = x-0.5, 0.25, 0.5-z

^{ii} = x, 0.5-y, z

^{iii} = x+0.5, 0.25, 0.5-z

TABLE 82

ANISOTROPIC THERMAL PARAMETERS FOR

$[Sr(15\text{-Crown-}5)_2]Cu_4I_6$ (**XVIII**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	62(1)	107(2)	72(1)	0	-5(1)	0
I(2)	62(1)	109(2)	62(1)	0	-2(1)	0
I(3)	66(1)	82(1)	77(1)	0	-7(1)	0
I(4)	60(1)	98(2)	66(1)	0	-10(1)	0
I(5)	71(1)	75(1)	108(1)	7(1)	-11(1)	-15(1)
Cu(1)	80(2)	80(3)	88(2)	0	-1(2)	0
Cu(2)	57(2)	122(5)	80(3)	-4(3)	-2(2)	6(3)
Cu(3)	99(3)	86(3)	130(3)	0	-43(3)	0
Cu(4)	88(3)	261(7)	81(2)	0	20(2)	0
Sr(1)	56(1)	48(1)	45(1)	0	1(1)	0
O(1)	158(24)	183(29)	104(16)	0	-62(16)	0
C(2)	139(28)	624(118)	139(25)	-161(47)	-16(23)	-183(48)
C(3)	389(107)	242(67	380(85)	-207(72)	-133(71)	167(60)
O(4)	177(18)	117(15)	96(10)	8(14)	6(12)	-61(11)
C(5)	412(67)	63(20)	127(23)	-107(31)	132(35)	-86(19)
C(6)	290(60)	156(41)	197(36)	-3(36)	-4(35)	-115(30)
O(7)	163(17)	119(17)	192(18)	-28(14)	75(15)	-67(14)
C(8)	65(13)	282(54	141(18)	11(20)	43(13)	57(23)
O(21)	265(38)	103(24)	198(28)	0	-167(28)	0
C(22)	115(19)	82(21)	142(20)	60(18)	-51(16)	-34(17)
C(23)	246(39)	79(23)	103(18)	43(25)	-46(22)	3(16)
O(24)	105(12)	116(14)	123(12)	4(11)	-1(10)	54(11)
C(25)	104(25)	234(48)	331(52)	62(30)	94(30)	158(39)
C(26)	153(29)	156(31)	155(25)	-70(25)	-33(23)	98(25)
O(27)	96(11)	124(15)	118(11)	-4(11)	20(9)	24(11)
C(28)	165(27)	113(27)	357(49)	-45(21)	151(31)	-62(27)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

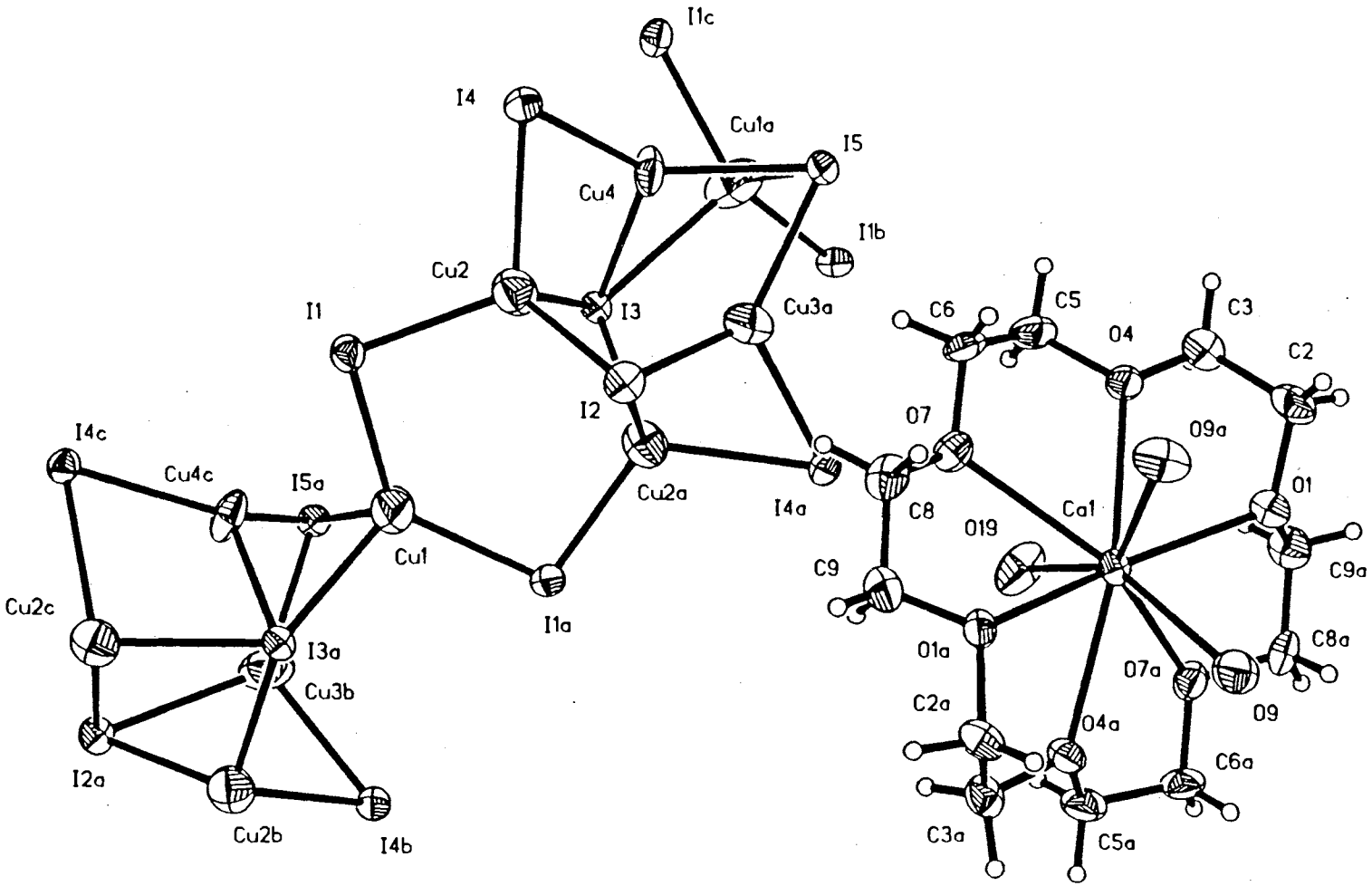


Figure 42. Projection View of $[Ca(18\text{-Crown-6})]Cu_5I_7 .3H_2O$ (**XIX**)

TABLE 83

CRYSTAL DATA FOR

[Ca(18-Crown-6)]Cu_5I_7 .$3H_2O$ (**XIX**)

Formula	$C_{12}H_{30}CaCu_5I_7O_9$
Space group	Pbcm
a	10.648(2) Å
b	14.444(5) Å
c	22.674(6) Å
V	3487.3(17) $Å^3$
Z	4
Mw	1564.4 g mol^{-1}
Density (calc.)	2.980 Mg m^{-3}
$\mu(MoK_\alpha)$	9.377 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	2840
Collected Reflections	6392
Independent Reflections	5211
Observed Reflections ($F > 5.0\ \sigma$)	1991
Number of parameters	171
Final R indices	R = 5.88 %, R_w = 6.62 %
R indices (all data)	R = 13.87 %, R_w = 9.00 %
GOF	1.29

TABLE 83

CRYSTAL DATA FOR

[Ca(18-Crown-6)]Cu_5I_7 .$3H_2O$ (**XIX**)

Formula	$C_{12}H_{30}CaCu_5I_7O_9$
Space group	Pbcm
a	10.648(2) Å
b	14.444(5) Å
c	22.674(6) Å
V	3487.3(17) $Å^3$
Z	4
Mw	1564.4 g mol^{-1}
Density (calc.)	2.980 Mg m^{-3}
$\mu(MoK_\alpha)$	9.377 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	2840
Collected Reflections	6392
Independent Reflections	5211
Observed Reflections ($F > 5.0\ \sigma$)	1991
Number of parameters	171
Final R indices	R = 5.88 %, R_w = 6.62 %
R indices (all data)	R = 13.87 %, R_w = 9.00 %
GOF	1.29

TABLE 85

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

[Ca(18-Crown-6)]$Cu_5I_7 .3H_2O$ (**XIX**)

I(1)-Cu(1)	2.547(3)	Cu(2)-Cu(4)	2.783(7)
I(1)-Cu(2)	2.602(3)	Cu(2)-Cu(2^{i})	3.007(6)
I(2)-Cu(2)	2.681(4)	Cu(3)-Cu(4^{i})	2.779(10)
I(2)-Cu(3)	2.718(8)	Cu(4)-Cu(1^{ii})	2.444(8)
I(2)-Cu(2^{i})	2.681(4)	Cu(4)-Cu(3^{i})	2.779(10)
I(2)-Cu(3^{i})	2.718(8)	Cu(4)-Cu(4^{i})	2.783(10)
I(3)-Cu(2)	2.804(4)	Ca(1)-O(1)	2.526(12)
I(3)-Cu(4)	2.712(6)	Ca(1)-O(4)	2.619(12)
I(3)-Cu(1^{ii})	2.874(6)	Ca(1)-O(7)	2.702(11)
I(3)-Cu(2^{i})	2.804(4)	Ca(1)-O(9)	2.446(14)
I(3)-Cu(4^{i})	2.712(6)	Ca(1)-O(19)	2.35(2)
I(4)-Cu(2)	2.716(3)	Ca(1)-O(1^{vi})	2.526(12)
I(4)-Cu(3)	2.620(7)	Ca(1)-O(4^{vi})	2.619(12)
I(4)-Cu(4)	2.527(6)	Ca(1)-O(7^{vi})	2.702(11)
I(5)-Cu(3)	2.520(8)	Ca(1)-O(9^{vi})	2.456(14)
I(5)-Cu(4)	2.600(6)	O(1)-C(2)	1.47(2)
I(5)-Cu(1^{ii})	2.979(7)	O(1)-C(9^{vi})	1.39(2)
I(5)-Cu(3^{i})	2.520(8)	C(2)-C(3)	1.53(3)
I(5)-Cu(4^{i})	2.600(6)	C(3)-O(4)	1.42(2)
Cu(1)-Cu(1^{ii})	2.547(3)	O(4)-C(5)	1.46(2)
Cu(2)-Cu(3^{i})	2.874(6)	C(5)-C(6)	1.48(3)
Cu(1)-I(5^{iii})	2.979(7)	C(6)-O(7)	1.43(2)
Cu(1)-Cu(4^{iv})	2.444(8)	O(7)-C(8)	1.43(2)
Cu(1)-Cu(4^{v})	2.444(8)	C(8)-C(9)	1.48(3)
Cu(2)-Cu(3)	2.387(9)	C(9)-O(1^{vi})	1.39(2)
Cu(1)-I(1)-Cu(2)	98.1(1)	O(1)-Ca(1)-O(4)	63.0(4)
Cu(1)-I(2)-Cu(2)	52.5(2)	O(1)-Ca(1)-O(7)	123.3(4)
Cu(2)-I(2)-Cu(2^{i})	68.2(1)	O(4)-Ca(1)-O(7)	60.3(4)
Cu(3)-I(2)-Cu(2^{i})	78.2(2)	O(1)-Ca(1)-O(9)	80.7(4)
Cu(2)-I(2)-Cu(3^{i})	78.2(2)	O(4)-Ca(1)-O(9)	129.6(5)
Cu(3)-I(2)-Cu(3^{i})	42.2(3)	O(7)-Ca(1)-O(9)	142.0(4)
Cu(2^{i})-I(2)-Cu(3^{i})	52.5(2)	O(1)-Ca(1)-O(19)	98.1(3)
Cu(2)-I(3)-Cu(4)	60.6(2)	O(4)-Ca(1)-O(19)	80.0(3)
Cu(2)-I(3)-Cu(1^{ii})	112.2(1)	O(7)-Ca(1)-O(19)	69.1(3)
Cu(4)-I(3)-Cu(1^{ii})	51.8(2)	O(9)-Ca(1)-O(19)	142.3(3)
Cu(2)-I(3)-Cu(2^{i})	64.9(1)	O(1)-Ca(1)-O(1^{vi})	163.7(6)
Cu(4)-I(3)-Cu(2^{i})	93.4(2)	O(4)-Ca(1)-O(1^{vi})	120.2(4)
Cu(1^{ii})-I(3)-Cu(2^{i})	112.2(1)	O(7)-Ca(1)-O(1^{vi})	63.4(4)

TABLE 85 (Continued)

Cu(2)-I(3)-Cu(4^{i})	93.4(2)	O(1)-Ca(1)-O(7^{vi})	63.4(4)
Cu(4)-I(3)-Cu(4^{i})	61.7(2)	O(4)-Ca(1)-O(7^{vi})	111.8(4)
Cu(1^{ii})-I(3)-Cu(4^{i})	51.8(2)	O(7)-Ca(1)-O(7^{vi})	138.1(6)
Cu(2^{i})-I(3)-Cu(4^{i})	60.6(2)	O(9)-Ca(1)-O(7^{vi})	77.2(4)
Cu(2)-I(4)-Cu(3)	53.1(2)	O(19)-Ca(1)-O(7^{vi})	69.1(3)
Cu(2)-I(4)-Cu(4)	64.0(2)	O(1^{vi})-Ca(1)-O(7^{vi})	123.3(4)
Cu(3)-I(4)-Cu(4)	34.0(2)	O(4^{vi})-Ca(1)-O(7^{vi})	60.3(4)
Cu(3)-I(5)-Cu(4)	34.2(3)	O(1)-Ca(1)-O(9^{vi})	86.4(4)
Cu(3)-I(5)-Cu(1^{ii})	80.5(3)	O(4)-Ca(1)-O(9^{vi})	68.8(4)
Cu(4)-I(5)-Cu(1^{ii})	51.4(2)	O(7)-Ca(1)-O(9^{vi})	77.2(4)
Cu(3)-I(5)-Cu(3^{ii})	45.7(3)	O(9)-Ca(1)-O(9^{vi})	75.5(7)
Cu(4)-I(5)-Cu(3^{i})	65.7(2)	O(19)-Ca(1)-O(9^{vi})	142.3(3)
Cu(1^{ii})-I(5)-Cu(3^{i})	80.5(3)	O(1^{vi})-Ca(1)-O(9^{vi})	80.7(4)
Cu(3)-I(5)-Cu(4^{i})	65.7(2)	O(4^{vi})-Ca(1)-O(9^{vi})	129.6(5)
Cu(4)-I(5)-Cu(4^{i})	64.7(2)	O(7^{vi})-Ca(1)-O(9^{vi})	142.0(4)
Cu(1^{ii})-I(5)-Cu(4^{i})	51.4(2)	C(2)-O(1)-C(9^{vi})	114.0(14)
Cu(3^{i})-I(5)-Cu(4^{i})	34.2(3)	O(1)-C(2)-C(3)	108(2)
O(9)-Ca(1)-O(1^{vi})	86.4(4)	C(2)-C(3)-O(4)	106.4(14)
O(19)-Ca(1)-O(1^{vi})	98.1(3)	C(3)-O(4)-C(5)	114.3(14)
O(1)-Ca(1)-O(4^{vi})	120.2(4)	O(4)-C(5)-C(6)	107(2)
O(4)-Ca(1)-O(4^{vi})	160.0(6)	C(5)-C(6)-O(7)	106.4(14)
O(7)-Ca(1)-O(4^{vi})	111.8(4)	C(6)-O(7)-C(8)	111.4(13)
O(9)-Ca(1)-O(4^{vi})	68.8(4)	O(7)-C(8)-C(9)	108.9(14)
O(19)-Ca(1)-O(4^{vi})	80.0(3)	C(8)-C(9)-O(1^{vi})	110(2)
O(1^{vi})-Ca(1)-O(4^{vi})	63.0(4)		

Symmetry operations:

^{i} = x, y, 0.5-z
^{ii} = 2-x, y-0.5, 0.25
^{iii} = 2-x, y+0.5, 0.25
^{iv} = 2-x, y+0.5, 0.5-z
^{v} = 2-x, y+0.5, z

TABLE 86

ANISOTROPIC THERMAL PARAMETERS FOR

[Ca(18-Crown-6)]Cu_5I_7 .$3H_2O$ (**XIX**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	53(1)	48(1)	46(1)	5(1)	6(1)	7(1)
I(2)	38(1)	57(1)	57(1)	-9(1)	0	0
I(3)	33(1)	37(1)	46(1)	-1(1)	0	0
I(4)	42(1)	50(1)	42(1)	-2(1)	8(1)	0(1)
I(5)	42(1)	42(1)	44(1)	9(1)	0	0
Cu(1)	156(5)	108(4)	75(3)	59(4)	0	0
Cu(2)	77(2)	76(2)	92(2)	11(2)	-7(2)	-1(2)
Cu(3)	165(8)	87(5)	81(4)	43(6)	-3(5)	16(4)
Cu(4)	76(4)	93(4)	51(3)	38(4)	18(3)	35(3)
Ca(1)	24(2)	36(3)	45(2)	0	0	3(2)
O(1)	47(7)	38(7)	50(7)	-4(6)	12(6)	2(6)
C(2)	84(16)	31(11)	77(14)	3(11)	6(12)	-3(10)
C(3)	37(10)	50(13)	71(12)	-7(10)	6(10)	-2(10)
O(4)	52(7)	36(7)	47(7)	-6(7)	-6(6)	-3(5)
C(5)	64(13)	56(13)	60(12)	-10(12)	-7(11)	-22(11)
C(6)	103(18)	52(12)	29(8)	-1(13)	-8(11)	-11(9)
O(7)	51(7)	59(9)	40(6)	-7(7)	2(6)	4(6)
C(8)	57(12)	68(14)	43(10)	-5(12)	15(9)	14(10)
C(9)	71(14)	48(12)	68(13)	8(12)	-7(12)	8(11)
O(9)	49(8)	70(10)	91(10)	11(8)	-16(8)	-22(8)
O(19)	32(10)	150(24)	61(11)	0	0	-3(14)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

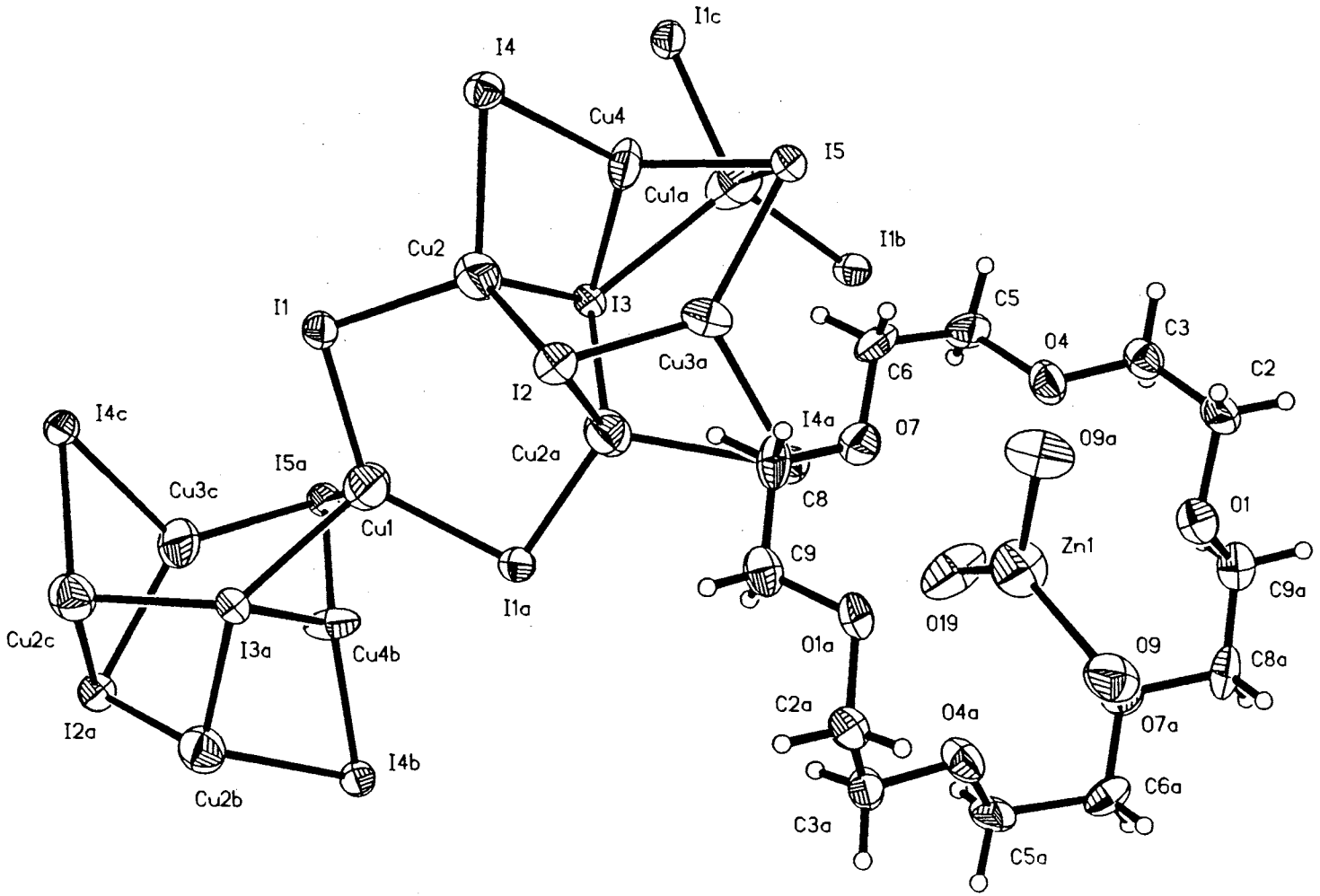


Figure 43. Projection View of $[Zn(18\text{-Crown-6})]Cu_5I_7.3H_2O$ (**XX**)

TABLE 87

CRYSTAL DATA FOR

[Zn(18-Crown-6)]Cu_5I_7 .$3H_2O$ (**XX**)

Formula	$C_{12}H_{30}Cu_5I_7O_9Zn$
Space group	Pbcm
A	10.881(9) Å
B	14.722(11) Å
C	22.16(2) Å
V	3706(5) $Å^3$
Z	4
Mw	1589.7 g mol^{-1}
Density (calc.)	2.849 Mg cm^{-3}
$\mu(MoK_\alpha)$	9.318 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	2880
Collected Reflections	6709
Independent Reflections	5508
Observed Reflections ($F > 4.0\ \sigma$)	1601
Number of parameters	171
Final R indices	R = 6.69 %, R_w = 7.57 %
R indices (all data)	R = 25.88 %, R_w = 15.20 %
GOF	1.31

TABLE 88

POSITIONAL PARAMETERS FOR

[Zn(18-Crown-6)]Cu_5I_7 .$3H_2O$ (**XX**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	1.0206(2)	0.5051(1)	0.1489(1)
I(2)	1.3542(2)	0.3968(1)	0.2500
I(3)	0.9822(2)	0.2565(1)	0.2500
I(4)	1.2292(1)	0.2520(1)	0.0941(1)
I(5)	1.3268(2)	0.0745(1)	0.2500
Cu(1)	0.9543(7)	0.5640(4)	0.2500
Cu(2)	1.1507(4)	0.3635(2)	0.1837(2)
Cu(3)	1.2786(12)	0.2322(6)	0.2061(4)
Cu(4)	1.1677(8)	0.1719(5)	0.1886(3)
Zn(1)	1.7270(6)	0.2500	0.5000
O(1)	1.7602(14)	0.0951(9)	0.5480(7)
C(2)	1.787(3	0.0198(15)	0.5064(9)
H(2A)	1.7956	-0.0367	0.5267
H(2B)	1.8633	0.0320	0.4868
C(3)	1.686(2)	0.0146(13)	0.4617(10)
H(3A)	1.6090	0.0025	0.4806
H(3B)	1.7015	-0.0327	0.4341
O(4)	1.683(2)	0.1036(9)	0.4335(7)
C(5)	1.597(3)	0.1094(15)	0.3856(10)
H(5A)	1.5140	0.1149	0.3994
H(5B)	1.6031	0.0562	0.3618
C(6)	1.636(2)	0.199(2)	0.3507(9)
H(6A)	1.5793	0.2104	0.3199
H(6B)	1.7166	0.1910	0.3345
O(7)	1.6360(15)	0.2730(10)	0.3897(7)
C(8)	1.676(2)	0.3563(15)	0.3614(10)
H(8A)	1.6190	0.3711	0.3311
H(8B	1.7558	0.3480	0.3446
C(9)	1.680(2)	0.430(2)	0.4045(10)
H(9A)	1.5988	0.4410	0.4187
H(9B)	1.7104	0.4843	0.3870
O(9)	1.903(2)	0.2886(12)	0.5608(8)
O(19)	1.504(2)	0.2500	0.5000

TABLE 89

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

[Zn(18-Crown-6)]Cu_5I_7 .$3H_2O$ (**XX**)

I(1)-Cu(1)	2.599(4)	Cu(1)-Cu(4^{iii})	2.510(10)
I(1)-Cu(2)	2.646(5)	Cu(1)-Cu(4^{iv})	2.510(10)
I(2)-Cu(2)	2.739(5)	Cu(2)-Cu(3)	2.438(11)
I(2)-Cu(3)	2.754(9)	Cu(2)-Cu(4)	2.830(9)
I(2)-Cu(2^{i})	2.739(5)	Cu(3)-Cu(4^{i})	2.861(12)
I(2)-Cu(3^{i})	2.754(9)	Cu(4)-Cu(1^{ii})	2.510(10)
I(3)-Cu(2)	2.864(5)	Cu(4)-Cu(3^{i})	2.861(12)
I(3)-Cu(4)	2.766(8)	Cu(4)-Cu(4^{i})	2.84(14)
I(3)-Cu(1^{ii})	2.918(7)	Zn(1)-O(9)	2.44(2)
I(3)-Cu(2^{i})	2.864(5)	Zn(1)-O(19)	2.43(3)
I(3)-Cu(4^{i})	2.766(8)	Zn(1)-O(9^{v})	2.44(2
I(4)-Cu(2)	2.780(5)	O(1)-C(2)	1.50(3)
I(4)-Cu(3)	2.666(9)	O(1)-C(9^{v})	1.45(3)
I(4)-Cu(4)	2.576(8)	C(2)-C(3)	1.52(4)
I(5)-Cu(3)	2.588(9)	C(3)-O(4)	1.46(2)
I(5)-Cu(4)	2.659(8)	O(4)-C(5)	1.45(3)
I(5)-Cu(1^{ii})	3.062(9)	C(5)-C(6)	1.60(3)
I(5)-Cu(3^{i})	2.588(9)	C(6)-O(7)	1.42(3)
I(5)-Cu(4^{i})	2.659(8)	O(7)-C(8)	1.46(3)
Cu(1)-Cu(1^{ii})	2.599(4)	C(8)-C(9)	1.47(3)
Cu(1)-Cu(3^{i})	2.918(7)	C(9)-O(1^{v})	1.45(3)
Cu(1)-I(5^{ii})	3.062(9)		
Cu(1)-I(1)-Cu(2)	97.9(2)	Cu(3)-I(5)-Cu(1^{ii})	81.0(3)
Cu(2)-I(2)-Cu(3)	52.7(3)	Cu(4)-I(5)-Cu(1^{ii})	51.5(2)
Cu(2)-I(2)-Cu(2^{i})	68.2(2)	Cu(3)-I(5)-Cu(3^{i})	46.2(4)
Cu(3)-I(2)-Cu(2^{i})	78.9(3)	Cu(4)-I(5)-Cu(3^{i})	66.1(3)
Cu(2)-I(2)-Cu(3^{i})	78.9(3)	Cu(1^{ii})-I(5)-Cu(3^{i})	81.0(3)
Cu(3)-I(2)-Cu(3^{i})	43.3(4)	Cu(3)-I(5)-Cu(4^{i})	66.1(3)
Cu(2^{i})-I(2)-Cu(3^{i})	52.7(3)	Cu(4)-I(5)-Cu(4^{i})	64.6(3)
Cu(2)-I(3)-Cu(4)	60.3(2)	Cu(1^{ii})-I(5)-Cu(4^{i})	51.5(2)
Cu(2)-I(3)-Cu(1^{ii})	112.5(2)	Cu(3^{i})-I(5)-Cu(4^{i})	34.4(3)
Cu(4)-I(3)-Cu(1^{ii})	52.3(2)	O(9)-Zn(1)-O(19)	141.5(4)
Cu(2)-I(3)-Cu(2^{i})	64.9(2)	O(9)-Zn(1)-O(9v)	76.9(9)
Cu(4)-I(3)-Cu(2^{i})	93.2(2)	O(19)-Zn(1)-O(9^{v})	141.5(4)
Cu(1^{ii})-I(3)-Cu(2^{i})	112.5(2)	C(2)-O(1)-C(9^{v})	115(2)
Cu(2)-I(3)-Cu(4^{i})	93.2(2)	O(1)-C(2)-C(3)	109(2)
Cu(4)-I(3)-Cu(4^{i})	61.8(3)	C(2)-C(3)-O(4)	106(2)
Cu(1^{ii})-I(3)-Cu(4^{i})	52.3(2)	C(3)-O(4)-C(5)	114(2)

TABLE 89 (Continued)

$Cu(2^{i})$-I(3)-$Cu(4^{i})$	60.3(2)	O(4)-C(5)-C(6)	105(2)
Cu(2)-I(4)-Cu(3)	53.1(2)	C(5)-C(6)-O(7)	108(2)
Cu(2)-I(4)-Cu(4)	63.7(2)	C(6)-O(7)-C(8)	111(2)
Cu(3)-I(4)-Cu(4)	34.4(3)	O(7)-C(8)-C(9)	109(2)
Cu(3)-I(5)-Cu(4)	34.4(3)	C(8)-C(9)-$O(1^{v})$	111(2)

Symmetry operations:

^{i} = x, y, 0.5-z
^{ii} = 2-x, y+0.5, 0.25
^{iii} = 2-x, y+0.5, 0.5-z
^{iv} = 2-x, y+0.5, z
^{v} = x, 0.5-y, 1-z

TABLE 90

ANISOTROPIC THERMAL PARAMETERS FOR

[Zn(18-Crown-6)]Cu_5I_7 .$3H_2O$ (**XX**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	64(1)	54(1)	55(1)	5(1)	7(1)	6(1)
I(2)	50(2)	67(1)	63(1)	-11(1)	0	0
I(3)	45(1)	41(1)	56(1)	0(1)	0	0
I(4)	53(1)	57(1)	52(1)	-3(1)	9(1)	-1(1)
I(5)	56(1)	49(1)	54(1)	9(1)	0	0
Cu(1)	175(7)	121(5)	84(4)	67(5)	0	0
Cu(2)	98(3)	82(2)	101(3)	14(2)	-6(2)	0(2)
Cu(3)	182(10)	84(5)	87(5)	42(6)	-8(6)	22(4)
Cu(4)	84(5)	102(5)	64(4)	36(5)	19(4)	38(4)
Zn(1)	96(4)	97(4)	108(4)	0	0	1(3)
O(1)	52(10)	44(8)	66(10)	-13(7)	6(9)	9(7)
C(2)	92(20)	37(12)	61(16)	6(13)	6(15)	4(11)
C(3)	59(16)	42(12)	58(15)	-1(11)	12(13)	6(11)
O(4)	74(12)	38(8)	74(11)	0(8)	-17(10)	5(7)
C(5)	79(19)	55(13)	55(14)	-18(14)	-20(15)	-17(12)
C(6)	66(17)	88(16)	30(11)	5(14)	-6(12)	-5(12)
O(7)	61(11)	64(10)	57(9)	2(8)	-5(8)	1(8)
C(8)	50(15)	67(15)	62(15)	7(13)	15(13)	34(13)
C(9)	43(15)	57(13)	73(17)	9(12)	6(13)	13(13)
O(9)	59(12)	84(12)	109(14)	23(10)	-23(11)	-30(10)
O(19)	44(16)	204(35)	68(15)	0	0	-16(19)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

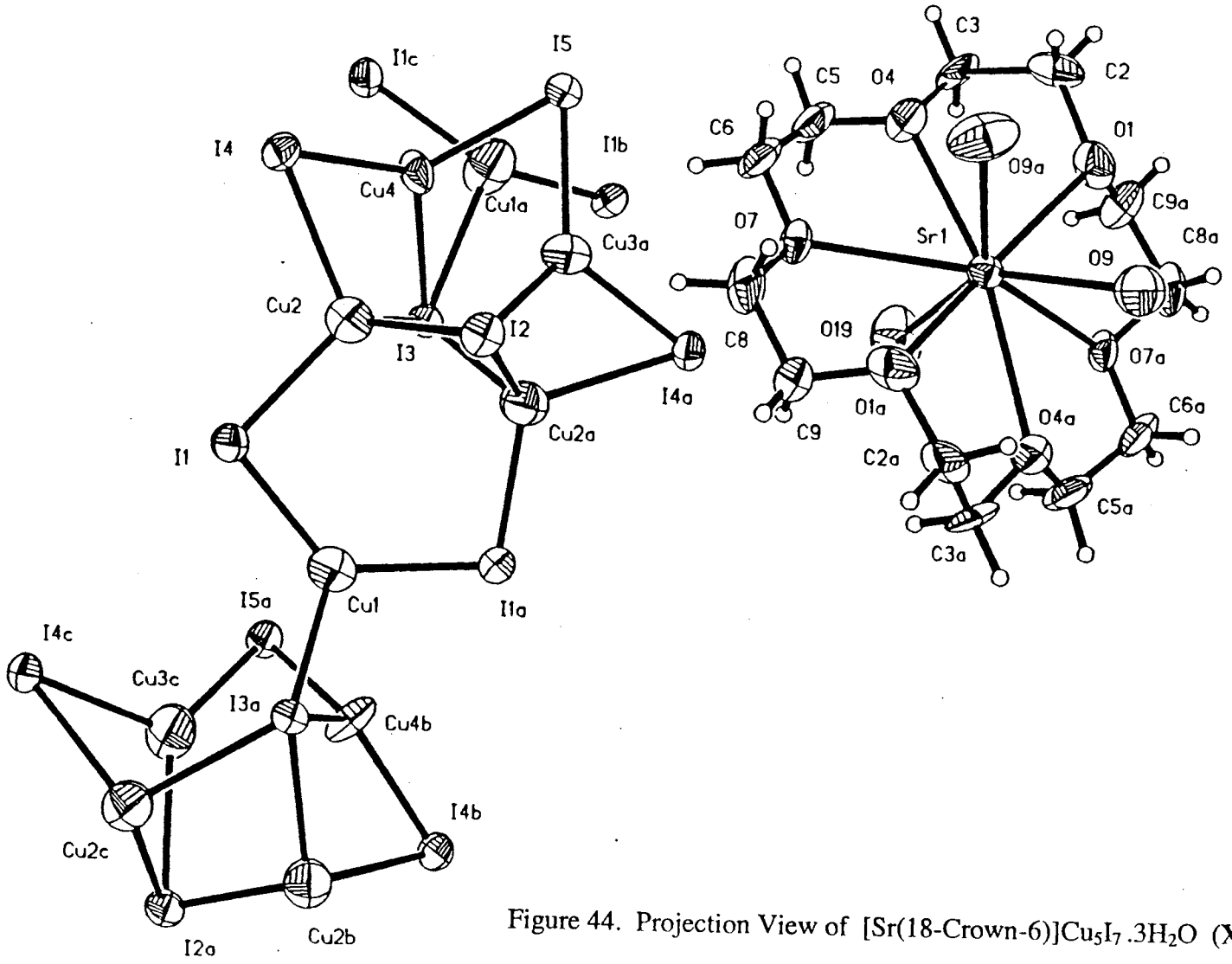


Figure 44. Projection View of $[Sr(18\text{-Crown-6})]Cu_5I_7 .3H_2O$ **(XXI)**

TABLE 91

CRYSTAL DATA FOR

[Sr(18-Crown-6)]Cu_5I_7 .$3H_2O$ (**XXI**)

Formula	$C_{12}H_{30}Cu_5I_7O_9Sr$
Space group	Pbcm
a	10.969(7) Å
b	14.708(9) Å
c	23.03(2) Å
V	3716(5) $Å^3$
Z	4
Mw	1612.0 g mol^{-1}
Density (Srlc.)	2.882 Mg m^{-3}
$\mu(MoK_\alpha)$	10.083 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	2912
Collected Reflections	6766
Independent Reflections	5545
Observed Reflections ($F > 4.0\ \sigma$)	1403
Number of parameters	171
Final R indices	$R = 6.84\ \%$, $R_w = 7.16\ \%$
R indices (all data)	$R = 23.68\ \%$, $R_w = 12.60\ \%$
GOF	1.47

TABLE 92

POSITIONAL PARAMETERS FOR

[Sr(18-Crown-6)]Cu_5I_7 .$3H_2O$ (**XXI**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	1.0180(2)	0.5025(1)	0.1497(1)
I(2)	1.3525(2)	0.3989(2)	0.2500
I(3)	0.9869(2)	0.2550(2)	0.2500
I(4)	1.2327(2)	0.2538(1)	0.0953(1)
I(5)	1.3288(3)	0.0776(2)	0.2500
Cu(1)	0.9560(8)	0.5646(5)	0.2500
Cu(2)	1.1509(4)	0.3645(3)	0.1843(2)
Cu(3)	1.2812(12)	0.2355(7)	0.2060(5)
Cu(4)	1.1698(8)	0.1735(7)	0.1901(3)
Sr(1)	1.7307(3)	0.2500	0.5000
O(1)	1.758(2)	0.0865(11)	0.5488(10)
C(2)	1.774(3)	0.0119(15)	0.5036(14)
H(2A)	1.7813	-0.0470	0.5213
H(2B)	1.8476	0.0235	0.4821
C(3)	1.676(3)	0.014(2)	0.4566(14)
H(3A)	1.6002	0.0127	0.4771
H(3B)	1.6794	-0.0347	0.4291
O(4)	1.686(2)	0.1043(12)	0.4293(10)
C(5)	1.611(3)	0.119(2)	0.3814(15)
H(5A)	1.5321	0.1302	0.3982
H(5B)	1.6058	0.0647	0.3580
C(6)	1.642(3)	0.204(2)	0.3489(12)
H(6A)	1.5835	0.2165	0.3187
H(6B)	1.7189	0.1912	0.3312
O(7)	1.6429(15)	0.2751(11)	0.3876(7)
C(8)	1.677(3)	0.364(2)	0.3592(14)
H(8A)	1.6378	0.3759	0.3228
H(8B	1.7631	0.3561	0.3521
C(9)	1.674(3)	0.434(2)	0.4062(14)
H(9A)	1.5917	0.4358	0.4205
H(9B)	1.6951	0.4920	0.3898
O(9)	1.916(2)	0.288(2)	0.5623(11)
O(19)	1.491(3)	0.2500	0.5000

TABLE 93

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

[Sr(18-Crown-6)]Cu_5I_7 .$3H_2O$ (**XXI**)

I(1)-Cu(1)	2.575(5)	Cu(2)-Cu(2^{i})	3.026(10)
I(1)-Cu(2)	2.622(5)	Cu(3)-Cu(4^{i})	2.837(14)
I(2)-Cu(2)	2.727(6)	Cu(4)-Cu(1^{ii})	2.525(11)
I(2)-Cu(3)	2.723(11)	Cu(4)-Cu(3^{i})	2.837(14)
I(2)-Cu(2^{i})	2.727(6)	Cu(4)-Cu(4^{i})	2.76(2)
I(2)-Cu(3^{i})	2.723(11)	Sr(1)-O(1)	2.67(2)
I(3)-Cu(2)	2.850(6)	Sr(1)-O(4)	2.74(2)
I(3)-Cu(4)	2.714(9)	Sr(1)-O(7)	2.79(2)
I(3)-Cu(1^{ii})	2.869(8)	Sr(1)-O(9)	2.55(2)
I(3)-Cu(2^{i})	2.850(6)	Sr(1)-O(19)	2.63(3)
I(3)-Cu(4^{i})	2.714(9)	Sr(1)-O(1^{vi})	2.67(2)
I(4)-Cu(2)	2.768(6)	Sr(1)-O(4^{vi})	2.74(2)
I(4)-Cu(3)	2.618(12)	Sr(1)-O(7^{vi})	2.79(2)
I(4)-Cu(4)	2.577(9)	Sr(1)-O(9^{vi})	2.55(2)
I(5)-Cu(3)	2.587(11)	O(1)-C(2)	1.52(3)
I(5)-Cu(4)	2.633(9)	O(1)-C(9^{vi})	1.42(4)
I(5)-Cu(3^{i})	2.587(11)	C(2)-C(3)	1.52(4)
I(5)-Cu(4^{i})	2.633(9)	C(3)-O(4)	1.47(4)
Cu(1)-I(1^{ii})	2.575(5)	O(4)-C(5)	1.39(4)
Cu(1)-I(3^{iii})	2.869(8)	C(5)-C(6)	1.50(4)
Cu(1)-Cu(4^{iv})	2.525(11)	C(6)-O(7)	1.37(4)
Cu(1)-Cu(4^{v})	2.525(11)	O(7)-C(8)	1.51(4)
Cu(2)-Cu(3)	2.428(12)	C(8)-C(9)	1.50(4)
Cu(2)-Cu(4)	2.821(11)	C(9)-O(1^{vi})	1.42(4)
Cu(1)-I(1)-Cu(2)	98.6(2)	O(1)-Sr(1)-O(1^{vi})	166.9(9)
Cu(1)-I(2)-Cu(2)	52.9(3)	O(4)-Sr(1)-O(1^{vi})	118.4(6)
Cu(2)-I(2)-Cu(2^{i})	67.4(2)	O(7)-Sr(1)-O(1^{vi})	61.9(6)
Cu(3)-I(2)-Cu(2^{i})	79.1(3)	O(9)-Sr(1)-O(1^{vi})	87.1(7)
Cu(2)-I(2)-Cu(3^{i})	79.1(3)	O(19)-Sr(1)-O(1^{vi})	96.5(5)
Cu(3)-I(2)-Cu(3^{i})	43.7(5)	O(1)-Sr(1)-O(4^{vi})	118.4(6)
Cu(2^{i})-I(2)-Cu(3^{i})	52.9(3)	O(4)-Sr(1)-O(4^{vi})	159.3(9)
Cu(2)-I(3)-Cu(4)	60.9(2)	O(7)-Sr(1)-O(4^{vi})	112.8(6)
Cu(2)-I(3)-Cu(1^{ii})	114.5(2)	O(9)-Sr(1)-O(4^{vi})	68.8(7)
Cu(4)-I(3)-Cu(1^{ii})	53.7(2)	O(19)-Sr(1)-O(4^{vi})	79.7(4)
Cu(2)-I(3)-Cu(2^{i})	64.1(2)	O(1^{vi})-Sr(1)-O(4^{vi})	64.3(6)
Cu(4)-I(3)-Cu(2^{i})	93.0(2)	O(1)-Sr(1)-O(7^{vi})	62.0(6)
Cu(1^{ii})-I(3)-Cu(2^{i})	114.5(2)	O(4)-Sr(1)-O(7^{vi})	112.8(6)
Cu(2)-I(3)-Cu(4^{i})	93.0(2)	O(7)-Sr(1)-O(7^{vi})	139.5(7)

TABLE 93 (Continued)

Cu(4)-I(3)-Cu(4^{i})	61.1(4)	O(9)-Sr(1)-O(7^{vi})	77.5(7)
Cu(1^{ii})-I(3)-Cu(4^{i})	53.7(2)	O(19)-Sr(1)-O(7^{vi})	69.8(3)
Cu(2^{i})-I(3)-Cu(4^{i})	60.9(2)	O(1^{vi})-Sr(1)-O(7^{vi})	123.3(6)
Cu(2)-I(4)-Cu(3)	53.5(3)	O(4^{vi})-Sr(1)-O(7^{vi})	59.2(6)
Cu(2)-I(4)-Cu(4)	63.6(2)	O(1)-Sr(1)-O(9^{vi})	87.1(7)
Cu(3)-I(4)-Cu(4)	35.1(3)	O(4)-Sr(1)-O(9^{vi})	68.8(7)
Cu(3)-I(5)-Cu(4)	34.9(3)	O(7)-Sr(1)-O(9^{vi})	77.5(7)
Cu(3)-I(5)-Cu(3^{i})	46.1(5)	O(9)-Sr(1)-O(9^{vi})	74.1(11)
Cu(4)-I(5)-Cu(3^{i})	65.8(3)	O(19)-Sr(1)-O(9^{vi})	143.0(5)
Cu(3)-I(5)-Cu(4^{i})	65.8(3)	O(1^{vi})-Sr(1)-O(9^{vi})	82.5(7)
Cu(4)-I(5)-Cu(4^{i})	63.2(4)	O(4^{vi})-Sr(1)-O(9^{vi})	130.4(7)
Cu(3^{i})-I(5)-Cu(4^{i})	34.9(3)	O(7^{vi})-Sr(1)-O(9^{vi})	140.3(7)
O(1)-Sr(1)-O(4)	64.3(6)	C(2)-O(1)-C(9^{vi})	115(2)
O(1)-Sr(1)-O(7)	123.3(6)	O(1)-C(2)-C(3)	113(2)
O(4)-Sr(1)-O(7)	59.2(6)	C(2)-C(3)-O(4)	106(2)
O(1)-Sr(1)-O(9)	82.5(7)	C(3)-O(4)-C(5)	116(2)
O(4)-Sr(1)-O(9)	130.4(7)	O(4)-C(5)-C(6)	113(3)
O(7)-Sr(1)-O(9)	140.3(7)	C(5)-C(6)-O(7)	108(2)
O(1)-Sr(1)-O(19)	96.5(5)	C(6)-O(7)-C(8)	112(2)
O(4)-Sr(1)-O(19)	79.7(4)	O(7)-C(8)-C(9)	106(2)
O(7)-Sr(1)-O(19)	69.8(3)	C(8)-C(9)-O(1^{vi})	111(3)
O(9)-Sr(1)-O(19)	143.0(5)		

Symmetry operations:

^{i} = x, y, 0.5-z
^{ii} = 2-x. y-0.5, 0.25
^{iii} = 2-x, y+0.5, 0.25
^{iv} = 2-x, y+0.5, 0.5-z
^{v} = 2-x, y+0.5, z
^{vi} = x, 0.5-y, 1-z

TABLE 94

ANISOTROPIC THERMAL PARAMETERS FOR

[Sr(18-Crown-6)]Cu_5I_7 .$3H_2O$ (**XXI**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	74(1)	62(1)	56(1)	5(1)	7(1)	6(1)
I(2)	59(2)	66(2)	69(2)	-14(1)	0	0
I(3)	49(1)	49(1)	58(1)	-2(1)	0	0
I(4)	62(1)	66(1)	51(1)	-1(1)	10(1)	-1(1)
I(5)	67(2)	57(2)	59(2)	13(1)	0	0
Cu(1)	188(8)	104(5)	100(5)	47(6)	0	0
Cu(2)	103(3)	91(3)	97(4)	14(3)	-8(3)	-2(3)
Cu(3)	173(10)	93(7)	102(7)	49(7)	4(8)	14(6)
Cu(4)	86(5)	112(7)	56(5)	40(5)	24(5)	38(5)
Sr(1)	41(2)	44(2)	51(2)	0	0	-1(2)
O(1)	103(17)	46(12)	86(18)	-3(11)	-19(15)	24(11)
C(2)	91(21)	25(13)	111(26)	5(14)	24(23)	8(20)
C(3)	89(23)	77(22)	65(22)	-5(20)	-20(19)	-52(19)
O(4)	92(15)	66(13)	51(14)	-11(12)	1(13)	-3(11)
C(5)	120(28)	72(20)	52(22)	-4(22)	-11(24)	-31(19)
C(6)	91(23)	101(24)	40(18)	5(20)	7(19)	-29(20)
O(7)	59(11)	76(13)	31(10)	-6(10)	3(9)	10(9)
C(8)	95(24)	116(26)	40(21)	-1(22)	8(19)	31(20)
C(9)	103(27)	91(23)	47(21)	26(22)	-6(20)	-5(20)
O(9)	77(15)	124(19)	136(21)	19(14)	-44(16)	-45(16)
O(19)	70(21)	214(45)	119(28)	0	0	18(32)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

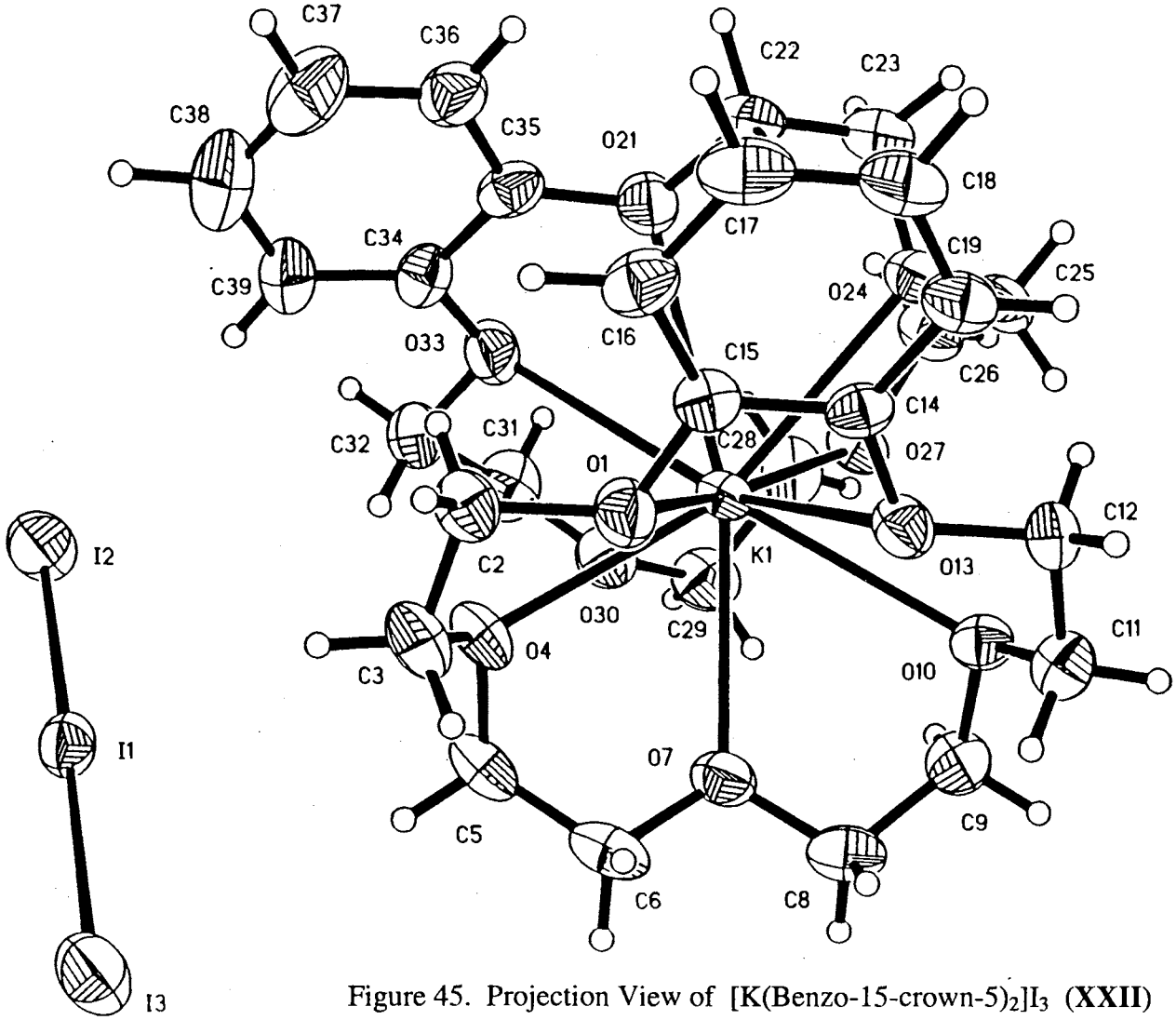


Figure 45. Projection View of $[K(Benzo\text{-}15\text{-}crown\text{-}5)_2]I_3$ (**XXII**)

TABLE 95

CRYSTAL DATA FOR

$[K(Benzo\text{-}15\text{-}crown\text{-}5)_2]I_3$ (**XXII**)

Formula	$C_{28}H_{40}I_3KO_{10}$
Space group	P1bar
a	11.362(3) Å
b	13.732(3) Å
c	13.955(4) Å
α	74.940(0)°
β	66.370(0)°
γ	80.030(0)°
V	1920.5(12) $Å^3$
Z	2
Mw	956.4 g $mole^{-1}$
Density (calc.)	1.654 Mg m^{-3}
$\mu(MoK_\alpha)$	2.594 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	932
Collected Reflections	12695
Independent Reflections	11136
Observed Reflections ($F > 4\ \sigma$)	3692
Number of parameters	380
Final R indices	R = 5.82 %, R_w = 7.23 %
R indices (all data)	R = 17.39 %, R_w = 15.14 %
GOF	1.61

TABLE 96

POSITIONAL PARAMETERS FOR

$[K(Benzo\text{-}15\text{-}crown\text{-}5)_2]I_3$ (**XXII**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.2403(1)	0.7544(1)	0.7501(1)
I(2)	0.0624(1)	0.5918(1)	0.8363(1)
I(3)	0.4205(1)	0.9145(1)	0.6670(1)
K(1)	0.3400(2)	0.6956(1)	0.2367(1)
O(1)	0.2875(6)	0.9184(4)	0.2439(5)
C(2)	0.2145(9)	0.9287(6)	0.3538(7)
H(2A)	0.1395	0.8911	0.3837
H(2B)	0.1878	0.9984	0.3571
C(3)	0.3032(11)	0.8828(7)	0.4160(8)
H(3A)	0.2620	0.8889	0.4893
H(3B)	0.3798	0.9188	0.3836
O(4)	0.3379(6)	0.7763(4)	0.4087(5)
C(5)	0.4528(10)	0.7342(7)	0.4318(8)
H(5A)	0.4475	0.6625	0.4582
H(5B)	0.4554	0.7627	0.4868
C(6)	0.5760(10)	0.7504(7)	0.3340(9)
H(6A)	0.5763	0.8210	0.3007
H(6B)	0.6506	0.7311	0.3528
O(7)	0.5790(6)	0.6922(4)	0.2590(5)
C(8)	0.6966(9)	0.6969(7)	0.1666(9)
H(8A)	0.7669	0.6636	0.1873
H(8B	0.7137	0.7664	0.1344
C(9)	0.6822(9)	0.6482(7)	0.0853(8)
H(9A)	0.6626	0.5793	0.1185
H(9B)	0.7621	0.6480	0.0249
O(10)	0.5810(5)	0.7006(4)	0.0465(4)
C(11)	0.6182(8)	0.7912(6)	-0.0337(7)
H(11A)	0.6762	0.7736	-0.1000
H(11B)	0.6617	0.8310	-0.0128
C(12)	0.4976(8)	0.8522(6)	-0.0466(7)
H(12A)	0.4507	0.8116	-0.0635
H(12B)	0.5199	0.9116	-0.1027
O(13)	0.4214(5)	0.8809(4)	0.0547(4)
C(14)	0.3056(7)	0.9414(6)	0.0634(7)
C(15)	0.2328(8)	0.9623(5)	0.1641(7)
C(16)	0.1136(8)	1.0232(6)	0.1850(8)
H(16A)	0.0648	1.0388	0.2541

TABLE 96 (Continued)

C(17)	0.0743(10)	1.0622(7)	0.0947(10)
H(17A)	-0.0053	1.1035	0.1054
C(18)	0.1466(10)	1.0406(7)	-0.0043(9)
H(18A)	0.1160	1.0674	-0.0616
C(19)	0.2616(9)	0.9799(6)	-0.0218(8)
H(19A)	0.3108	0.9643	-0.0909
O(21)	0.0570(6)	0.7102(5)	0.2738(5)
C(22)	0.0359(8)	0.7563(6)	0.1742(7)
H(22A)	0.0711	0.8211	0.1445
H(22B)	-0.0544	0.7652	0.1869
C(23)	0.1083(8)	0.6861(7)	0.0972(8)
H(23A)	0.0762	0.6204	0.1292
H(23B)	0.0949	0.7105	0.0310
O(24)	0.2441(5)	0.6788(4)	0.0790(4)
C(25)	0.3155(9)	0.5930(7)	0.0314(7)
H(25A)	0.2811	0.5839	-0.0180
H(25B)	0.4038	0.6081	-0.0079
C(26)	0.3139(9)	0.4953(7)	0.1135(8)
H(26A)	0.2256	0.4838	0.1582
H(26B)	0.3517	0.4389	0.0796
O(27)	0.3803(5)	0.5042(4)	0.1801(5)
C(28)	0.3804(10)	0.4137(6)	0.2611(8)
H(28A)	0.2941	0.3941	0.3013
H(28B	0.4313	0.3597	0.2275
C(29)	0.4350(10)	0.4348(7)	0.3375(9)
H(29A)	0.4441	0.3735	0.3869
H(29B)	0.5191	0.4586	0.2958
O(30)	0.3558(6)	0.5115(4)	0.3961(5)
C(31)	0.2447(10)	0.4744(7)	0.4866(8)
H(31A)	0.2018	0.4339	0.4659
H(31B)	0.2706	0.4327	0.5428
C(32)	0.1493(10)	0.5614(7)	0.5276(7)
H(32A)	0.0750	0.5380	0.5890
H(32B)	0.1919	0.6039	0.5464
O(33)	0.1116(6)	0.6170(5)	0.4382(5)
C(34)	0.0132(9)	0.6953(6)	0.4587(7)
C(35)	-0.0172(8)	0.7473(6)	0.3662(8)
C(36)	-0.1158(9)	0.8254(7)	0.3762(8)
H(36A)	-0.1370	0.8592	0.3150
C(37)	-0.1817(11)	0.8537(8)	0.4742(11)
H(37A)	-0.2480	0.9083	0.4800
C(38)	-0.1546(13)	0.8022(9)	0.5667(10)
H(38A)	-0.2045	0.8194	0.6349
C(39)	-0.0504(10)	0.7247(7)	0.5554(8)
H(39A)	-0.0253	0.6934	0.6151

TABLE 97

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[K(Benzo\text{-}15\text{-}crown\text{-}5)_2]I_3$ (**XXII**)

I(1)-I(2)	2.956(1)	C(14)-C(15)	1.392(12)
I(1)-I(3)	2.949(1)	C(14)-C(19)	1.415(15)
K(1)-O(1)	3.034(6)	C(15)-C(16)	1.427(11)
K(1)-O(4)	2.885(8)	C(16)-C(17)	1.45(2)
K(1)-O(7)	2.846(8)	C(17)-C(18)	1.38(2)
K(1)-O(10)	2.948(5)	C(18)-C(19)	1.391(13)
K(1)-O(13)	3.058(5)	O(21)-C(22)	1.465(12)
K(1)-O(21)	3.023(7)	O(21)-C(35)	1.398(12)
K(1)-O(24)	2.890(8)	C(22)-C(23)	1.522(14)
K(1)-O(27)	2.849(6)	C(23)-O(24)	1.449(11)
K(1)-O(30)	2.935(6)	O(24)-C(25)	1.459(11)
K(1)-O(33)	3.058(5)	C(25)-C(26)	1.518(12)
O(1)-C(2)	1.453(11)	C(26)-O(27)	1.450(15)
O(1)-C(15)	1.437(12)	O(27)-C(28)	1.446(10)
C(2)-C(3)	1.54(2)	C(28)-C(29)	1.54(2)
C(3)-O(4)	1.467(11)	C(29)-O(30)	1.455(12)
O(4)-C(5)	1.456(14)	O(30)-C(31)	1.435(10)
C(5)-C(6)	1.513(13)	C(31)-C(32)	1.529(13)
C(6)-O(7)	1.461(15)	C(32)-O(33)	1.464(12)
O(7)-C(8)	1.434(10)	O(33)-C(34)	1.405(10)
C(8)-C(9)	1.53(2)	C(34)-C(35)	1.446(15)
C(9)-O(10)	1.464(12)	C(34)-C(39)	1.380(14)
O(10)-C(11)	1.435(9)	C(35)-C(36)	1.400(12)
C(11)-C(12)	1.528(13)	C(36)-C(37)	1.39(2)
C(12)-O(13)	1.446(10)	C(37)-C(38)	1.42(2)
O(13)-C(14)	1.408(9)	C(38)-C(39)	1.436(15)
I(2)-I(1)-I(3)	178.8(1)	O(1)-C(2)-C(3)	106.5(7)
O(1)-K(1)-O(4)	56.1(2)	C(2)-C(3)-O(4)	108.5(10)
O(1)-K(1)-O(7)	90.0(2)	C(3)-O(4)-C(5)	113.4(9)
O(4)-K(1)-O(7)	62.2(2)	O(4)-C(5)-C(6)	113.0(9)
O(1)-K(1)-O(10)	100.4(1)	C(5)-C(6)-O(7)	109.1(9)
O(4)-K(1)-O(10)	117.3(2)	C(6)-O(7)-C(8)	113.4(8)
O(7)-K(1)-O(10)	60.7(2)	O(7)-C(8)-C(9)	109.4(9)
O(1)-K(1)-O(13)	50.6(2)	C(8)-C(9)-O(10)	113.0(7)
O(4)-K(1)-O(13)	98.9(2)	C(9)-O(10)-C(11)	114.2(6)
O(7)-K(1)-O(13)	87.5(2)	O(10)-C(11)-C(12)	109.0(6)
O(10)-K(1)-O(13)	55.6(1)	C(11)-C(12)-O(13)	106.2(8)
O(1)-K(1)-O(21)	83.6(2)	C(12)-O(13)-C(14)	117.9(7)

TABLE 97 (Continued)

O(4)-K(1)-O(21)	102.6(2)	O(13)-C(14)-C(15)	115.5(8)
O(7)-K(1)-O(21)	164.4(2)	O(1)-C(15)-C(14)	124.3(7)
O(10)-K(1)-O(21)	134.5(2)	O(13)-C(14)-C(19)	124.3(7)
O(13)-K(1)-O(21)	99.3(2)	C(15)-C(14)-C(19)	120.2(7)
O(1)-K(1)-O(24)	103.9(2)	O(1)-C(15)-C(14)	114.8(7)
O(4)-K(1)-O(24)	154.5(2)	O(1)-C(15)-C(16)	123.3(8)
O(7)-K(1)-O(24)	139.5(2)	C(14)-C(15)-C(16)	121.9(10)
O(10)-K(1)-O(24)	79.3(2)	C(15)-C(16)-C(17)	115.7(9)
O(13)-K(1)-O(24)	73.8(2)	C(16)-C(17)-C(18)	121.9(9)
O(21)-K(1)-O(24)	56.1(2)	C(17)-C(18)-C(19)	121.1(12)
O(1)-K(1)-O(27)	165.6(2)	C(14)-C(19)-C(18)	119.2(9)
O(4)-K(1)-O(27)	138.3(2)	C(22)-O(21)-C(35)	119.4(7)
O(7)-K(1)-O(27)	98.0(2)	O(21)-C(22)-C(23)	106.5(7)
O(10)-K(1)-O(27)	73.6(2)	C(22)-C(23)-O(24)	108.8(9)
O(13)-K(1)-O(27)	117.5(2)	C(23)-O(24)-C(25)	112.6(8)
O(21)-K(1)-O(27)	91.4(2)	O(24)-C(25)-C(26)	113.3(7)
O(24)-K(1)-O(27)	62.4(2)	C(25)-C(26)-O(27)	110.3(8)
O(1)-K(1)-O(30)	133.1(2)	C(26)-O(27)-C(28)	112.9(7)
O(4)-K(1)-O(30)	77.7(2)	O(27)-C(28)-C(29)	109.3(8)
O(7)-K(1)-O(30)	73.9(2)	C(28)-C(29)-O(30)	112.6(9)
O(10)-K(1)-O(30)	108.5(2)	C(29)-O(30)-C(31)	114.0(7)
O(13)-K(1)-O(30)	160.5(2)	O(30)-C(31)-C(32)	111.3(7)
O(21)-K(1)-O(30)	100.2(2)	C(31)-C(32)-O(33)	105.6(8)
O(24)-K(1)-O(30)	117.0(2)	C(32)-O(33)-C(34)	117.0(7)
O(27)-K(1)-O(30)	61.1(2)	O(33)-C(34)-C(35)	113.6(8)
O(1)-K(1)-O(33)	98.1(2)	O(33)-C(34)-C(39)	125.8(9)
O(4)-K(1)-O(33)	71.9(2)	C(35)-C(34)-C(39)	120.6(8)
O(7)-K(1)-O(33)	117.3(2)	O(21)-C(35)-C(34)	113.9(7)
O(10)-K(1)-O(33)	161.4(2)	O(21)-C(35)-C(36)	126.6(10)
O(13)-K(1)-O(33)	141.8(2)	C(34)-C(35)-C(36)	119.5(9)
O(21)-K(1)-O(33)	50.1(2)	C(35)-C(36)-C(37)	119.9(11)
O(24)-K(1)-O(33)	98.4(2)	C(36)-C(37)-C(38)	121.3(10)
O(27)-K(1)-O(33)	89.0(2)	C(37)-C(38)-C(39)	118.6(11)
O(30)-K(1)-O(33)	55.8(2)	C(34)-C(39)-C(38)	119.8(11)
C(2)-O(1)-C(15)	119.3(6)		

TABLE 98

ANISOTROPIC THERMAL PARAMETERS FOR

$[K(Benzo\text{-}15\text{-}crown\text{-}5)_2]I_3$ (**XXII**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	67(1)	75(1)	53(1)	-2(1)	-19(1)	-13(1)
I(2)	107(1)	113(1)	81(1)	-39(1)	-32(1)	-12(1)
I(3)	131(1)	120(1)	78(1)	-52(1)	-32(1)	-20(1)
K(1)	55(1)	52(1)	58(1)	-3(1)	-30(1)	-15(1)
O(1)	70(4)	77(4)	61(4)	11(3)	-27(3)	-23(3)
C(2)	83(7)	54(5)	70(6)	0(5)	-32(5)	-22(5)
C(3)	115(9)	78(7)	75(7)	-12(6)	-45(7)	-32(5)
O(4)	100(5)	65(4)	68(4)	-6(3)	-46(4)	-26(3)
C(5)	109(9)	89(7)	75(7)	-7(6)	-63(7)	-19(6)
C(6)	94(8)	75(6)	110(9)	-3(6)	-70(7)	-29(6)
O(7)	67(4)	74(4)	80(5)	-9(3)	-36(4)	-25(3)
C(8)	67(7)	75(6)	108(9)	2(5)	-51(7)	-16(6)
C(9)	67(6)	66(6)	79(7)	10(5)	-31(5)	-19(5)
O(10)	56(3)	54(3)	72(4)	-1(3)	-27(3)	-16(3)
C(11)	67(6)	56(5)	71(6)	-2(5)	-19(5)	-17(5)
C(12)	69(6)	60(5)	49(5)	-4(4)	-18(4)	-16(4)
O(13)	68(4)	65(3)	59(4)	5(3)	-31(3)	-16(3)
C(14)	44(5)	48(5)	66(6)	1(4)	-25(5)	-5(4)
C(15)	57(5)	43(5)	62(6)	-2(4)	-25(5)	-3(4)
C(16)	58(6)	63(6)	90(7)	7(5)	-26(5)	-24(5)
C(17)	71(7)	72(7)	125(10)	11(5)	-57(7)	-14(7)
C(18)	78(7)	74(6)	95(9)	-1(6)	-55(7)	-5(6)
C(19)	68(6)	61(5)	74(7)	-4(5)	-40(5)	-5(5)
O(21)	70(4)	102(5)	70(5)	27(4)	-37(4)	-28(4)
C(22)	56(5)	69(5)	82(7)	3(4)	-46(5)	-20(5)
C(23)	65(6)	76(6)	93(8)	-5(5)	-46(6)	-17(5)
O(24)	62(4)	65(4)	69(4)	1(3)	-34(3)	-22(3)
C(25)	79(7)	85(7)	74(7)	3(5)	-41(5)	-39(6)
C(26)	84(7)	66(6)	91(7)	7(5)	-47(6)	-35(5)
O(27)	77(4)	56(3)	73(4)	-5(3)	-42(3)	-14(3)
C(28)	99(8)	55(6)	74(7)	0(5)	-30(6)	-8(5)
C(29)	91(8)	72(6)	94(8)	13(6)	-52(7)	-5(6)
O(30)	83(4)	68(4)	71(5)	-2(3)	-35(4)	-10(3)
C(31)	100(8)	73(7)	76(7)	-2(6)	-32(7)	4(6)
C(32)	84(7)	99(7)	52(6)	-14(6)	-23(5)	-2(5)
O(33)	81(4)	88(4)	55(4)	7(4)	-30(3)	-18(3)
C(34)	63(6)	57(5)	62(6)	-6(5)	-12(5)	-17(5)

TABLE 98 (Continued)

C(35)	48(5)	59(5)	84(7)	-9(4)	-19(5)	-23(5)
C(36)	61(6)	72(6)	87(7)	2(5)	-26(5)	-30(5)
C(37)	87(8)	71(7)	136(12)	11(6)	-17(8)	-45(8)
C(38)	128(11)	93(9)	84(9)	-8(8)	-4(8)	-37(7)
C(39)	94(8)	78(6)	56(6)	-16(6)	-13(6)	-17(5)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

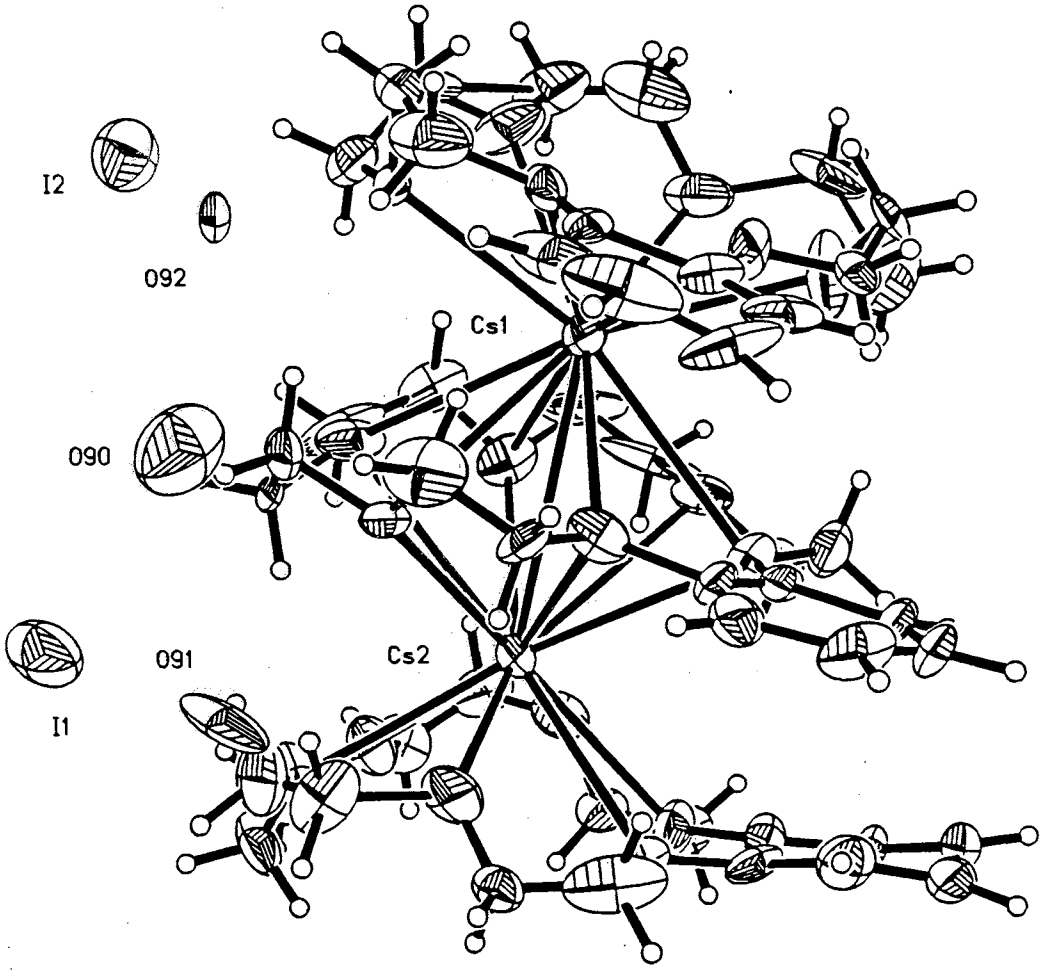


Figure 46. Projection View of $[Cs_2(Benzo\text{-}18\text{-}crown\text{-}6)_3]I_2.3H_2O$ **(XXIII)**

TABLE 99

CRYSTAL DATA FOR

$[Cs(Benzo\text{-}18\text{-}crown\text{-}6)]_2I_2.3H_2O$ (**XXIII**)

Formula	$C_{48}H_{78}Cs_2I_2O_{21}$
Space group	Cc
A	23.216(3) Å
B	18.247(2) Å
C	14.177(2) Å
β	98.490(10)°
V	5943.6(13) $Å^3$
Z	4
Mw	1510.7 g mol^{-1}
Density (calc.)	1.688 Mg m^{-3}
$\mu(MoK_\alpha)$	2.336 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	3000
Collected Reflections	9808
Independent Reflections	9253
Observed Reflections ($F > 5.0\sigma$)	4268
Number of parameters	648
Final R indices	$R = 6.53$ %, $R_w = 7.48$ %
R indices (all data)	$R = 12.53$ %, $R_w = 10.21$ %
GOF	1.66

TABLE 100

POSITIONAL PARAMETERS FOR

$[Cs(Benzo\text{-}18\text{-}crown\text{-}6)]_2I_2.3H_2O$ (**XXIII**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	0.2621(1)	0.3235(2)	0.6720(2)
I(2)	0.5157(2)	0.3314(2)	0.7818(3)
Cs(1)	0.4800	0.3002(1)	0.2644
Cs(2)	0.2962(1)	0.3012(1)	0.1908(1)
O(1)	0.5545(6)	0.1467(6)	0.3176(10)
C(2)	0.5586(7)	0.1063(10)	0.2398(12)
H(2A)	0.5214	0.0955	0.2030
H(2B)	0.5792	0.0611	0.2544
C(3)	0.5899(8)	0.1441(14)	0.174(2)
H(3A)	0.6090	0.1173	0.1288
H(3B)	0.6186	0.1706	0.2161
O(4)	0.5487(9)	0.2054(9)	0.1327(10)
C(5)	0.5559(17)	0.213(2)	0.044(2)
H(5A)	0.5211	0.2286	0.0044
H(5B)	0.5743	0.1739	0.0143
C(6)	0.5998(8)	0.283(2)	0.0747(15)
H(6A)	0.6321	0.2637	0.1175
H(6B)	0.6149	0.3022	0.0202
O(7)	0.5673(7)	0.3575(11)	0.1219(12)
C(8)	0.6148(13)	0.401(2)	0.181(2)
H(8A)	0.6391	0.4191	0.1375
H(8B)	0.6383	0.3725	0.2296
C(9)	0.6004(15)	0.455(2)	0.231(2)
H(9A)	0.5673	0.4735	0.1894
H(9B)	0.6269	0.4940	0.2515
O(10)	0.5740(8)	0.4288(11)	0.2950(14)
C(11)	0.5824(9)	0.472(2)	0.365(2)
H(11A)	0.5773	0.5196	0.3346
H(11B)	0.6203	0.4701	0.4023
C(12)	0.5336(10)	0.4529(15)	0.427(2)
H(12A)	0.4967	0.4666	0.3921
H(12B)	0.5401	0.4820	0.4842
O(13)	0.5301(4)	0.3780(8)	0.4569(8)
C(14)	0.5817(8)	0.3575(11)	0.514(2)
H(14A)	0.5947	0.3894	0.5672
H(14B)	0.6116	0.3529	0.4748

TABLE 100 (Continued)

C(15)	0.5631(12)	0.280(2)	0.547(2)
H(15A)	0.5266	0.2825	0.5709
H(15B)	0.5919	0.2571	0.5936
O(16)	0.5561(5)	0.2281(8)	0.4651(7)
C(17)	0.5457(6)	0.1616(11)	0.4848(11)
C(18)	0.5398(7)	0.1146(11)	0.3919(13)
C(19)	0.5334(7)	0.0386(12)	0.402(2)
H(19A)	0.5352	0.0069	0.3488
C(20)	0.5151(11)	0.0101(15)	0.481(2)
H(20A)	0.5030	-0.0402	0.4821
C(21)	0.5266(12)	0.051(2)	0.562(3)
H(21A)	0.5174	0.0257	0.6175
C(22)	0.5287(9)	0.122(3)	0.554(2)
H(22A)	0.5291	0.1451	0.6146
O(31)	0.3898(10)	0.1683(12)	0.1364(13)
C(32)	0.402(2)	0.179(2)	0.029(2)
H(32A)	0.3848	0.1389	-0.0085
H(32B)	0.4438	0.1755	0.0311
C(33)	0.3799(13)	0.2398(15)	-0.009(2)
H(33A)	0.3382	0.2435	-0.0154
H(33B)	0.3917	0.2437	-0.0707
O(34)	0.4044(9)	0.2986(12)	0.0440(15)
C(35)	0.4084(13)	0.3794(29)	0.014(3)
H(35A)	0.3692	0.3888	-0.0153
H(35B)	0.4325	0.3793	-0.0351
C(36)	0.4262(14)	0.430(2)	0.063(4)
H(36A)	0.4239	0.4755	0.0297
H(36B)	0.4654	0.4225	0.0945
O(37)	0.3871(12)	0.4343(13)	0.128(2)
C(38)	0.414(2)	0.491(2)	0.186(2)
H(38A)	0.4105	0.5325	0.1432
H(38B)	0.4544	0.4867	0.2133
C(39)	0.378(2)	0.503(2)	0.259(4)
H(39A)	0.3381	0.5051	0.2316
H(39B)	0.3886	0.5484	0.2913
O(40)	0.3822(10)	0.4352(11)	0.322(2)
C(41)	0.3466(12)	0.423(2)	0.400(2)
H(41A)	0.3087	0.4045	0.3756
H(41B)	0.3417	0.4674	0.4350
C(42)	0.3775(13)	0.366(2)	0.467(2)
H(42A)	0.3623	0.3609	0.5261
H(42B)	0.4184	0.3765	0.4796
O(43)	0.3609(9)	0.3037(11)	0.4031(14)
C(44)	0.398(2)	0.246(3)	0.450(2)
H(44A)	0.3961	0.2460	0.5172

TABLE 100 (Continued)

H(44B)	0.4377	0.2516	0.4413
C(45)	0.3816(10)	0.166(2)	0.411(2)
H(45A)	0.3405	0.1603	0.4118
H(45B)	0.4019	0.1257	0.4451
O(46)	0.3895(9)	0.1729(13)	0.3202(15)
C(47)	0.3866(12)	0.094(2)	0.271(3)
C(48)	0.3894(12)	0.1103(15)	0.173(3)
C(49)	0.3904(14)	0.036(2)	0.126(4)
H(49A)	0.3901	0.0368	0.0583
C(50)	0.3880(15)	-0.028(2)	0.168(3)
H(50A)	0.3908	-0.0744	0.1359
C(51)	0.382(2)	-0.0249(15)	0.255(3)
H(51A)	0.3764	-0.0704	0.2865
C(52)	0.3781(13)	0.038(2)	0.313(2)
H(52A)	0.3713	0.0365	0.3779
O(61)	0.2202(6)	0.2356(7)	-0.0057(9)
C(62)	0.2094(8)	0.2813(9)	-0.0903(10)
H(62A)	0.1747	0.2651	-0.1302
H(62B)	0.2408	0.2786	-0.1273
C(63)	0.2009(8)	0.3474(11)	-0.0629(13)
H(63A)	0.1664	0.3500	-0.0330
H(63B)	0.1932	0.3750	-0.1210
O(64)	0.2486(6)	0.3853(9)	-0.0080(10)
C(65)	0.2428(11)	0.4585(12)	0.010(2)
H(65A)	0.2333	0.4845	-0.0493
H(65B)	0.2803	0.4754	0.0394
C(66)	0.2025(11)	0.4721(11)	0.0677(2)
H(66A)	0.1639	0.4627	0.0350
H(66B)	0.2055	0.5235	0.0821
O(67)	0.2091(7)	0.4281(9)	0.1579(12)
C(68)	0.1696(14)	0.453(2)	0.209(3)
H(68A)	0.1330	0.4669	0.1724
H(68B)	0.1826	0.4939	0.2492
C(69)	0.1548(9)	0.387(2)	0.2930(15)
H(69A)	0.1281	0.3541	0.2562
H(69B)	0.1359	0.4051	0.3442
O(70)	0.2009(8)	0.3550(11)	0.3198(11)
C(71)	0.2103(15)	0.314(2)	0.406(2)
H(71A)	0.1784	0.3235	0.4407
H(71B)	0.2442	0.3384	0.4396
C(72)	0.2166(13)	0.2526(14)	0.4036(15)
H(72A)	0.2476	0.2445	0.4553
H(72B)	0.1826	0.2311	0.4236
O(73)	0.2358(8)	0.2011(11)	0.3298(12)
C(74)	0.1980(8)	0.1550(13)	0.2955(14)

TABLE 100 (Continued)

H(74A)	0.1618	0.1768	0.2674
H(74B)	0.1902	0.1246	0.3474
C(75)	0.2174(12)	0.106(2)	0.228(2)
H(75A)	0.1922	0.0655	0.2102
H(75B)	0.2559	0.0889	0.2507
O(76)	0.2210(5)	0.1528(7)	0.1353(9)
C(77)	0.2320(8)	0.1154(10)	0.055(2)
C(78)	0.2370(9)	0.1548(15)	-0.006(2)
C(79)	0.2426(7)	0.1321(9)	-0.1142(10)
H(79A)	0.2386	0.1687	-0.1634
C(80)	0.2648(9)	0.0620(15)	-0.119(2)
H(80A)	0.2780	0.0454	-0.1764
C(81)	0.2546(9)	0.0223(15)	-0.057(2)
H(81A)	0.2557	-0.0296	-0.0684
C(82)	0.2547(5)	0.0473(5)	0.0483(8)
H(82A)	0.2616	0.0161	0.1032
O(90)	0.3936	0.2171	0.7365
O(91)	0.2691	0.1662	0.6416
O(92)	0.5074	0.1761	0.8343

TABLE 101

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

$[Cs(Benzo\text{-}18\text{-}crown\text{-}6)]_2I_2.3H_2O$ (**XXIII**)

Cs(1)-O(1)	3.320(11)	O(31)-C(32)	1.61(4)
Cs(1)-O(4)	3.15(2)	O(31)-C(48)	1.18(4)
Cs(1)-O(7)	3.24(2)	C(32)-C(33)	1.30(4)
Cs(1)-O(10)	3.19(2)	C(33)-O(34)	1.38(3)
Cs(1)-O(13)	3.144(12)	O(34)-C(35)	1.54(6)
Cs(1)-O(16)	3.386(11)	C(35)-C(36)	1.19(6)
Cs(1)-O(31)	3.51(2)	C(36)-O(37)	1.38(6)
Cs(1)-O(34)	3.35(2)	O(37)-C(38)	1.42(4)
Cs(1)-O(37)	3.63(2)	C(38)-C(39)	1.44(7)
Cs(1)-O(40)	3.52(2)	C(39)-O(40)	1.52(5)
Cs(1)-O(43)	3.62(2)	O(40)-C(41)	1.50(4)
Cs(1)-O(46)	3.31(2)	C(41)-C(42)	1.52(4)
Cs(2)-O(31)	3.42(2)	C(42)-O(43)	1.47(3)
Cs(2)-O(34)	3.49(2)	O(43)-C(44)	1.46(5)
Cs(2)-O(37)	3.42(3)	C(44)-C(45)	1.58(6)
Cs(2)-O(40)	3.51(2)	C(45)-O(46)	1.33(3)
Cs(2)-O(43)	3.16(2)	O(46)-C(47)	1.59(4)
Cs(2)-O(46)	3.52(2)	C(47)-C(48)	1.44(6)
Cs(2)-O(61)	3.292(12)	C(47)-C(52)	1.22(5)
Cs(2)-O(64)	3.255(15)	C(48)-C(49)	1.51(5)
Cs(2)-O(67)	3.06(2)	C(49)-C(50)	1.32(6)
Cs(2)-O(70)	3.22(2)	C(50)-C(51)	1.27(6)
Cs(2)-O(73)	3.16(2)	C(51)-C(52)	1.41(5)
Cs(2)-O(76)	3.255(12)	O(61)-C(62)	1.45(2)
O(1)-C(2)	1.34(2)	O(61)-C(78)	1.52(3)
O(1)-C(18)	1.30(2)	C(62)-C(63)	1.29(3)
C(2)-C(3)	1.44(3)	C(63)-O(64)	1.43(2)
C(3)-O(4)	1.53(3)	O(64)-C(65)	1.37(3)
O(4)-C(5)	1.29(4	C(65)-C(66)	1.35(4)
C(5)-C(6)	1.65(4)	C(66)-O(67)	1.50(3)
C(6)-O(7)	1.74(4)	O(67)-C(68)	1.33(4)
O(7)-C(8)	1.51(4)	C(68)-C(69)	1.77(5)
C(8)-C(9)	1.29(5)	C(69)-O(70)	1.23(3)
C(9)-O(10)	1.26(4)	O(70)-C(71)	1.42(3)
O(10)-C(11)	1.26(4)	C(71)-C(72)	1.14(4)
C(11)-C(12)	1.58(4)	C(72)-O(73)	1.52(3)
C(12)-O(13)	1.43(3)	O(73)-C(74)	1.26(3)
O(13)-C(14)	1.40(2)	C(74)-C(75)	1.43(4)
C(14)-C(15)	1.58(4)	C(75)-C(76)	1.57(3)
C(15)-O(16)	1.48(3)	C(76)-C(77)	1.38(3)

TABLE 101 (Continued)

O(16)-C(17)	1.28(2)	C(77)-C(78)	1.15(3)
C(17)-C(18)	1.56(2)	C(77)-C(82)	1.36(2)
C(17)-C(22)	1.32(4)	C(78)-C(79)	1.61(3)
C(18)-C(19)	1.41(3)	C(79)-C(80)	1.38(3)
C(19)-C(20)	1.36(4)	C(80)-C(81)	1.19(4)
C(20)-C(21)	1.37(5)	C(81)-C(82)	1.56(3)
C(21)-C(22)	1.30(6)		
O(1)-Cs(1)-O(4)	51.6(4)	O(40)-Cs(2)-O(70)	82.6(5)
O(1)-Cs(1)-O(7)	93.5(4)	O(43)-Cs(2)-O(70)	74.0(5)
O(4)-Cs(1)-O(7)	52.3(5)	O(46)-Cs(2)-O(70)	109.1(5)
O(1)-Cs(1)-O(10)	105.4(4)	O(61)-Cs(2)-O(70)	105.3(4)
O(4)-Cs(1)-O(10)	95.1(5)	O(64)-Cs(2)-O(70)	100.0(4)
O(7)-Cs(1)-O(10)	50.9(5)	O(67)-Cs(2)-O(70)	50.5(4)
O(1)-Cs(1)-O(13)	94.0(3)	O(31)-Cs(2)-O(73)	94.9(5)
O(4)-Cs(1)-O(13)	127.5(4)	O(34)-Cs(2)-O(73)	142.0(5)
O(7)-Cs(1)-O(13)	102.1(4)	O(37)-Cs(2)-O(73)	156.9(5)
O(10)-Cs(1)-O(13)	52.5(4)	O(40)-Cs(2)-O(73)	110.0(6)
O(1)-Cs(1)-O(16)	44.9(3)	O(43)-Cs(2)-O(73)	66.9(5)
O(4)-Cs(1)-O(16)	92.2(4)	O(46)-Cs(2)-O(73)	65.5(5)
O(7)-Cs(1)-O(16)	110.7(3)	O(61)-Cs(2)-O(73)	94.9(4)
O(10)-Cs(1)-O(16)	84.8(4)	O(64)-Cs(2)-O(73)	133.4(4)
O(13)-Cs(1)-O(16)	50.6(3)	O(67)-Cs(2)-O(73)	100.8(5)
O(1)-Cs(1)-O(31)	77.9(4)	O(70)-Cs(2)-O(73)	54.4(5)
O(4)-Cs(1)-O(31)	68.4(5)	O(31)-Cs(2)-O(76)	72.0(4)
O(7)-Cs(1)-O(31)	106.2(5)	O(34)-Cs(2)-O(76)	104.6(4)
O(10)-Cs(1)-O(31)	156.6(5)	O(37)-Cs(2)-O(76)	149.0(5)
O(13)-Cs(1)-O(31)	150.9(4)	O(40)-Cs(2)-O(76)	161.8(5)
O(16)-Cs(1)-O(31)	111.4(4)	O(43)-Cs(2)-O(76)	113.9(4)
O(1)-Cs(1)-O(34)	112.9(4)	O(46)-Cs(2)-O(76)	80.7(4)
O(4)-Cs(1)-O(34)	71.5(5)	O(61)-Cs(2)-O(76)	44.9(3)
O(7)-Cs(1)-O(34)	73.2(5)	O(64)-Cs(2)-O(76)	94.7(3)
O(10)-Cs(1)-O(34)	112.8(5)	O(67)-Cs(2)-O(76)	105.9(4)
O(13)-Cs(1)-O(34)	152.8(5)	O(70)-Cs(2)-O(76)	90.1(4)
O(16)-Cs(1)-O(34)	156.5(5)	O(73)-Cs(2)-O(76)	53.0(4)
O(31)-Cs(1)-O(34)	47.3(5)	C(2)-O(1)-C(18)	118.6(14)
O(1)-Cs(1)-O(37)	159.9(4)	O(1)-C(2)-C(3)	112(2)
O(4)-Cs(1)-O(37)	111.6(5)	C(2)-C(3)-O(4)	104(2)
O(7)-Cs(1)-O(37)	80.0(5)	C(3)-O(4)-C(5)	106(2)
O(10)-Cs(1)-O(37)	85.3(5)	O(4)-C(5)-C(6)	90(2)
O(13)-Cs(1)-O(37)	105.9(5)	C(5)-C(6)-O(7)	115(2)
O(16)-Cs(1)-O(37)	155.0(5)	C(6)-O(7)-C(8)	108(2)
O(31)-Cs(1)-O(37)	85.7(5)	O(7)-C(8)-C(9)	119(3)
O(34)-Cs(1)-O(37)	47.1(5)	C(8)-C(9)-O(10)	107(3)
O(1)-Cs(1)-O(40)	150.3(5)	C(9)-O(10)-C(11)	107(2)

TABLE 101 (Continued)

O(4)-Cs(1)-O(40)	157.1(5)	O(10)-C(11)-C(12)	105(2)
O(7)-Cs(1)-O(40)	113.7(5)	C(11)-C(12)-O(13)	117(2)
O(10)-Cs(1)-O(40)	84.6(5)	C(12)-O(13)-C(14)	110.2(14)
O(13)-Cs(1)-O(40)	69.6(5)	O(13)-C(14)-C(15)	100(2)
O(16)-Cs(1)-O(40)	110.5(5)	C(14)-C(15)-O(16)	110(2)
O(31)-Cs(1)-O(40)	104.1(5)	C(15)-O(16)-C(17)	116(2)
O(34)-Cs(1)-O(40)	87.4(6)	O(16)-C(17)-C(18)	109.5(14)
O(37)-Cs(1)-O(40)	45.6(6)	O(16)-C(17)-C(22)	140(2)
O(1)-Cs(1)-O(43)	107.8(4)	C(18)-C(17)-C(22)	109(2)
O(4)-Cs(1)-O(43)	145.7(5)	O(1)-C(18)-C(17)	116(2)
O(7)-Cs(1)-O(43)	158.6(5)	O(1)-C(18)-C(19)	125(2)
O(10)-Cs(1)-O(43)	118.4(5)	C(17)-C(18)-C(19)	117(2)
O(13)-Cs(1)-O(43)	74.6(4)	C(18)-C(19)-C(20)	121(2)
O(16)-Cs(1)-O(43)	84.0(4)	C(19)-C(20)-C(21)	116(3)
O(31)-Cs(1)-O(43)	81.3(5)	C(20)-C(21)-C(22)	118(4)
O(34)-Cs(1)-O(43)	99.7(5)	C(17)-C(22)-C(21)	129(4)
O(37)-Cs(1)-O(43)	80.6(5)	C(32)-O(31)-C(48)	123(3)
O(40)-Cs(1)-O(43)	45.0(5)	O(31)-C(32)-C(33)	112(3)
O(1)-Cs(1)-O(46)	71.4(4)	C(32)-C(33)-O(34)	109(2)
O(4)-Cs(1)-O(46)	98.7(5)	C(33)-O(34)-C(35)	129(2)
O(7)-Cs(1)-O(46)	148.7(5)	O(34)-C(35)-C(36)	128(4)
O(10)-Cs(1)-O(46)	158.5(5)	C(35)-C(36)-O(37)	103(3)
O(13)-Cs(1)-O(46)	106.0(4)	C(36)-O(37)-C(38)	99(3)
O(16)-Cs(1)-O(46)	78.3(4)	O(37)-C(38)-C(39)	106(3)
O(31)-Cs(1)-O(46)	44.9(5)	C(38)-C(39)-O(40)	108(3)
O(34)-Cs(1)-O(46)	87.3(5)	C(39)-O(40)-C(41)	124(3)
O(37)-Cs(1)-O(46)	104.7(6)	O(40)-C(41)-C(42)	108(2)
O(40)-Cs(1)-O(46)	89.0(5)	C(41)-C(42)-O(43)	95(2)
O(43)-Cs(1)-O(46)	47.1(5)	C(42)-O(43)-C(44)	101(2)
O(31)-Cs(2)-O(34)	47.1(5)	O(43)-C(44)-C(45)	115(2)
O(31)-Cs(2)-O(37)	90.4(6)	C(44)-C(45)-O(46)	101(2)
O(34)-Cs(2)-O(37)	47.8(6)	C(45)-O(46)-C(47)	109(2)
O(31)-Cs(2)-O(40)	106.4(5)	O(46)-C(47)-C(48)	104(2)
O(34)-Cs(2)-O(40)	85.5(6)	O(46)-C(47)-C(52)	124(3)
O(37)-Cs(2)-O(40)	47.1(6)	C(48)-C(47)-C(52)	132(3)
O(31)-Cs(2)-O(43)	89.8(5)	O(31)-C(48)-C(47)	128(3)
O(34)-Cs(2)-O(43)	106.6(5)	O(31)-C(48)-C(49)	128(4)
O(37)-Cs(2)-O(43)	90.8(5)	C(47)-C(48)-C(49)	104(3)
O(40)-Cs(2)-O(43)	48.1(6)	C(48)-C(49)-C(50)	127(4)
O(31)-Cs(2)-O(46)	44.2(5)	C(49)-C(50)-C(51)	114(4)
O(34)-Cs(2)-O(46)	82.0(5)	C(50)-C(51)-C(52)	129(3)
O(37)-Cs(2)-O(46)	104.6(6)	C(47)-C(52)-C(51)	112(4)
O(40)-Cs(2)-O(46)	85.9(5)	C(62)-O(61)-C(78)	124.2(14)
O(43)-Cs(2)-O(46)	48.9(5)	O(61)-C(62)-C(63)	107.7(14)
O(31)-Cs(2)-O(61)	80.3(4)	C(62)-C(63)-O(64)	118(2)

TABLE 101 (Continued)

O(34)-Cs(2)-O(61)	80.4(4)	C(63)-O(64)-C(65)	119(2)
O(37)-Cs(2)-O(61)	108.2(5)	O(64)-C(65)-C(66)	113(2)
O(40)-Cs(2)-O(61)	153.2(5)	C(65)-C(66)-O(67)	115(2)
O(43)-Cs(2)-O(61)	158.5(4)	C(66)-O(67)-C(68)	107(2)
O(46)-Cs(2)-O(61)	114.3(4)	O(67)-C(68)-C(69)	110(2)
O(31)-Cs(2)-O(64)	106.6(4)	C(68)-C(69)-O(70)	107(2)
O(34)-Cs(2)-O(64)	70.9(4)	C(69)-O(70)-C(71)	122(2)
O(37)-Cs(2)-O(64)	65.4(5)	O(70)-C(71)-C(72)	120(2)
O(40)-Cs(2)-O(64)	102.9(5)	C(71)-C(72)-O(73)	133(2)
O(43)-Cs(2)-O(64)	150.5(5)	C(72)-O(73)-C(74)	115(2)
O(46)-Cs(2)-O(64)	150.4(5)	O(73)-C(74)-C(75)	114(2)
O(61)-Cs(2)-O(64)	50.8(3)	C(74)-C(75)-O(76)	107(2)
O(31)-Cs(2)-O(67)	158.3(4)	C(75)-O(76)-C(77)	117(2)
O(34)-Cs(2)-O(67)	115.9(5)	O(76)-C(77)-C(78)	112(2)
O(37)-Cs(2)-O(67)	80.9(5)	O(76)-C(77)-C(82)	129(2)
O(40)-Cs(2)-O(67)	82.3(5)	C(78)-C(77)-C(82)	116(2)
O(43)-Cs(2)-O(67)	110.1(5)	O(61)-C(78)-C(77)	123(2)
O(46)-Cs(2)-O(67)	157.5(5)	O(61)-C(78)-C(79)	108(2)
O(61)-Cs(2)-O(67)	83.5(4)	C(77)-C(78)-C(79)	126(2)
O(64)-Cs(2)-O(67)	51.7(4)	C(78)-C(79)-C(80)	112(2)
O(31)-Cs(2)-O(70)	148.8(5)	C(79)-C(80)-C(81)	114(2)
O(34)-Cs(2)-O(70)	163.0(5)	C(80)-C(81)-C(82)	124(2)
O(37)-Cs(2)-O(70)	115.7(6)	C(77)-C(82)-C(81)	113.0(15)

TABLE 102

ANISOTROPIC THERMAL PARAMETERS FOR

$[Cs(Benzo\text{-}18\text{-}crown\text{-}6)]_2I_2.3H_2O$ (**XXIII**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	95(2)	217(4)	89(2)	-14(2)	30(2)	10(2)
I(2)	115(2)	84(1)	117(2)	4(2)	20(2)	-7(2)
Cs(1)	54(1)	56(1)	61(1)	1(1)	2(1)	-7(1)
Cs(2)	44(1)	61(1)	63(1)	6(1)	11(1)	-9(1)
O(1)	94(9)	18(6)	98(10)	-2(6)	25(8)	-16(6)
C(2)	38(8)	53(10)	71(11)	13(7)	4(7)	-1(9)
C(3)	40(9)	129(21)	126(18)	43(11)	9(10)	-64(16)
O(4)	195(19)	94(12)	54(8)	83(12)	15(10)	1(8)
C(5)	178(34)	106(25)	129(28)	1(23)	-17(24)	-30(20)
C(6)	35(8)	256(37)	68(12)	21(16)	26(8)	31(18)
O(7)	61(9)	156(17)	106(13)	-18(10)	-4(9)	4(11)
C(8)	87(19)	213(42)	135(30)	-18(24)	51(20)	86(28)
C(9)	129(26)	182(38)	83(20)	-105(27)	29(17)	13(20)
O(10)	121(14)	124(16)	98(12)	-83(12)	7(11)	2(11)
C(11)	44(11)	169(31)	125(23)	-33(15)	-18(13)	49(22)
C(12)	80(14)	101(21)	97(16)	7(13)	-19(12)	-42(15)
O(13)	42(6)	74(9)	65(7)	15(6)	-7(5)	-36(6)
C(14)	53(10)	75(14)	110(16)	-4(10)	18(11)	-32(12)
C(15)	79(16)	198(32)	87(18)	-13(19)	0(14)	22(20)
O(16)	46(6)	88(9)	37(6)	11(6)	10(5)	-10(6)
C(17)	27(7)	69(12)	38(8)	4(7)	-14(6)	3(8)
C(18)	46(9)	66(13)	68(11)	-17(9)	-8(8)	17(10)
C(19)	28(8)	50(12)	196(27)	7(8)	-29(12)	25(15)
C(20)	93(18)	78(18)	143(24)	-57(15)	-63(17)	46(17)
O(21)	75(18)	140(33)	250(49)	-5(20)	17(23	131(35)
C(22)	45(12)	318(56)	69(15)	2(23)	3(11)	37(25)
O(31)	91(15)	51(11)	48(10)	6(12)	-17(9)	5(10)
C(32)	108(24)	104(27)	104(27)	-44(20)	48(20)	-62(22)
C(33)	79(18)	58(15)	51(15)	27(14)	19(13)	16(12)
O(34)	46(10)	92(15)	69(12)	1(10)	-7(8)	30(11)
C(35)	15(11)	250(57)	189(47)	31(20)	1(18)	165(43)
C(36)	56(19)	56(17)	311(62)	-36(15)	-26(25)	28(25)
O(37)	95(17)	83(15)	90(14)	-15(13)	-9(12)	11(12)
C(38)	115(25)	58(21)	78(16)	-14(20)	-34(17)	40(16)
C(39)	125(44)	50(15)	252(65)	-15(22)	-105(45)	-18(26)
O(40)	47(9)	51(11)	180(24)	9(9)	-23(12)	4(13)
C(41)	32(15)	251(50)	126(25)	-13(20)	7(15)	-163(32)

TABLE 102 (Continued)

C(42)	68(16)	94(17)	46(9)	7(13)	16(10)	-25(12)
O(43)	37(8)	82(12)	64(10)	-16(8)	5(6)	-11(9)
C(44)	119(30)	234(46)	41(17)	-20(33)	-7(16)	34(23)
C(45)	67(13)	81(16)	44(11)	-34(13)	-6(9)	-13(11)
O(46)	69(13)	74(13)	80(15)	-1(11)	30(11)	34(12)
C(47)	53(13)	41(17)	85(17)	-8(11)	-2(11)	-31(14)
C(48)	36(13)	26(12)	113(27)	-7(10)	12(13)	-20(15)
C(49)	50(15)	101(26)	192(39)	13(16)	-24(18)	-109(28)
C(50)	78(19)	68(19)	128(26)	-13(14)	7(17)	-67(19)
C(51)	91(23)	24(12)	191(55)	0(15)	-35(31)	12(18)
C(52)	58(15)	61(17)	103(19)	12(13)	11(14)	-5(15)
O(61)	92(9)	52(8)	80(9)	12(7)	6(7)	-22(7)
C(62)	75(11)	53(12)	35(7)	3(8)	2(7)	32(7)
C(63)	57(10)	87(15)	50(10)	12(10)	-24(8)	13(10)
O(64)	62(8)	83(11)	95(10)	15(8)	8(7)	33(8)
C(65)	97(17)	56(14)	105(17)	-4(13)	-19(14)	27(12)
C(66)	114(18)	39(11)	120(18)	19(12)	14(15)	35(12)
O(67)	91(11)	83(11)	119(12)	33(9)	26(9)	-4(9)
C(68)	102(21)	84(22)	375(59)	32(18)	20(29)	-14(30)
C(69)	58(12)	199(30)	70(13)	61(17)	1(10)	-42(16)
O(70)	125(14)	138(16)	70(9)	53(12)	41(9)	-10(9)
C(71)	152(27)	131(27)	66(16)	8(20)	38(16)	-17(16)
C(72)	181(27)	71(18)	61(13)	-49(18)	21(15)	24(12)
O(73)	98(11)	189(20)	89(10)	-47(12)	66(9)	-28(12)
C(74)	46(10)	87(17)	63(12)	6(10)	6(9)	-1(11)
C(75)	113(21)	127(24)	143(24)	-49(19)	-38(18)	102(21)
O(76)	53(7)	68(9)	65(7)	-8(6)	2(6)	-10(6)
C(77)	52(10)	33(10)	102(16)	-11(8)	-22(10)	1(10)
C(78)	58(12)	99(20)	83(15)	34(13)	-22(11)	-46(14)
C(79)	64(10)	36(9)	48(8)	10(8)	-2(7)	-14(7)
C(80)	58(12)	97(20)	96(16)	-2(13)	15(12)	-52(14)
C(81)	47(11)	78(19)	159(26)	9(12)	-4(14)	-47(18)
C(82)	83(14)	60(14)	116(18)	-6(11)	8(12)	1(13)
C(90)	171(18)	110(14)	199(19)	13(26)	-25(15)	-18(25)
C(91)	27(8)	330(34)	54(8)	24(13)	2(6)	34(14)
C(92)	45(8)	124(13)	74(10)	16(8)	6(7)	-73(9)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

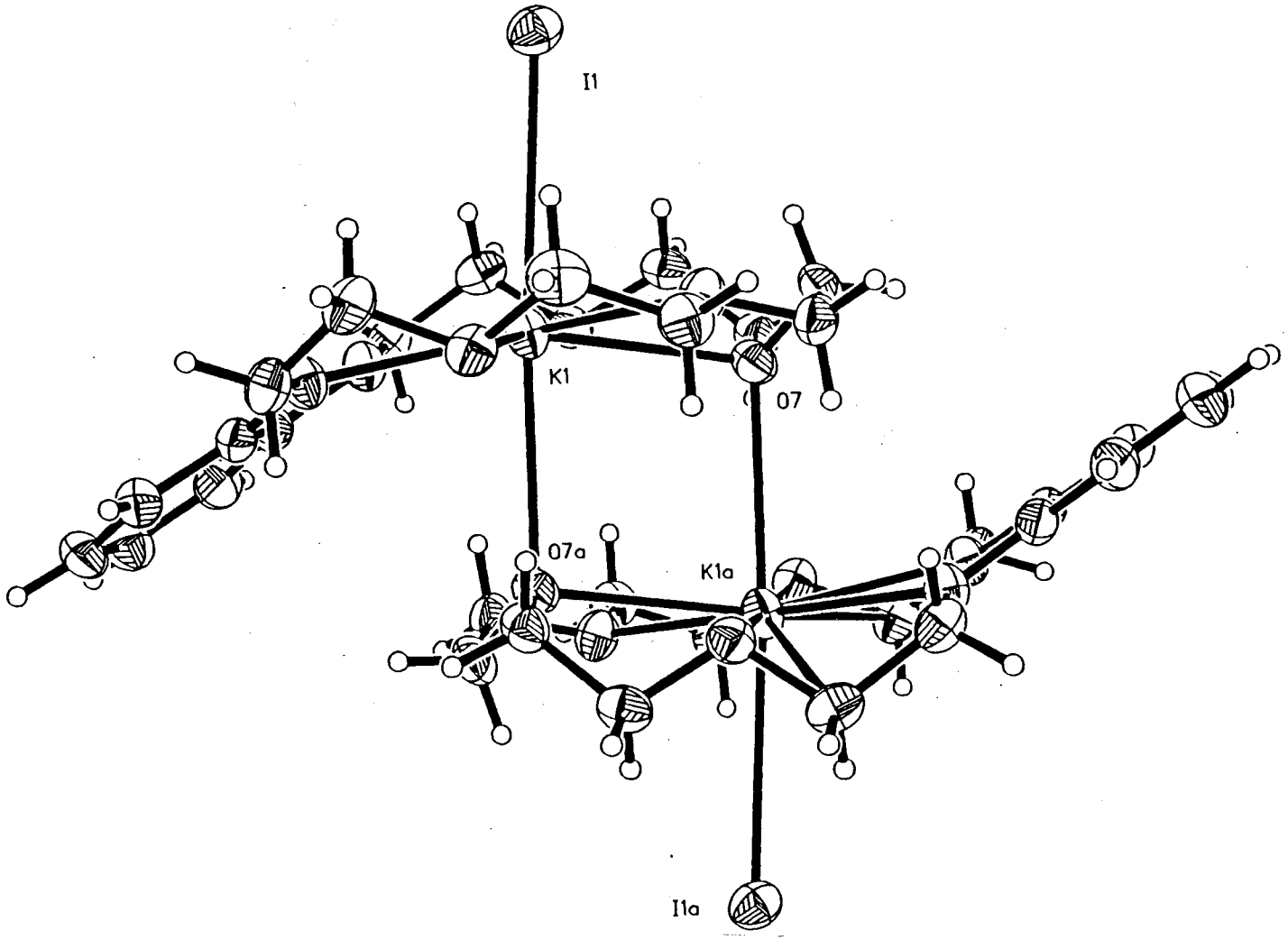


Figure 47. Projection View of [K(Benzo-18-crown-6)]I (**XXIV**)

TABLE 103

CRYSTAL DATA FOR

[K(Benzo-18-crown-6)]I (**XXIV**)

Formula	$C_{16}H_{24}IKO_6$
Space group	P1bar
a	9.793(4) Å
b	10.129(5) Å
c	12.796(5) Å
α	71.83(2)°
β	69.890(10)°
γ	62.73(2)°
V	1040.1(8) $Å^3$
Z	2
Mw	478.4 g $mole^{-1}$
Density (calc.)	1.527 Mg m^{-3}
$\mu(MoK_\alpha)$	1.764 mm^{-1}
$\lambda(MoK_\alpha)$	0.71073 Å
F(000)	480
Collected Reflections	6876
Independent Reflections	5941
Observed Reflections ($F > 4\sigma$)	2991
Number of parameters	218
Final R indices	$R = 3.55$ %, $R_w = 4.46$ %
R indices (all data)	$R = 10.81$ %, $R_w = 7.47$ %
GOF	1.06

TABLE 104

POSITIONAL PARAMETERS FOR

[K(Benzo-18-crown-6)]I (**XXIV**)

ATOM	x(σ(x))	y(σ(y))	z(σ(z))
I(1)	-0.0121(1)	0.2386(1)	0.2386(1)
K(1)	0.0982(1)	0.4101(1)	0.8344(1)
O(1)	0.1211(3)	0.6560(3)	0.6680(2)
C(2)	-0.0245(5)	0.7776(4)	0.6392(3)
H(2A)	-0.0068	0.8132	0.5588
H(2B)	-0.0574	0.8605	0.6759
C(3)	-0.1515(5)	0.7143(5)	0.6820(3)
H(3A)	-0.1134	0.6250	0.6514
H(3B)	-0.2470	0.7858	0.6588
O(4)	-0.1830(3)	0.6752(3)	0.8051(2)
C(5)	-0.3038(5)	0.6148(5)	0.8561(4)
H(5A)	-0.2702	0.5222	0.8311
H(5B)	-0.4005	0.6853	0.8343
C(6)	-0.3278(5)	0.5821(5)	0.9852(4)
H(6A)	-0.4186	0.5570	1.0221
H(6B)	-0.3472	0.6725	1.0075
O(7)	-0.1902(3)	0.4582(3)	1.0233(2)
C(8)	-0.2039(5)	0.3119(5)	1.0560(4)
H(8A)	-0.2125	0.2874	0.9924
H(8B	-0.2973	0.3171	1.1155
C(9)	-0.0576(5)	0.1903(5)	1.0946(3)
H(9A)	-0.0729	0.0980	1.1310
H(9B)	-0.0376	0.2242	1.1479
O(10)	0.0770(3)	0.1660(3)	0.9973(2)
C(11)	0.2208(5)	0.0463(4)	1.0250(4)
H(11A)	0.2038	-0.0446	1.0644
H(11B)	0.2552	0.0761	1.0724
C(12)	0.3479(6)	0.0202(4)	0.9141(4)
H(12A)	0.3062	0.0059	0.8625
H(12B)	0.4411	-0.0682	0.9263
O(13)	0.3874(3)	0.1522(3)	0.8651(2)
C(14)	0.4884(5)	0.1474(5)	0.7511(3)
H(14A)	0.4336	0.1470	0.7018
H(14B)	0.5826	0.0565	0.7515
C(15)	0.5298(5)	0.2846(5)	0.7077(3)
H(15A)	0.6061	0.2767	0.6363
H(15B)	0.5743	0.2916	0.7609

TABLE 104 (Continued)

O(16)	0.3861(3)	0.4187(3)	0.6951(2)
C(17)	0.4019(5)	0.5584(4)	0.6446(3)
C(18)	0.2574(5)	0.6863(4)	0.6318(3)
C(19)	0.2605(6)	0.8318(5)	0.5870(4)
H(19A)	0.1626	0.9177	0.5827
C(20)	0.4024(7)	0.8501(6)	0.5512(4)
H(20A)	0.4036	0.9492	0.5209
C(21)	0.5458(7)	0.7245(7)	0.5583(4)
H(21A)	0.6436	0.7384	0.5307
C(22)	0.5469(5)	0.5763(6)	0.6070(4)
H(22A)	0.6442	0.4902	0.6132

TABLE 105

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR

[K(Benzo-18-crown-6)]I (**XXIV**)

I(1)-K(1)	3.589(2)	O(7)-K(1^{i})	3.107(4)
K(1)-O(1)	2.768(3)	C(8)-C(9)	1.518(6)
K(1)-O(4)	2.871(3)	C(9)-O(10)	1.454(5)
K(1)-O(7)	2.973(3)	O(10)-C(11)	1.445(5)
K(1)-O(10)	2.731(3)	C(11)-C(12)	1.533(6)
K(1)-O(13)	2.888(3)	C(12)-O(13)	1.454(6)
K(1)-O(16)	2.794(3)	O(13)-C(14)	1.455(5)
K(1)-O(7^{i})	3.107(4)	C(14)-C(15)	1.511(7)
O(1)-C(2)	1.468(5)	C(15)-O(16)	1.456(4)
O(1)-C(18)	1.397(6)	O(16)-C(17)	1.416(5)
C(2)-C(3)	1.517(8)	C(17)-C(18)	1.433(5)
C(3)-O(4)	1.457(5)	C(17)-C(22)	1.411(8)
O(4)-C(5)	1.444(6)	C(18)-C(19)	1.415(7)
C(5)-C(6)	1.536(6)	C(19)-C(20)	1.387(10)
C(6)-O(7)	1.465(5)	C(20)-C(21)	1.406(7)
O(7)-C(8)	1.465(6)	C(21)-C(22)	1.432(9)
O(1)-K(1)-O(4)	60.5(1)	O(4)-C(5)-C(6)	108.3(4)
O(1)-K(1)-O(7)	118.5(1)	C(5)-C(6)-O(7)	112.6(3)
O(4)-K(1)-O(7)	61.0(1)	C(6)-O(7)-C(8)	112.7(4)
O(1)-K(1)-O(10)	179.5(1)	O(7)-C(8)-C(9)	109.3(5)
O(4)-K(1)-O(10)	119.8(1)	C(8)-C(9)-O(10)	109.1(3)
O(7)-K(1)-O(10)	61.9(1)	C(9)-O(10)-C(11)	113.1(3)
O(1)-K(1)-O(13)	117.9(1)	O(10)-C(11)-C(12)	107.9(3)
O(4)-K(1)-O(13)	177.3(1)	C(11)-C(12)-O(13)	109.3(4)
O(7)-K(1)-O(13)	119.7(1)	C(12)-O(13)-C(14)	112.9(3)
O(10)-K(1)-O(13)	61.8(1)	O(13)-C(14)-C(15)	109.9(4)
O(1)-K(1)-O(16)	56.9(1)	C(14)-C(15)-O(16)	108.7(4)
O(4)-K(1)-O(16)	117.3(1)	C(15)-O(16)-C(17)	117.5(3)
O(7)-K(1)-O(16)	160.8(1)	O(16)-C(17)-C(18)	115.3(4)
O(10)-K(1)-O(16)	122.9(1)	O(16)-C(17)-C(22)	124.4(3)
O(13)-K(1)-O(16)	61.1(1)	C(18)-C(17)-C(22)	120.3(4)
O(1)-K(1)-O(7^{i})	84.5(1)	O(1)-C(18)-C(17)	115.9(4)
O(4)-K(1)-O(7^{i})	94.0(1)	O(1)-C(18)-C(19)	124.8(3)
O(7)-K(1)-O(7^{i})	82.3(1)	C(17)-C(18)-C(19)	119.3(5)
O(10)-K(1)-O(7^{i})	95.8(1)	C(18)-C(19)-C(20)	120.5(4)
O(13)-K(1)-O(7^{i})	83.5(1)	C(19)-C(20)-C(21)	120.6(6)
O(21)-K(1)-O(7^{i})	78.8(1)	C(20)-C(21)-C(22)	120.5(6)
C(2)-O(1)-C(18)	117.8(3)	C(17)-C(22)-C(21)	118.7(4)

Symmetry operation: ^{i} = -x, 1-y, 2-z

TABLE 106

ANISOTROPIC THERMAL PARAMETERS FOR

[K(Benzo-18-crown-6)]I (**XXIV**)

ATOM	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	83(1)	55(1)	65(1)	-22(1)	-21(1)	-15(1)
K(1)	46(1)	44(1)	61(1)	-16(1)	-12(1)	0(1)
O(1)	53(2)	44(1)	58(2)	-17(1)	-11(1)	-2(1)
C(2)	65(3)	48(2)	50(2)	-12(2)	-19(2)	-4(2)
C(3)	62(3)	54(2)	58(2)	-9(2)	-27(2)	-12(2)
O(4)	51(2)	62(2)	57(2)	-23(1)	-15(1)	-12(1)
C(5)	47(2)	56(2)	75(3)	-14(2)	-19(2)	-20(2)
C(6)	43(2)	59(2)	74(3)	-19(2)	-4(2)	-26(2)
O(7)	55(2)	56(2)	67(2)	-27(1)	-11(1)	-15(1)
C(8)	67(3)	62(3)	72(3)	-42(2)	-6(2)	-9(2)
C(9)	79(3)	62(2)	47(2)	-38(2)	-6(2)	-4(2)
O(10)	64(2)	56(2)	51(1)	-20(1)	-12(1)	-1(1)
C(11)	82(3)	43(2)	64(2)	-26(2)	-24(2)	3(2)
C(12)	76(3)	38(2)	86(3)	-11(2)	-22(2)	-15(2)
O(13)	61(2)	41(1)	56(1)	-14(1)	-11(1)	-11(1)
C(14)	57(3)	51(2)	60(2)	-4(2)	-5(2)	-19(2)
C(15)	49(2)	64(2)	55(2)	-14(2)	0(2)	-19(2)
O(16)	46(1)	50(1)	65(2)	-17(1)	-6(1)	-10(1)
C(17)	62(2)	59(2)	42(2)	-33(2)	-4(2)	-10(2)
C(18)	55(2)	53(2)	44(2)	-24(2)	-6(2)	-9(2)
C(19)	86(3)	53(2)	61(2)	-34(2)	-13(2)	-6(2)
C(20)	108(4)	79(3)	76(3)	-62(3)	-22(3)	1(2)
C(21)	97(4)	116(4)	64(3)	-79(4)	-13(3)	-8(3)
C(22)	68(3)	85(3)	56(2)	-41(3)	-11(2)	-12(2)

The anisotropic displacement exponent takes the form:
$\exp[-2\pi^2(U_{11}h^2a^{*2}+ U_{22}k^2b^{*2}+ U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)] \times 10^3$

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