CORRELATION OF CRYSTALLOGRAPHIC SYMMETRY AND EMISSION IN SOLID STATE ANIONIC COPPER(I) COMPLEXES; LINEAR $[CuX_2]^-$, X=Cl, Br, I

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TABLE OF CONTENTS

LIST OF TABLES

Table Page

Table Page

Table Page

LIST OF FIGURES

CHAPTER I

INTRODUCTION AND BACKGROUND

Early interest in the copper(I) halides of type, $Cu_aX_b(ligand)_x$, ($b \geq a$; X=Cl, Br, I), arose because of their varied colors of visible solid state emission when excited in the ultraviolet. Luminescence of cuprous halides was observed for the first time in 1938 by J. T. Randall.[1,2] Further studies of emission behavior of cuprous halides, however, were not performed until the 1970's. H. D. Hardt et al.[3,4] synthesized many complexes of copper(I) with Lewis bases and reported their emission properties. Ligands used in these studies were simple hetero aromatic and nonaromatic rings, including pyridine, morpholine, piperidine, quinoline, pyrroline and their derivatives.[5-11] Early studies merely reported the color of emission observed for the various complexes without structural characterization of the solid state material. The observation of a change in the color of emission upon cooling was termed "fluorescent thermochromism" and a series of reports left the impression of a moving of the emission wavelength under the influence of lowered temperatures.

$Cu_aX_b(ligand)_c$ complexes can be either ligand-based or anionic complexes, depending on the values of a, b and c. When a is equal to b and c>0, the $Cu_aX_b(ligand)_c$ cluster is neutral and the Cu atom is coordinated to electron pair donor atoms such as N, P, etc. of the ligand. These compounds are called ligand-based complexes. When b>a and c=0, Cu_aX_b is negatively charged species $[Cu_aX_b]^{-(b-a)}$, the complexes are anionic ones, formed by electrostatic force between $[Cu_aX_b]^{-(b-a)}$ anions and cations deriving from the "ligand".

The $(Cu_aX_b(ligand)_x)$ complexes have been the subject of a review.[12]

Their emission has been studied by previous workers in this laboratory.[13] It has been established that the presence or absence of crystallographic symmetry elements influences the wavelength of maximum emission.

Ab Initio studies of a series of ligand-based complexes, Cu_2I_2(ligand)$_4$, both with and without centers of symmetry were performed by Bao and coworkers.[14] These studies established that the excitation and emission transitions were forced to involve different orbitals when crystallographic symmetry made the HOMO to LUMO transition forbidden. A further conclusion was that the HOMO level was halide dominated and the LUMO level was copper dominated and thus excitation involved electron donation from the halide to copper. The imposition of forbiddances upon the orbital system caused excitation from the HOMO to a higher but copper dominated orbital followed by radiative decay to a lower, also copper dominated orbital. Thus, while the excitation wavelength is seen to depend upon the identity of the halide atom, emission in centrosymmetric cases may take place between copper dominated orbitals and therefore be independent of the identity of the halide. Furthermore, emission is of lower energy and occurs at longer wavelengths.

Hu et al.[15] studied ligand-based complex systems of the type $Cu_4I_4(CH_3CN)_2$(ligand)$_2$, where ligand = aniline derivatives. In these complexes, Cu_4I_4 form cubic clusters, with the copper atom being coordinated with N atoms of the ligands. However the presence of a center of symmetry was not possible. This work sought to establish the influence of symmetry elements other than 1 bar. The major conclusions drawn from this investigation were: (i) Complexes with no symmetry, mirror symmetry or 2-fold axis symmetry elements which do not undergo a phase change emit at about the same range (565 - 585 nm) at both room and low (10K) temperatures; (ii) Some complexes with no symmetry or 2-fold axis symmetry undergo a phase change at low temperature and gain two mirror symmetry elements if the substituent on aniline is simple and at *para-* or one *ortho-* position. These complexes emit at lower energy at low temperature than at room temperature; (iii) The HOMO level is dominated by p orbitals of iodine atoms whereas the LUMO orbitals are dominated by contribution from Cu based p orbitals. Metal to ligand charge transfer (MLCT) is not involved; (iv) Emission may be partially correlated with symmetry elements. Further examination of low temperature crystal structures is necessary to substantiate this hypothesis.

Anionic complexes, $[Cu_4X_6]^{-2}$ and $[Cu_2X_4]^{-2}$ were studied by Fields, et al.[16] Their results showed that the λ_{max} of the emission spectrum shifts to longer wavelengths as iodine is replaced by bromine in any particular motif, suggesting that the change to a more electronegative halide may lower the energy level of the emitting state. The presence or absence of a symmetry element passing through copper atoms of the motif appears to influence λ_{max} in the emission spectra of $[Cu_4X_6]^{-2}$ clusters. It was found that a compound involving a symmetry element displayed changed emission (i.e emitting at two different wavelengths). However, no theoretical explanation was given to account for these experimental results.

It has been well established that cuprous halides react with many quaternary halides such as ammonium, phosphonium and arsonium salts to form anionic $[Cu_aX_b]^{-(b-a)}$ complexes. These complexes consist of the quaternary cations and copper(I) halide anions, which are held together by electrostatic forces. These complexes are more stable than the neutral ligand-based copper(I) halide complexes probably due to binding of copper solely to halogen atoms and to ionic lattice interactions.

In $[Cu_aX_b]^{-(b-a)}$ (b>a) complexes, many ratios of b to a are possible, and thus many different motifs. Discrete anionic $[Cu_aX_b]^{-(b-a)}$ complexes have been observed to be mononuclear ($[CuX_3]^{-2}$, $[CuX_4]^{-3}$),[17-21] dinuclear ($[Cu_2X_4]^{-2}$, $[Cu_2X_5]^{-3}$, $[Cu_2X_6]^{-4}$),[22-26] trinuclear ($[Cu_3X_6]^{-3}$),[27-29] tetranuclear ($[Cu_4X_6]^{-2}$),[30-33] pentanuclear ($[Cu_5X_7]^{-2}$),[34,35] hexanuclear ($[Cu_6X_9]^{-3}$, $[Cu_6X_{11}]^{-5}$),[36,37] heptanuclear ($[Cu_7X_{10}]^{-3}$),[38] and octanuclear ($[Cu_8X_{13}]^{-5}$).[32] Polymeric anions such as $[CuX_2]^-$, $[CuX_3]^{-2}$, $[Cu_2X_3]^-$, $[Cu_3X_4]^-$, $[Cu_5X_7]^{-2}$, $[Cu_6X_{11}]^{-5}$ and $[Cu_7X_{10}]^{-3}$ have also been observed.[20,33,37,38,39-45]

Copper atoms have been observed to show three different types of coordination: four-coordinate (tetrahedral), tricoordinate (trigonal planar), and dicoordinate. It has been suggested that cation size might be a key factor for the determination of the copper coordination number.[46-50] Large cations with a low, well-screened positive charge seem to stabilize the formation of discrete anions in the solid state. It has been pointed out that there is an increased tendency towards polymerization of the iodocuprates(I) as compared with the bromo- and chlorocuprates(I).[50]

DICOORDINATE

The dicoordinate species are of two types: discrete monomers, often linear, and X-Cu-X linkages existing as part of infinite chains (Figure 1). The linear dicoordinate complex, $[CuX_2^-][L^+]$, (where L^+ = quaternary ammonium, phosphonium and arsonium cations, etc.) has been a focus of many researchers. Numerous linear dicoordinate monomeric complexes have been reported in the literature (Table 1). They are observed to form with X=Cl, Br and I, but not with X=F, the majority forming with Cl or Br atoms. Only two compounds of this type are known with X=I.[51] This is because CuI_2^- seems more likely to incorporate into a polymeric species.

In a linear dicoordinate compound, a copper atom is bonded to two terminal halides, forming an anionic species $[X\text{-}Cu\text{-}X]^-$ (CuX_2^-), which is

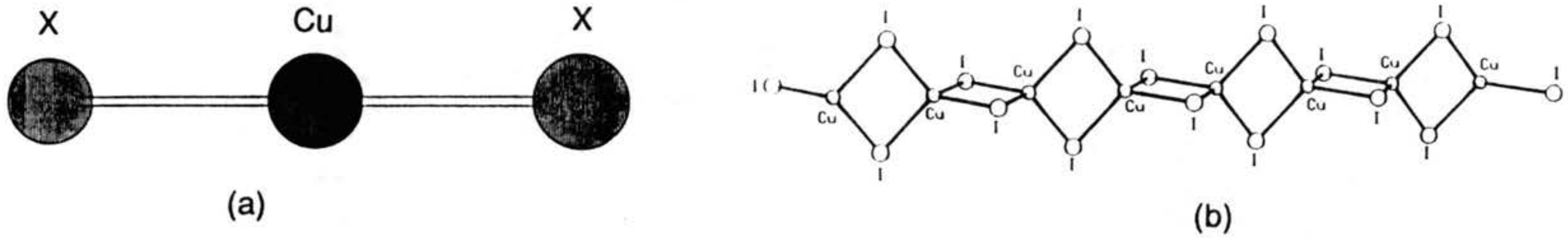


Figure 1. Two Types of $[X\text{-}Cu\text{-}X]^-$: (a) Discrete Monomers and (b) Infinite Chains.

TABLE 1

The Cu-X Bond Distances, X-Cu-X Angles, Non-bonded Interactions And Their Averages in Linear Dicoordinate Anionic Copper(I) Complexes

Compound	Cu-X distance (Å)	X-Cu-X angle(°)	Cu-X average(Å)	X-Cu-X average(°)	Comments	Ref.
Center of symmetry						
X=Cl						
$[Cu(bipy)_2][CuCl_2]_2$	2.091(2)	180				52
$[Cu(tmeda)_2][CuCl_2]$[a]	2.084(4),2.088(4)	180				53
$[N(C_4H_9)_4][CuCl_2]$	2.069(3),2.072(3)	180				54
$[BEDT\text{-}TTF][CuCl_2]$[b]	2.108(1)	180				55
$[BEDT\text{-}TTF]_2[CuCl_2]$	2.084(2)	180				56
$[Cu(2,4,6\text{-}tmpy)_2][CuCl_2]$[c]	2.084(1)	180				57
$[Rb(15\text{-}crown\text{-}5)_2][CuCl_2]$	2.041(7)	180	2.090(2)	180		58
X=Br						
$[N(C_4H_9)_4][CuBr_2]$	2.226(1)	180	2.226(1)	180		54
X=Br,Cl						
$[N(C_4H_9)_4][CuBrCl]$	2.104(17),2.195(6)	180				59
X=I						
$[K(dicyclohexano\text{-}18\text{-}crown\text{-}6)][CuI_2]$	2.394(2)	180				51
$[K(18\text{-}crown\text{-}6)][CuI_2]$	2.383(1)	180	2.388(2)	180		51
2-fold axis symmetry						
X=Cl						
$[N_6P_6(N(CH_3)_2)_{12}CuCl][CuCl_2]$	2.06(1)[d],2.11(1)[d]	179.5(2)				60
$[N(C_3H_7)_4][CuCl_2]$	2.071(2)	178.5(1)	2.152(6)	179.0(2)		61
X=Br						
$[Cu(phen)_2][CuBr_2]$[e]	2.209(2),2.223(2)	180				62
$[N(C_3H_7)_4][CuBr_2]$	2.194(1)	178.4(1)	2.209(2)	179.2(2)		47
Mirror symmetry						
$[N(C_6H_5)(CH_3)_3][CuCl_2]$	2.105(2),2.117(2)	179.63(7)				63

TABLE 1 (Continued)

No symmetry					
X=Cl					
$[(C_6H_5)_2PO(CH)_2NH(C_2H_5)_2][CuCl_2]$	2.086(4),2.095(4)	175.8(2)			64
$[Cu_4(C_{24}H_{20}NPS_2)_3][CuCl_2]$	1.96(1)[d],2.906(1)	177			65
$[Cu(C_{18}H_{15}AsO)_4][CuCl_2]_2$	2.079(2)	178.65(8)			66
$[CuCl(C_{44}H_{60}N_4)][CuCl_2]$	2.066(7),2088(8)	179.0(3)			67
$[CuCl(C_{44}H_{60}N_4)][CuCl_2]\cdot 3C_2H_6O$	2.046(9),2.10(2)	169.5(1)			68
$[P(C_6H_5)_4][MoOS_3(CuCl)_3][CuCl_2]_2$	2.091(2),2.095(2)	178.1(1)			69
$[As(C_6H_5)_4][CuCl_2]$	2.088(2),2.090(2)	176.4(1)			48
$[P(C_6H_5)_4][CuCl_2]$	2.088(2),2.090(2)	174.7(1)			48
[(MeCN)Cu(meso-L)]$[CuCl_2]$[f]	2.096(6),2.083(6)	178.0(3)			70
$[\{(mad)_2Cu\}_2Cl][CuCl_2]$[g]	2.09[h]	177.2[g]			68
$[((C_6H_5)CH_2CO)(C_6H_5)_3P][CuCl_2]$	2.095(8),2.086(9)	175.0(4)			16
$[(C_6H_5)CH_2(C_6H_5)_3P][CuCl_2]$	2.088(3),2.097(3)	175.4(2)			16
$[((C_6H_5)_3P)_2N][CuCl_2]$	2.086(5),2.084(6)	178.9(6)	2.074(5)	177.4(3)	16
X=Br					
[TSeT]$[CuBr_2]$[i]	2.267(2),2.282(3)	153.8(1)			74
$[\{CH_3C(CH_2P(C_6H_5)_2)_3IrP_3\}_3Cu_5Br_4][CuBr_2]$	2.221(10)	178.4(3)			71
$[P(C_6H_5)_4][CuBr_2]$	2.211(2),2.216(2)	173.62(7)			48
$[P(C_4H_9)(C_6H_5)_3][CuBr_2]$	2.213(2),2.220(1)	177.67(6)			49
$[P(C_3H_7)(C_6H_5)_3][CuBr_2]$	2.225(1),2.232(1)	173.18(4)			72
$[P(C_2H_5)(C_6H_5)_3][CuBr_2]$	2.207(2),2.224(2)	175.0(1)			73
$[P(CH_3)(C_6H_5)_3][CuBr_2][Br]$	2.228(1),2.233(1)	175.29(4)			17
$[(Br(C_6H_4)CH_2CO)(C_6H_5)_3P][CuBr_2]$	2.207(8),2.229(8)	178.0(5)			16
[Rb(15-crown-5)$_2$]$[CuBr_2]$	2.197(4),2.200(4)	179.0(1)	2.204(2)	175.6(4)	58

[a] tmeda, Tetramethylethylenediamine.
[b] BEDT-TTF, 3,4;3',4' bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalene.
[c] 2,4,6-tmpy, 2,4,6-Trimethylpyridine.
[d] the error is for second digit after the decimal.
[e] phen, 1,10-Phenanthroline.
[f] L, 2,6-bis[1-phenyl-1-(pyridin-2-yl)-ethyl]pyridine.
[g] mad, $C_6H_5CH{=}CH{-}{-}CH{=}N{-}{-}C_6H_4{-}{-}p{-}{-}CH_3$.
[h] no errors are available in the liteature.
[i] TSeT, Tetraselenotetracene.

approximately linear (in the case of the presence of center of symmetry at Cu, X-Cu-X is exactly linear). The few cases where the X-Cu-X angle is seriously distorted from 180° involve a fourth atom close to copper. If any atom which is positively charged is found near the X-Cu-X species, then interaction between this atom and X of X-Cu-X is possible. This fourth atom attracts the X atom away from its linear position in X-Cu-X. $[CuCl(C_{44}H_{60}N_4)][CuCl_2]\cdot 3C_2H_6O$ provides an exception to this expectation.[75] The anion ($CuCl_2^-$) is severely bent (X-Cu-X angle, 169.5(8)°), however there is no close interaction <3.5 Å between Cl and any other atom. In [TSeT][$CuBr_2$], the $CuBr_2^-$ is severely distorted, with the Br-Cu-Br angle equal to 153.8(1)°. There is an interatomic Cu···Br distance of 2.829(2) Å.[74]

The Cu-X bond lengths in the linear dicoordinate monomeric complexes were found to be shorter than those in the multinuclear dicoordinate copper atoms and also shorter that those seen in compounds with three and four coordinate copper atoms. The distances of Cu-Cl, Cu-Br and Cu-I in the linear dicoordinate complexes are 1.960-2.110, 2.194-2.233 and 2.383-2.394 Å, respectively, while those in the compounds with other motifs are 2.250, 2.380, 2.560 Å.[50] This suggests that the Cu-X bonds in the linear dicoordinate complexes have double bond character. Bonding in linear X-Cu-X anion has been investigated in terms of ds hybridization of the copper atom.[76-80] A theoretical study of the bonding and nuclear quadrupole coupling in $[CuCl_2]^-$ and $[CuBr_2]^-$ has shown the existence of involvement of Cu $4p_z$, which undergoes contraction relative to the free-atom orbital on bond formation.[81]

The linear dicoordinate complexes are of special interest in conjunction with their emission properties, because they may crystallize with a variety of different symmetry elements within the $[CuX_2]^-$ cluster (Figure 2). The copper atom can be situated on a center of symmetry or point of inversion, on a 2-fold axis (which might pass through the halide atoms as well or be situated perpendicular to the X-Cu-X axis) , and on a mirror plane (which might be perpendicular to the X-Cu-X axis or which might pass through all three atoms). Furthermore, the $[CuX_2]^-$ motif might crystallize with no internal crystallographic symmetry element.

Center of Symmetry. A complex in this category forms an anion with a center of symmetry element passing through the copper atom, therefore, X-Cu-X is exactly linear. In order for a complex to have a center of symmetry element at the copper atom, the cation itself (the quaternary ammonium and phosphonium salts) must be centrosymmetrically substituted, for example $(Butyl)_4NCl$, etc. However, a $[CuX_2]^-$ compound formed with a centrosymmetric cation does not necessarily possess a center of symmetry within the $[CuX_2]^-$ cluster.

$[(Butyl)_4N][CuBrCl]$ should be specially addressed because it is a mixed halide complex. The Cu-Br distance appears to be slightly shorter than the average of Cu-Br distances calculated from other complexes containing only bromide. The shorter Cu-Br distance suggests a disorder of Br and Cl and thus a Cu-X distance shorter that the normal Cu-Br distance but longer than the normal Cu-Cl bond should be expected. Unfortunately, the X-ray crystal structure determination was not of sufficient quality to permit much interpretation of the Cu-X distances in $[CuBrCl]^-$.

In the compound $[BEDT\text{-}TTF][CuCl_2]$, the dicuprate anions are a mixture of $Cu^ICl_2^-$, and $Cu^{II}Cl_2$. That is, the Cu atoms in $CuCl_2$ are in a mixed-valence state consisting of mono- and divalent cations.

In the two previously known iodocuprate(I) complexes,[51] copper(I) lies on a center of symmetry, with Cu-I distances of 2.383(1) and 2.394(3) Å, respectively. The iodine atoms are further involved in ionic interactions with potassium, K-I distances being 3.598(1) and 3.656(3) Å, respectively.

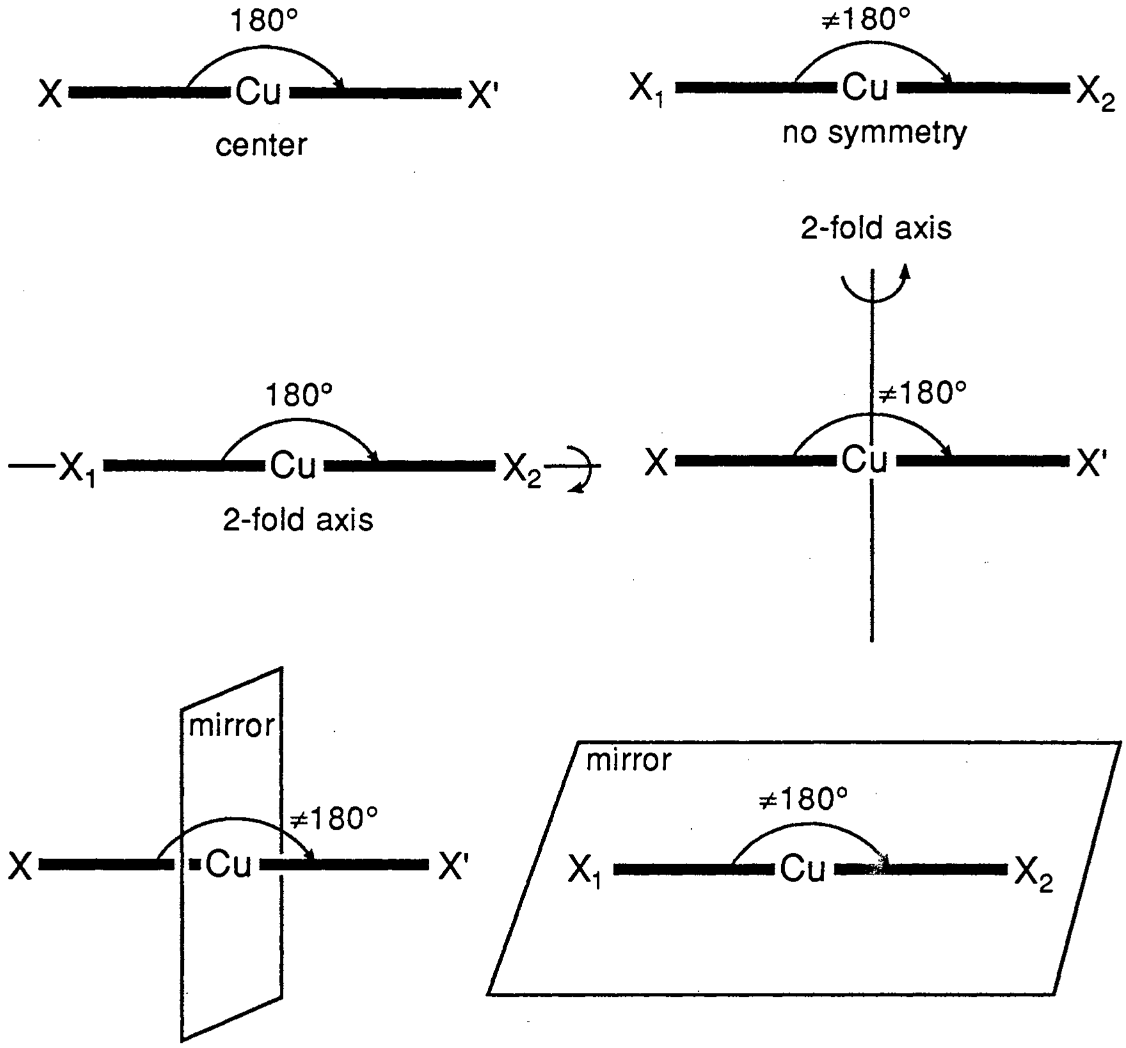


Figure 2. The Possible Symmetry Elements within $[CuX_2]^-$.

2-fold Axis Symmetry. There have been four clusters with 2-fold axis symmetry elements reported in the literature. In these complexes, Cu atoms sit on 2-fold axis symmetry elements with X-Cu-X angle close to 180°. The average Cu-Cl distance and Cl-Cu-Cl angle are 2.152(6) Å, 179.0(2)°, respectively, while the corresponding values for bromide are 2.209(2) Å and 179.2(2)°. $[N_6P_6(N(CH_3)_2)_{12}CuCl][CuCl_2]$ has both Cu(I) and Cu(II) in the molecule, but the copper atom of the anion, $CuCl_2^-$, is Cu(I), which lies on a 2-fold axis. In the compound $[Cu(phen)_2][CuBr_2]$, the Cu and both Br atoms lie on a 2-fold axis, making the $CuBr_2^-$ species truly linear. Cu-Br distances are 2.209(2) and 2.223(2) Å.

Mirror Symmetry. There is only one known compound with the Cu atom on a mirror, $[(PhMe_3)N][CuCl_2]$.[61] In this compound, the copper atom, two chlorine atoms, the phenyl ring, the nitrogen atom and one of the methyl carbons lie in the crystallographic mirror plane. The mean Cu-Cl distance and the Cl-Cu-Cl angle are 2.111(2) Å, 179.63(7)°, respectively. The shortest halogen-carbon distance, which represents the shortest anion-cation contact, Cu-Cl, is 3.417(5) Å. The closest distance between Cu and carbon is 3.623(7) Å.

No internal Symmetry. Although some cations possess at least one symmetry element, the complexes formed from them do not necessarily have a symmetry element present in the solid state. Most of the known $[CuX_2]^-$ complexes fall in this category. Both $[P(C_6H_5)_4][CuBr_2]$ and $[P(C_2H_5)(C_6H_5)_3]$-$[CuBr_2]$ crystallize with monomeric dibromocuprate(I) anions. Replacement of a single phenyl group by the appreciably smaller ethyl group would thus not appear to affect the configuration of the anion in the solid state.

The existence of a large number of linear dicoordinate complexes with a variety of different crystallographic symmetry elements provides an opportunity to observe the influence of many different types of symmetry elements upon emission behavior. It has been possible to add a significant number of new compounds to these groups.

A cuprous compound has to be excited before it can emit. There are five possible mechanisms for excitation: (i) metal to ligand charge transfer, existing when an electron in a *3d* orbital of Cu is excited into a π^* orbital of the ligand ($3d^{10}$-$3d^9\pi^*$); (ii) ligand-ligand interaction, describing a π-π^* transition between adjacent π systems; (iii) metal-metal interaction, occuring when two copper atoms are close (<2.6 Å); (iv) single metal excitation, resulting from a *d* to *s* transition on a single Cu when two Cu are widely separated; (v) donor acceptor pair, existing when an atom coordinated to Cu can donate an electron to the metal atom.

The possible excitation mechanisms may be simplified for linear complexes due to the absence of copper-copper, metal to ligand and ligand-ligand interactions. In these systems, only the excitation mechanisms arising from a single Cu atom or from a donor acceptor pair are possible. Furthermore, the $[CuX_2]^-$ is reasonably stable for X=I, Br or Cl, allowing the investigation of the influence of a change of halide upon the emission properties.

Previous studies of the emission behavior of the linear complexes are essentially nonexistent. This thesis study, thus, set out to accomplish: (1) a systematic study of the emission of the $[CuX_2]^-$ complexes, involving the synthesis of new complexes of this type with a variety of internal symmetry elements; (2) their characterization using single crystal X-ray diffraction; (3) measurement of their emission spectra at room and low temperatures and (4) a correlation of the influence of the multiple symmetry elements possible upon the wavelength of maximum emission with the aid of *ab initio* calculations.

CHAPTER II

X - RAY CRYSTALLOGRAPHY

X-ray crystallography permits investigation of the three-dimensional structures of molecules in crystalline materials using X-ray diffraction. A crystal is a solid substance having an ordered arrangement of atoms, ions or molecules in its lattice. This arrangement can be represented by a unit or motif called the unit cell, which is defined as the smallest, repeating unit of the crystal structure. A unit cell is characterized by three edges: a, b and c, and three angles between these edges: α, β and γ. The relationships between the edges and angles establish the crystal system to which the unit cell belongs.[82] There are seven crystal systems possible (Table 2).

A crystal lattice is an array or repetition of atoms, ions or molecules in a crystal. The lattice can be classified as primitive, P, face centered (A, B, C, or F) or body centered, I, according to the number of lattice points that lattice contains. There are fourteen *Bravais lattices* possible when crystal systems are combined with lattice types. Atoms or molecules within a unit cell may be related to each other by point symmetry elements such as rotation axes, inversion axes or mirror planes, and space symmetry elements such as screw axes and glide planes. Combination of the fourteen *Bravais lattices* with possible point and space symmetry elements gives rise to a total of 230 possible space groups. The space group is a fundamental characteristic of a crystal and its structure. All crystalline materials have a structure which is characterized in one of these space groups.

TABLE 2

THE SEVEN CRYSTAL SYSTEMS[62]

Crystal system	Unit cell shape	Essential symmetry
Triclinic	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$	1, $\bar{1}$
Monoclinic	$a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$	2, m, 2/m
Orthorhombic	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$	222, mm2, mmm
Tetragonal	$a = b \neq c$, $\alpha = \beta = \gamma = 90°$	4, $\bar{4}$, 4/m,422,4mm, $\bar{4}$2m, 4/mmm
Rhombohedral	$a = b = c$, $\alpha = \beta = \gamma < 120° \neq 90°$	3, $\bar{3}$, 32, 3m, $\bar{3}$m
Hexagonal	$a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$	6, $\bar{6}$, 6/m, 622 6mm, $\bar{6}$m$\bar{2}$, 6/mmm
Cubic	$a = b = c$, $\alpha = \beta = \gamma = 90°$	23, m3, 432 $\bar{4}$3m, m3m

Because crystals have infinitely, ordered repeating lattices, they diffract X-ray beams like an optical grating. When crystals diffract X-rays, it is the core electrons of the atoms or ions in the crystal which act as secondary point sources and scatter the X-rays. The diffraction of a beam of X-ray by a crystal is governed by Bragg's law:

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

where λ is the wavelength of the radiation, θ is the angle of incidence and the angle of diffraction of the X-ray beam with the set of planes diffracting, d is the perpendicular distance between the lattice planes diffracting, and n is the diffraction order. Bragg's law gives the relationship between the wavelength of X-ray radiation, distance between parallel planes of the scattering crystal, and the scattering angles at which specific diffracted beams are observed. It also defines the conditions necessary for diffraction of an X-ray beam of a fixed wavelength by a set of parallel lattice planes of interplanar spacing, d. Bragg's law implies that crystals are built up in layers or planes such that each layer acts as a semi-transparent mirror. Some of the X-rays are reflected off a plane with angle of reflection equal to the angle of incidence, and the rest are transmitted to be subsequently reflected by succeeding planes. The condition of Bragg's law must be met in order for a beam to be diffracted.

When an X-ray beam is diffracted by the lattice of a crystal, the specific diffraction pattern (reflection distribution and intensities) results from specific aspects of the structure. The distribution of diffracted reflections is governed by the unit cell of the particular crystal, while the intensities of reflections are determined by the types of atoms present and the relative positions of these atoms in that unit cell. Every different structure has its own characteristic diffraction pattern. Atoms of different elements have different abilities to scatter X-rays and the same atoms at different positions in the cell diffract X-ray beams differently. Two crystals having different contents may have the same unit cells, and thus give rise to diffraction at the same positions, however the intensities of the diffracted beams will differ due to the difference in cell content. The diffracted intensity data from a crystal contains total information about the structure of the crystal, X-ray crystallography simply attempts to "extract" structural information in terms of three-dimensional positional parameters from intensity data obtained experimentally using mathematical procedures. With a modern diffractometer equipped with a computer, the solution process is automated and is relatively simple, although the principles on which the methods are based are complicated. Figure 3 gives a diagram of the process of solving a structure with a typical diffractometer.[83]

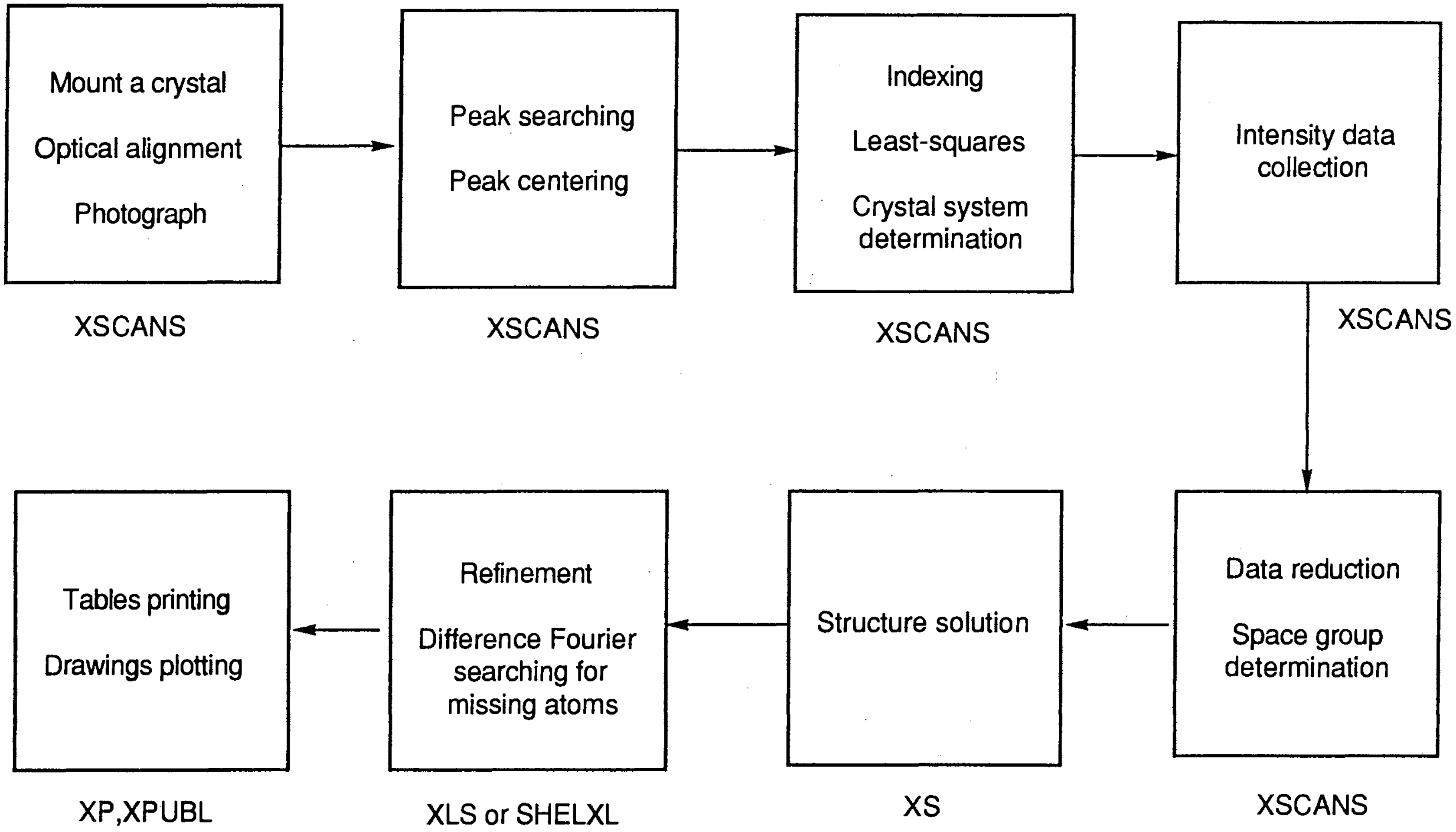


Figure 3. A Typical Process of Solving a Crystal Structure.

A photograph of the crystal is taken to check the quality of the crystal. High crystalline quality gives rise to a photograph with many sharp diffraction spots extending well out towards the edges of the film. The photograph shows both horizontal and vertical mirror symmetry about the center of the film. After the suitability of the crystal is confirmed, the automated four-circle diffractometer searches for a specified number of strong reflections (usually twenty-five to fifty) and establishes the optimum settings of the four angles to maximize peak intensity. The optimum angles (2θ, ω, χ, ϕ) used to determine unit cell dimensions are then refined by least squares methods. When the accurate cell is obtained, a full set of intensity data is collected and used to solve the structure. The diffractometer will record the intensity ($I_{meas}(hkl)$) for each reflection within the possible collection range. Individual reflections are distinguished from one another by their Miller indices (h k l). These indices provide a useful way of labeling the planes that pass through the so-called reciprocal lattice. The reciprocal lattice is expressed with axes a*, b*, and c* that can be related to the the direct lattice cell axes a, b and c. The process from determination of a unit cell to intensity data collection is performed with the software named XSCANS.[84]

The raw intensity data (I_{meas} is corrected for background, polarization, Lorentz effect, and crystal decomposition effects.[85] The correction for left and right background is calculated by:

$$I_{int} = (I_{meas} - L_{bg} - R_{bg}) \times \text{Scan speed} \qquad (2)$$

$$\sigma I_{int} = (I_{meas} + L_{bg} - R_{bg})^{1/2} \times \text{Scan speed} \qquad (3)$$

where:

I_{int} = Integrated Intensity

I_{meas} = Measured Intensity

L_{bg} = Left Background

R_{bg} = Right Background

σI_{int} = Standard Deviation of I_{int}

If $I_{int} \geq 2\sigma(I_{in})$, then the reflection is considered observed. Intensities measured by the diffractometer are always lower than their real values because of the effects of several factors:[86]

(i) *Polarization factor* ----- the factor taking care of the difference in diffraction efficiency at different magnitudes of θ. The unpolarized vector of the X-ray beam has a parallel component (I_{para}) and a perpendicular component (I_{para}). The parallel and perpendicular components of the incident beam are diffracted with differing efficiencies. The difference of efficiency is based on the magnitude of the angle, θ, at which diffraction is taking place. At lower 2θ angles, the perpendicular component of the beam is diffracted with higher efficiency.

$$I_{para} = KI_o \tag{4}$$

$$I_{perp} = KI_o\cos^2 2\theta \tag{5}$$

Considering these two components, the scattered intensity of an incident X-ray beam (I) can be described as an average of the two:

$$I = (I_{para} + I_{perp}) / 2 = KI_o / (1 + \cos^2 2\theta) / 2 \tag{6}$$

where I_o is the intensity of the incident X-ray beam and K, the reflection factor for the crystal planes. The term $(1 + \cos^2 2\theta) / 2$, known as the polarization factor, P, is a function of 2θ only and therefore it is independent of the geometry of data collection.

$$P = (1 + \cos^2 2\theta) / 2 \tag{7}$$

(ii) *Lorentz factor* ----- the factor dealing with the geometric positions relative to the 2θ values. The reflections measured at different 2θ values spend different amounts of time in diffraction position. When the crystal is rotated at a constant speed, reflections with low 2θ spend more time in optimum diffraction geometry than those reflections with high 2θ. The Lorentz factor (L) is defined so as to correct this effect:

$$L = (\sin 2\theta)^{-1} \tag{8}$$

Combining the Lorentz and polarization factors results in the Lorentz-polarization factor (LP) :

$$LP = (1 + \cos^2 2\theta) / 2\sin 2\theta \tag{9}$$

(iii) *Absorption factor* ----- the factor due to the reduction of intensity of the diffracted beam by absorption of the crystal. As an X-ray beam passes through a crystal, its intensity is reduced by absorption. The extent of the absorption depends on the path length of the beam through the crystal, the nature of the atoms in the crystal, and the wavelength of the incident X-ray beam. The absorption factor, A, is defined by:

$$A = (1 / V) \int e^{-\mu L}\, dv \tag{10}$$

where μ is the linear absorption coefficient, L is the path length through the crystal of a beam diffracted from the volume dv, and V is the volume of the crystal.[87]

(iv) *Decomposition factor* ----- the factor reflecting the decrease in intensity as the data collection proceeds due to the decomposition of the crystal. This correction assumes that decomposition is linear with respect to time and thus the correction factor is indicated by:

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

where I_{orig} is the starting intensity of a standard reflection and I_{ave} is the average current intensity of the std. reflection in between any two observations.

With all factors mentioned above taken into account, a general expression for the corrected integrated intensity, I_{corr}, is:

$$I_{corr} = I_{int} \times (LP)^{-1} \times A^{-1} \times D \qquad (12)$$

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

The structure factor, F_{hkl}, expresses the combined scattering of all atoms in the cell compared to that of a single electron. Its amplitude, $|F_{hkl}|$, is proportional to the square root of the corrected integrated intensity, I_{corr}:

$$|F_{hkl}| = K_s (I_{corr})^{1/2} \qquad (13)$$

where K_s is a scale factor. This is the observed structure factor and is usually designated $|F_{obs}|$. $|F_{obs}|$ is the actual data used to solve a structure. The error in $|F_{hkl}|$ is σF and is calculated according to the following:

$$\begin{aligned}\sigma F = (1/2) (k/LP)^{1/2} [N_t + N_{rbg} + N_{lbg} \\ + (0.01 N_{pk})^2] / (N_t - N_{lbg} - N_{rbg})^{1/2}\end{aligned} \qquad (14)$$

where:

N_t = no. of counts

N_{lbg} = no. of left background counts

N_{rbg} = no. of right background counts

$N_{pk} = N_t - N_{rbg} - N_{lbg}$

The structure factor, F_{hkl}, may also be expressed as a function of the positions of atoms in the cell, their abilities to scatter radiation and the phase angle, $\alpha(hkl)$:

$$|F_{hkl}| = [(A_{hkl})^2 + (B_{hkl})^2]^{1/2} \qquad (15)$$

$$A_{hkl} = \Sigma f_j \cos 2\pi (hx_j + ky_j + lz_j) \qquad (16)$$

$$B_{hkl} = \Sigma f_j \sin 2\pi (hx_j + ky_j + lz_j) \qquad (17)$$

$$F_{hkl} = A_{hkl} + iB_{hkl} = | F_{hkl}| e^{i\alpha(hkl)} \qquad (18)$$

$$\alpha = \tan^{-1} (B/A) \tag{19}$$

where f_j represents individual atomic scattering factors, and x_j, y_j, z_j represent the positional parameters in the unit cell of atom j.

The electron density or the number of electrons per unit volume at any point x, y, z represented by $\rho (xyz)$, is given by the following equation:

$$\rho (xyz) = (1/V_c)\sum_{h,k,l}\sum\sum F_{hkl}\, e^{-i\phi} \tag{20}$$

where, $\phi = 2\pi (hx + ky + lz)$, is the relative phase.

By combining $e^{\pm i\phi} = \cos\phi \pm i\sin\phi$

$$F_{hkl} = A_{hkl} + iB_{hkl}$$

$$F_{hkl} = |F_{hkl}|\, e^{i\alpha(hkl)}$$

with Friedel's law (X-ray diffraction adds centrosymmetry to the diffraction pattern whether or not a crystal has a center of symmetry. This means that hkl and -h-k-l cannot be distinguished, and that the intensities of hkl and -h-k-l are equal.):

$$F_{hkl} = F_{-h-k-l} \tag{21}$$

(20) becomes

$$\rho (xyz) = (2 / V_c) \sum_{h,k,l}\sum\sum |F_{hkl}| \cos [2\pi(hx + ky + lz) - \alpha] \tag{22}$$

where:

$\rho (xyz)$ = the electron density at some point x y z in the cell

V_c = unit cell volume

$|F_{hkl}|$ = amplitudes of structure factors

α = phase angle

Thus, to obtain a three dimensional electron density map, amplitudes of the structure factors and their phases must be known. Unfortunately, only the structure factor, F_{hkl}, may be obtained experimentally, the phase, α, is not measurable[88] directly from an experiment. The phase has to be derived either from values of A and B that are computed from known structures, or by purely analytical methods.

The so called "phase problem" in X-ray crystallography[82,88,89] says that the phase angles must be determined approximately for a number of reflections in order to have a first trial model from which to complete the structure. Direct methods and Patterson methods are two approaches to this problem (Figure 4). These two methods are based on different ideas of dealing with the phase problem.

The Patterson method works well only for molecules containing heavy atoms. This method evaluates a Fourier series for which only the indices and the $|F_{hkl}|^2$ value of each diffracted intensity are needed; these quantities are directly derivable from the experiment. The Patterson function, P (u, v, w), is given by:[89]

$$P(u, v, w) = 1 / V_c \sum\sum\sum_{k,k,l} |F_{hkl}|^2 \cos 2\pi (hu + kv + lw) \qquad (23)$$

or

$$P(u, v, w) = V \iiint \rho(xyz)\, \rho(x+u, y+v, z+w)\, dxdydz \qquad (24)$$

The Patterson function is always centrosymmetric. It defines a map which gives interatomic distances plotted from the origin. When any two atoms in the unit cell are separated by a vector (u, v, w), then there will be a peak on the Patterson map at (u, v, w). Therefore the orientation and length of every interatomic vector in the structure is represented on the Patterson map. A peak (uvw) in Patterson map is called a vector. When one of the values, u, v, w is fixed (e.g. 0vw, uv1/2), the vector is referred to as a Harker plane; when two of the values, u, v, w are fixed (e.g. u00, 0v1/2), the vector is called a Harker line.

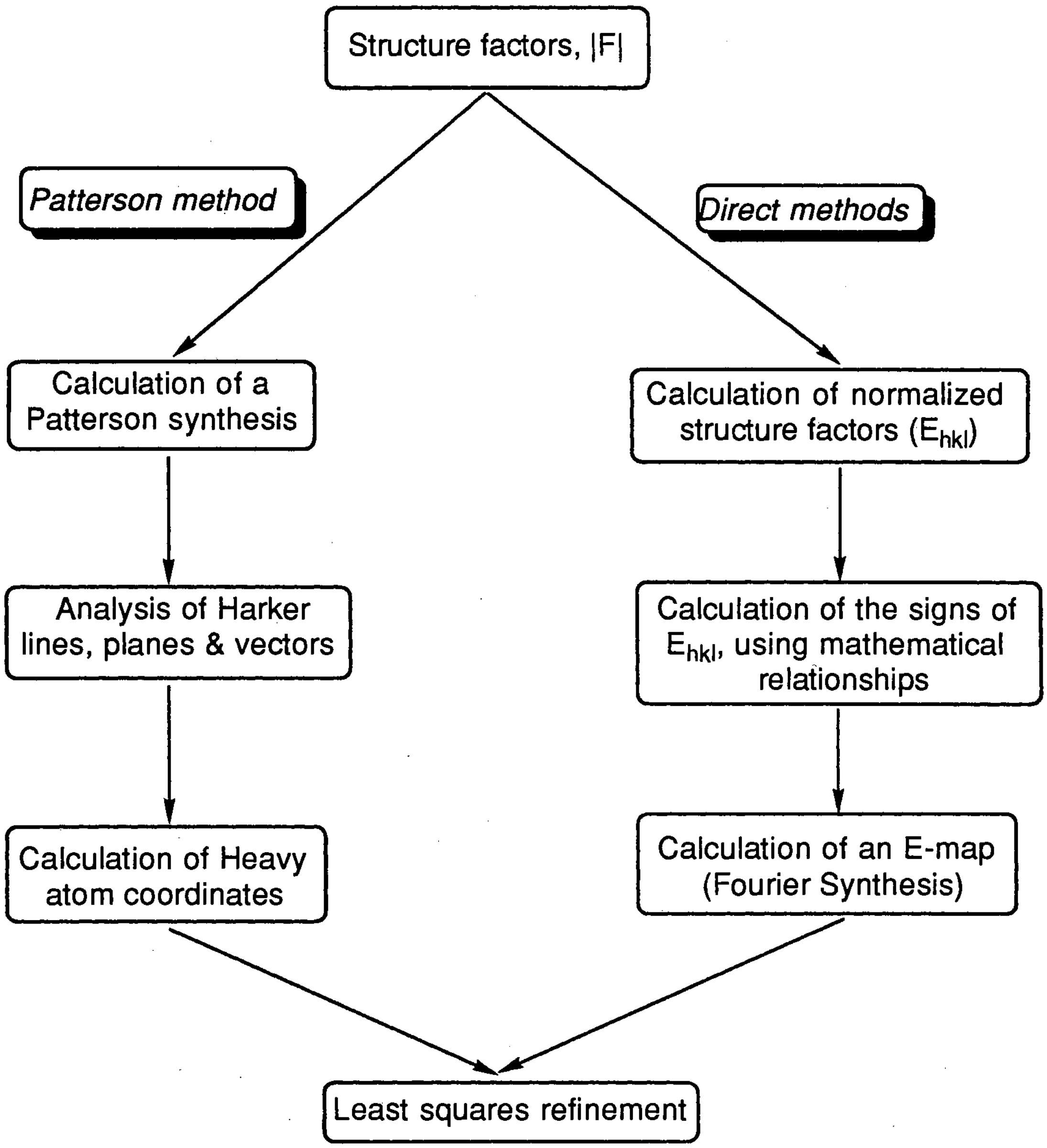


Figure 4. The Patterson Method and Direct Methods to Solve a Structure.

The height of a Patterson peak is proportional to Z_jZ_k , where Z_j and Z_k are the atomic numbers of atoms j and k, respectively. The vectors formed between atoms with larger atomic numbers, i.e. heavy atoms, are much more easily visible than those formed between light atoms on the Patterson map. The coordinates of heavy atoms may be derived[85,90] from the map by analysis of Patterson vectors, Harker lines and planes using the general equivalent positions of the space group to which the crystal belongs. Table 3 shows some Harker lines and planes. Using $P2_1$ as an example, the space group has one 2-fold screw parallel to b, and two equivalent positions x, y, z and x, y+1/2, z. The interatomic vector is expected to be found on the Harker plane (u, 1/2, w) and at the position (2x, 1/2, 2z). The x and z coordinates of the atom can, thus, be calculated from the position of this peak, but the y coordinate cannot be determined. However, y can be assigned arbitrarily. Coordinates derived from the Harker lines and planes for heavy atoms give a first trial model.

TABLE 3

Some Harker Lines and Planes[85]

Symmetry Elements	Harker Lines & Planes
2-Fold axis || a, b, c	0 v w; u 0 w; u v 0
2-Fold screw || a, b, c	1/2 v w; u 1/2 w; u v 1/2
m plane ⊥ a, b, c	u 0 0; 0 v 0; 0 0 w
a glide ⊥ a, b, c	1/2 v 0; 1/2 0 w
b glide ⊥ a, b, c	u 1/2 0; 0 1/2 w
c glide ⊥ a, b, c	u 0 1/2; 0 v 1/2

The other approach, direct methods, was developed later than the Patterson method, however it is now the more powerful technique for solving crystal structures. This method is applicable to any structure, including both light and heavy atom structures. As the name, "direct methods", implies, these methods derive the phases of a subset of the structure factors directly from the magnitudes of the $|F_{hkl}|^2$, by using analytical techniques to obtain an approximate set of phases from which an electron density map can be calculated. A trial model suitable for the structure may then be derived from interpretation of this map. Direct methods are based on the premise that the electron density in a real crystal can never be negative anywhere and that electron density consists of discrete spherically symmetric atoms. For centrosymmetric structures, with each atom at x, y, z, matched by an equivalent atom in the structure at -x, -y, -z, the phase angle can only be either 0° or 180°. This can be illustrated by substituting A and B values in (19). In other words, $\cos \alpha = +1$ or -1 and $\sin \alpha = 0$. Therefore, $|F_{hkl}| \cos \alpha = F_{hkl} = +|F_{hkl}|$ or $-|F_{hkl}|$. Because of this, the word "sign" is often used to refer the phase of a structure factor, which can either be +1 or -1. In this situation, (22) can be further simplified as:

$$\rho(xyz) = (2/V_c) \sum_{h,k,l}\sum\sum \pm |F_{hkl}| \cos 2\pi (hx + ky + lz) \qquad (25)$$

Notice there are two signs in front of $|F_{hkl}|$ in equation (25). Equation (25) takes a positive sign when $\alpha = 0°$, and a negative sign when $\alpha = 180°$ for a given structure factor. Thus, the electron density map may be calculated from (25) when the signs of a significant number of structure factors are known. Sign determination, therefore, is a key step to get a trial structure in direct methods. There exist relationships among the signs, which means that signs or relative phases of many F_{hkl}'s can be determined from a few known phases. These relationships are illustrated by the so-called Sayre equation:[89,91]

$$s(h_1, k_1, l_1) \cdot s(h_2, k_2, l_2) \approx s(h_1 + h_2, k_1 + k_2, l_1 + l_2) \qquad (26)$$

which is also known as triplet product sign relationship, where s is "sign of", ≈ means "is probably equal to", s (h, k, l) is $F_{hkl} / |F_{hkl}|$ and is either + or -, and (h_1, k_1, l_1), (h_2, k_2, l_2), and $(h_1 + h_2, k_1 + k_2, l_1 + l_2)$ are reflections with high $|E|$ values. This triplet product sign relationship can be used to expand the number of phases. If two of the signs in the equation are known, the third can be deduced from the equation. For example, if the signs of 601 and 133 are each +1, then 734 is generated by the combination of 601 and 133 and its sign will be positive:

$$s(734) \approx s(601) \cdot s(133) = (+1) \cdot (+1) = +1$$

Several such vector triplets for a given hkl can exist, for instance,

$$s(734) \approx s(589) \cdot s(145)$$

$$s(734) \approx s(444) \cdot s(290)$$

However, only a limited number of signs can be determined from the triplet relationship. In order to determine more signs, the technique of symbolic signs (a, b, etc.) is employed. The technique assigns symbolic signs to certain reflections and generates the signs of other reflections in terms of these symbols. With more and more symbolic signs assigned, the signs of these symbols may become clear eventually. The signs of more reflections can be determined in a symbolic way and it is often possible to derive phases for almost all strong reflections.

The probability concepts associated with these sign relationships should be taken into account. The higher the probability for a triplet product is, the more reliable the sign will be. Therefore, ideally, only those triplet products with high probabilities should be chosen. The probability that a triplet product is positive is[88]

$$P_{+}(hkl) = 1/2 + (1/2)\tanh[(s_3/s_2^{3/2})\alpha'] \qquad (27)$$

where α' is given by

$$\alpha' = |E_{hkl}| \sum_{h'k'l'} E(h', k', l')\, E(h-h', k-k', l-l') \qquad (28)$$

and σ_n by

$$\sigma_n = \Sigma Z_j^n \qquad (29)$$

and Z_j is the atomic number of the j^{th} atom. $|E_{hkl}|$ is called the normalized structure factor, which is defined by the equation:

$$|E_{hkl}|^2 = |F_{hkl}|^2 / \Sigma f_i^2 \tag{30}$$

For a structure containing N identical atoms, $\sigma_3/\sigma_2^{3/2}$ is equal to $N^{-1/2}$. It is easy to notice that the probability is strongly dependent upon the magnitudes of the | E | values. Thus, in order to maintain a high probability for a triplet product, only the high | E | values, usually the strongest 10 percent or so, should be used.

The start of the sign determination procedure relies upon the establishment of phases for three reflections. This set of three known phases can be obtained by defining the unit-cell origin. In centrosymmetric crystals, the origin is placed on one of the eight centers of symmetry in the unit cell. These origin-fixing reflections should not form a "triplet product", instead they should essentially differ with respect to the evenness or oddness of their individual indices, and h, k, and l must not all be even. In any primitive, centrosymmetric space group in the triclinic, monoclinic, or orthorhombic systems, arbitrary signs can be allocated to three reflections in order to specify the origin. These signs form a basic set. More signs can be derived from this basic set by using triplet product sign relationships.

When a large enough number of phases is known, an electron density map, E-map, is calculated with | E | values rather than | F | values (so that atoms are sharper, corresponding to point atoms):

$$\rho(xyz) = (2 / V_c) \Sigma\Sigma\Sigma \pm |E_{hkl}| \cos 2\pi (hx + ky + lz) \tag{31}$$

A trial model for the structure can be derived from the E-map.

For noncentrosymmetric structures, additional formulae may be used to derive approximate values for the phase angle. The phase angle can take any value between 0 and 2π. The so-called tangent formula[86]

$$\tan \phi_H \approx \frac{< |E_K| |E_{H-K}| \sin (\phi_K + \phi_{H-K}) >_k}{< |E_K| |E_{H-K}| \cos (\phi_K + \phi_{H-K}) >_k} \qquad (32)$$

is used extensively to calculate and also to refine phases for noncentrosymmetric structures, where, H ≡ h, k, l, K≡ h', k', l', f is the phase angle of the structure factor. The brackets refer to an average overall value of K, where H = (K) + (H - K). Just as equation (26) is the key formula for phase determination in the centric case, the tangent formula is the formula for phase determination in the accentric case.

Because the methods to deal with centrosymmetric and noncentrosymmetric structures are different, determination of centeredness or noncenteredness should be done prior to looking for a structure solution. This can be done by analysis of the statistical distribution of | E | values which can be calculated using equation (30). The mean value of | E | is 0.798 for a centrosymmetric structure and 0.886 for a noncentrosymmetric one.

Least-squares refinement attempts to improve the R factor by altering atomic positions. The least squares program compares the observed structure amplitudes with those calculated from the model. Then the atomic parameters of the calculated structure factors are modified so that the least squares fit improves. The agreement factor, R_f, is calculated to evaluate the correctness of the model. R_f is given by:

$$R_f = (\Sigma | |F_{obs}| - |F_{calc}| |) / (\Sigma |F_{obs}|) \qquad (33)$$

After least-squares refinement, a difference Fourier synthesis is made to locate missing atoms. The difference Fourier is defied as:

$$\Delta\rho (xyz) = (2 / V_c) \Sigma\Sigma\Sigma (|F_{obs}| - |F_{calc}|) \cos [2\pi (hx + ky + lz) - \phi_c] \qquad (34)$$

h,k,l

where $$\phi_c = \tan^{-1} [B_c'(hkl) / A_c'(hkl)] \qquad (35)$$

$A_c'(hkl)$ and $B_c'(hkl)$ are the real and imaginary components, respectively, of the calculated structure factor, F_{calc}, which can be calculated from (15), (16), (17) with a known structure (a partially known structure, such as a trial structure, or a completely known structure) with atoms j at known positions x_j, y_j, z_j. The cycle involving refinement of atomic positional parameters and difference Fourier searching for missing atoms is repeated until all nonhydrogen atoms have been found and a relatively low R factor is obtained. Up to this point, refinement is performed using isotropic temperature parameters. The temperature factor, a measure of the thermal vibration of the atom, effectively spreads the electron cloud over a larger volume. The temperature parameter causes the decrease in the atomic scattering factor as 2θ increases. The scattering factor for an atom at rest is given by the expression:

$$\exp [-B_{iso} (\sin^2\theta) / l^2] \qquad (36)$$

where B_{iso} is the isotropic thermal parameter. It is equal to $8\pi^2 <u^2>$, where $<u^2>$ is the mean square amplitude of displacement of the atom from its equilibrium position. The atomic scattering behavior may be more accurately expressed by the anisotropic thermal parameter:

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

where b_{ij} is the individual anisotropic thermal parameter. Refinement is then continued anisotropically to give more accurate positional parameters and a better R factor for the structure. Use of anisotropic parameters describes an ellipsoidal volume of electron density.

Hydrogen atom positions are usually calculated using ideal geometry except where intensity data is good enough to allow them to be located from a difference Fourier map. When all atoms have been located, an appropriate weighting scheme and extinction correction may be selected. As the model approaches completion, differences between F_{obs} and F_{calc} are expected to be small and R_f to be low. For an acceptable solution to a structural problem, the R factor is normally between 3 - 6% and bond angles and distances should be reasonable. At this stage, a difference Fourier map phased with final parameters for the refined structure should reveal no fluctuations in electron density greater than those expected on the basis of the estimated precision of the electron density. Then the structure is considered completed.

Tables of crystal information, data collection conditions, positional parameters, anisotropic thermal parameters and bond distances and angles are prepared. The table of final F_{obs} and F_{calc} structure factors is also printed. Appropriate drawings of the molecular and the unit cell are prepared.

CHAPTER III

LUMINESCENCE

Luminescence is the general term to describe the emission of light by a material following absorption of energy. There are several types of luminescence, based upon the energy source used for excitation of the material and distinguished verbally by the addition of a prefix to denote the type of energy involved.[92,93] *Photoluminescence* results from absorption of photons or light, often UV; *electroluminescence* involves of use of electrical energy, *cathodoluminescence* is caused by cathode rays of electrons; *chemiluminescence* results from energy supplied by a chemical reaction; *bioluminescence* is the result of a biological process; and *radioluminescence* is caused by interaction of radioactive particles. Of these six types, *photoluminescence* is the most common and may be either fluorescence or phosphorescence. Phosphorescence has a longer lifetime than fluorescence. Both processes involve the excitation of molecules into electronic excited states and the emission procedure competes with other processes by which the molecules can lose excess energy.

Figure 5 shows the electronic configuration of a simple molecule having a π-system and a lone pair of electrons. Before absorption of energy, electrons in the molecule occupy the orbitals of lowest energy and the molecule is said to exist in the ground state. In the ground state two electrons occupy the same orbital with different spins. These two electrons are said to be paired. Since the spin of every electron in the molecule is cancelled out by the spin of its companion in the same orbital, the total electron spin of the ground state molecule is zero and the state is referred to as a "singlet state". When the molecule absorbs photons of UV radiation, one of the the paired electrons is promoted to an upper excited state, S_1 or S_2. The transitions of electrons to T_1 or T_2 cannot occur, because these transitions would involve in spin change which is forbidden according to the "selection rule", which states that the electron spin cannot change during a transition associated with absorption or emission of radiation. In S_1 or S_2, the electron spin is still paired with that of the electron left behind and so a whole series of excited states exists in which the total electron spin is still zero. Like the ground state, these excited states are also singlet states. Although a transition from the ground state to an excited state involving a triplet

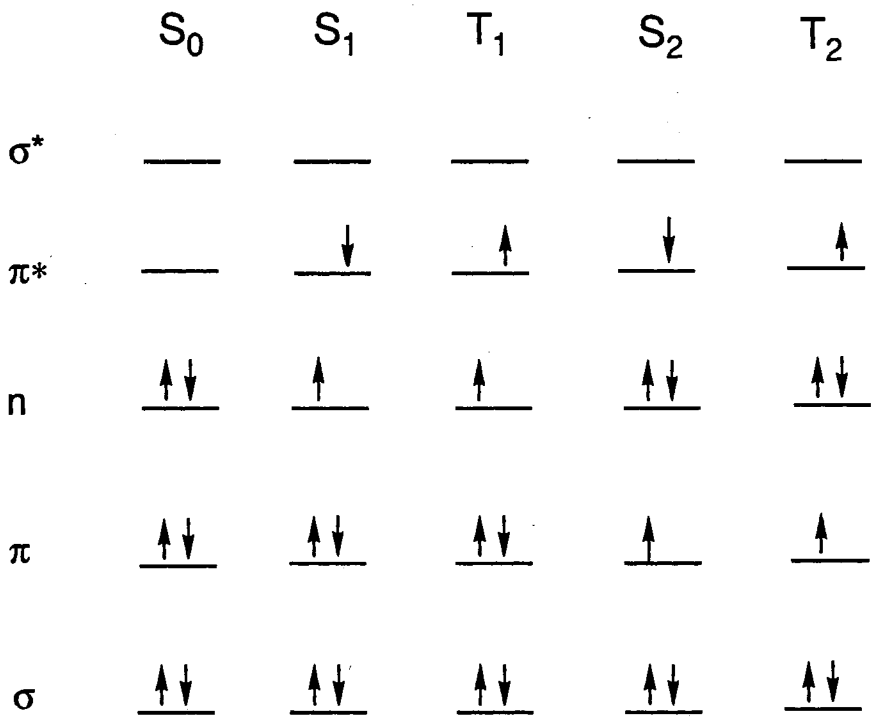


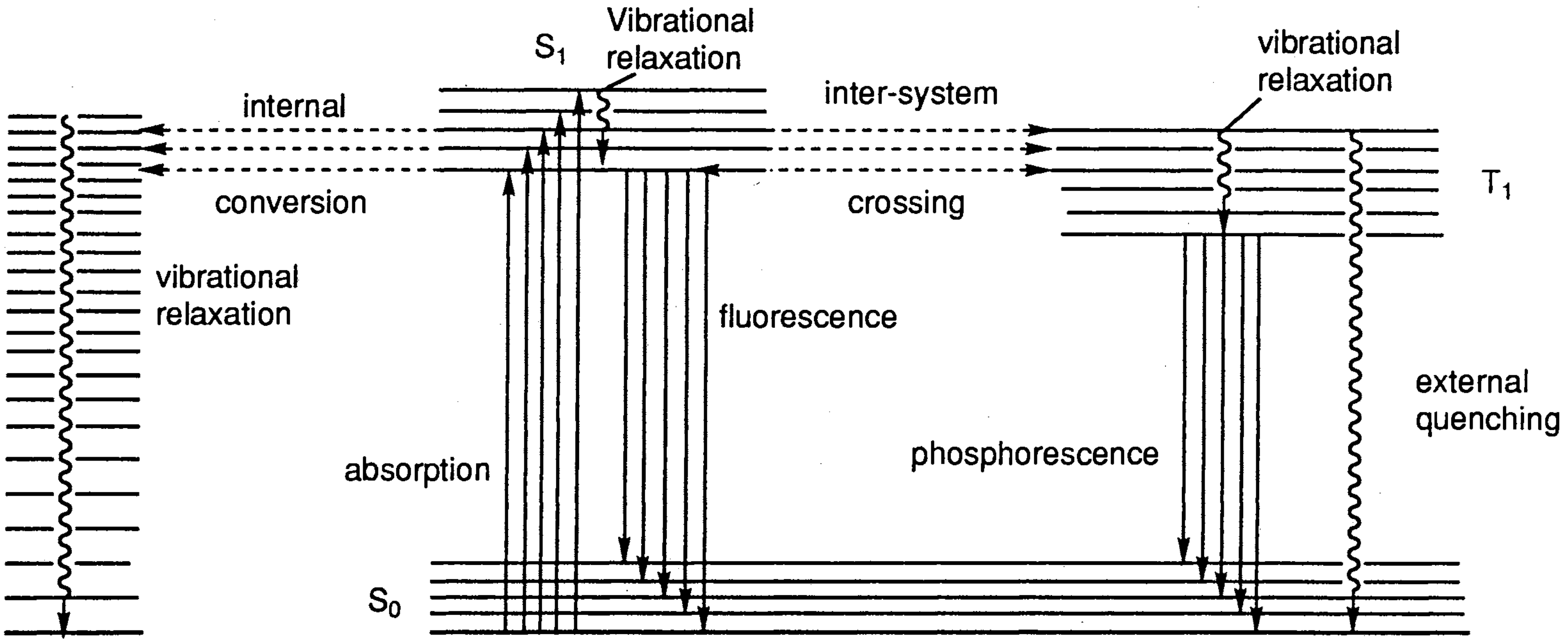
Figure 5. A Diagram of Electronic State Configurations.

state is spin-forbidden, molecules can arrive in triplet states by inter-system crossing from a singlet state or, in some case, by some other non-radiative process such as a chemical reaction. Phosphorescence is emission from a triplet state and fluorescence is emission from a singlet state.

Molecules possess vibrational energy which is quantized to give a series of vibrational energy levels. Absorption of UV light can also affect vibrational energy levels. The excess vibrational energy of the excited molecules will be rapidly dissipated through thermal motion (intermolecular collisions) and other processes by partition of vibrational energy to other modes of rotation and vibration within the molecule until the lowest vibrational energy level of the excited singlet state, S_1, is reached. This process is called *vibrational relaxation* (Figure 6).

There are three possible pathways (Figure 6) for an excited molecule from the lowest vibrational state, S_1, to return to the ground state. When it returns directly to the ground state, visible light will be given off as an emission. This process is called fluorescence.

If an excited molecule does not fluoresce, it must have disposed of the excess energy by some other means in order to return to the ground state. There are several mechanisms by which the energy can be dissipated without the emission of radiation. Such processes are referred to as radiationless transfer of energy. Radiationless transfer can occur in one of two ways. One way is by intra-molecular redistribution of the energy between the available electronic and vibrational states. This can be considered to take place in the two stages, the first being called internal conversion and the second vibrational relaxation. The conversion of electronic energy to vibrational energy and its subsequent degradation is much easier if the molecule is loose and floppy



S_0 --- Ground state
S_1 --- Excited singlet state
T_1 --- Excited triplet state

Figure 6. Energy Level Diagram Showing Fluorescence and Phosphorescence Transitions.

because it can reorient itself in ways which help to promote the internal transfer of energy. A rigid molecule cannot make efficient use of internal conversion to return to the ground state and so is more likely to emit a photon. However, not all rigid molecules are fluorescent, because the possibility of inter-system crossing is still open to them. The other mechanism of radiationless transfer of energy is by a combination of inter-system crossing, which leads to the lowest triplet state, T_1. In the lowest triplet state, the two electrons occupying separate orbitals are no longer restricted by the Pauli principle and their spins are "parallel" (i.e. aligned in the same direction). In a magnetic field, the excited state is split up into three sub-states of different energies. Such an state is therefore referred to as a "triplet state" because they have a "multiplicity" of three. Since according to the "selection rule", singlet - triplet transitions are "forbidden" in both directions, a molecule arriving in the lowest triplet state, T_1, cannot return to the ground state, S_0, by emitting a photon. However, in practice, the selection rule is not quite rigorous and there is a small probability that such a forbidden transition can take place. Thus, a molecule crossing from S_1 to T_1 can eventually return to the ground state with emission of radiation if deactivation can be prevented prior to the emission process. Lowering temperature seems to slow down the lattice thermal vibration and the molecules would be restricted in a more rigid lattice. This would allow the electron of the molecule to stay in the T_1 state for a longer time, and thus emission is more likely to be given off at a lower temperature than at a higher temperature.

It will be useful to establish a method of quantifying the extent to which a given molecule fluoresces. This is done by means of the *quantum yield* or *fluorescence efficiency*, ϕ_f, which is defined as the fraction of the incident radiation which is re-emitted as fluorescence.

$$\phi_f = \frac{\text{no. of photons emitted}}{\text{no. of photons absorbed}} = \frac{\text{intensity of fluorescence}}{\text{intensity of absorption}}$$

The time during which a molecule remains in an excited state before it returns spontaneously, with light emission, to a lower state, is called the lifetime of the excited energy level. The lifetime of fluorescence is 10^{-8} seconds or less. Therefore, it is impossible for the eye to perceive fluorescence once the source of the excitation has been removed. Phosphorescence persists for a longer period of time when excitation is discontinued. The lifetime of phosphorescence is usually between 10^{-6} to 100 seconds.

The luminescence of a material is usually studied using a fluorometer which measures the light emitted at right angles to the path of the incident or excitation beam. A typical fluorometer consists of the following components: i) a source of UV radiation; ii) a wavelength selector to choose the wavelength of the radiation to be used to excite the sample molecules; iii) an optical system to direct the exciting radiation onto the sample and to collect the emitted radiation; iv) a second wavelength selector to observe the radiation emitted at a particular wavelength; v) a sensitive detector to respond to the emitted radiation; vi) a read-out system to record the intensity of the fluorescence. scheme showing the essential components of a fluorometer is indicated in Figure 7.[92-94]

i) *Radiation Source:* The radiation source is commonly a mercury or xenon arc lamp; both bright and powerful sources of ultraviolet radiation. The mercury lamp has the advantage of giving radiation with very high intensity, however, it has a less continuous spectrum than a xenon arc lamp. A xenon arc lamp gives radiation with lower intensity and produces a small number of lines in the 4000 Å and 6600 - 8000 Å region. These may result in errors in high resolution work but have little effect on low resolution studies. Radiation sources are cooled by water or forced air to avoid overheating.

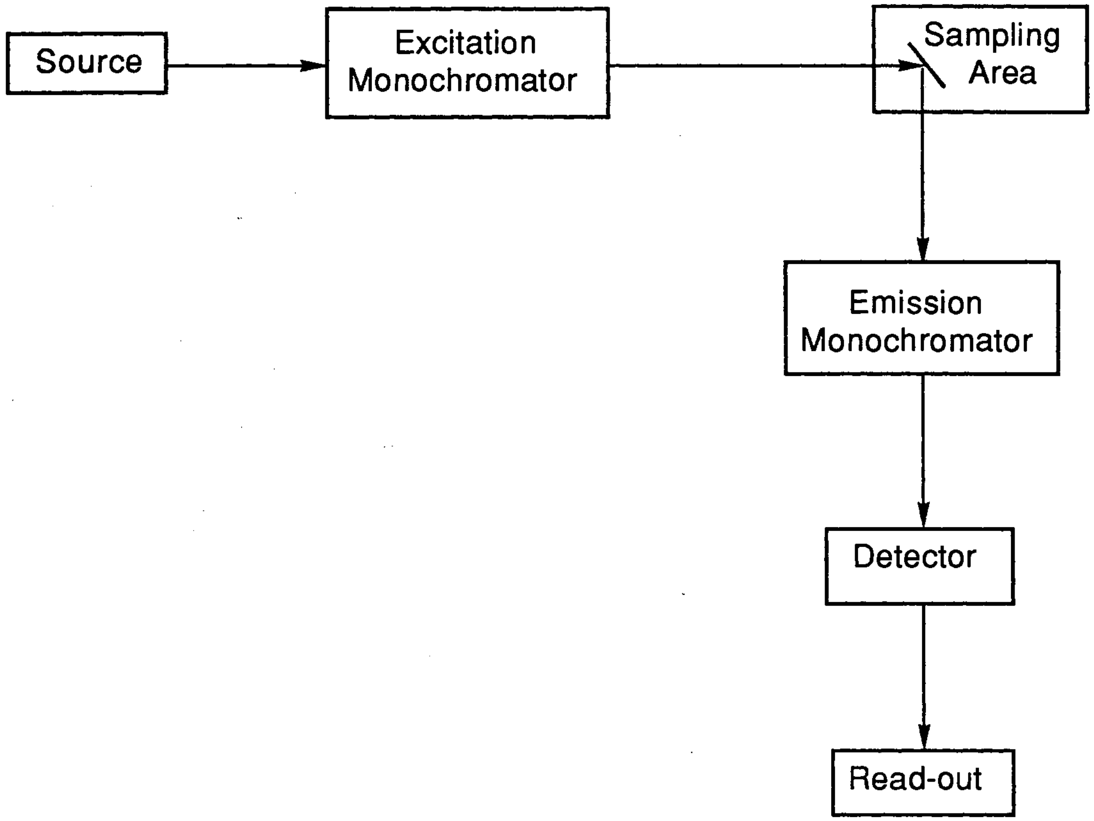


Figure 7. A Schematic Diagram of a Typical Fluorometer.

ii) *Excitation & Emission Monochromators :* Two monochromators are placed before and after the sample chamber to select the excitation and the emission wavelengths desired. The beam of light is separated into a band of narrow wavelength by the monochromator using gratings or prisms. Grating monochromators result in a lower loss of intensity than prism ones which absorb radiation. However, grating monochromators transmit light of shorter wavelength in the visible or red regions. Materials used for prisms should be selected so that absorbance in the region of interest is minimal. Quartz prisms are appropriate when measurement is made in the ultraviolet region of the spectrum. Wavelength calibration of monochromators should be done using a known standard such as the emission lines from a low pressure mercury lamp. Resolution is improved at the expense of sensitivity and controlled by the monochromator slit width. The smaller the slit width, the better the resolution. However, sensitivity will be reduced due to the decrease in intensity which is caused by the narrowed band of light allowed to pass through the monochromator.

iii) *Sample chamber:* The sample cell is situated in the sample chamber in such a way that the angle between the incident and emission beam is 90°. The material used for windows of the sample cell must not emit and must be transparent to wavelengths of interest. Pyrex glass or fused synthetic silica and quartz are suitable for this purpose.

iv) *Detector:* High gain photomultiplier tubes with high voltage power supplies are the most commonly used detection systems although semiconductor photodiodes also offer good performance. The wavelength response of a photomultiplier varies depending on the material of the photocathode, so it is necessary to choose a photomultiplier tube with maximum response in the spectral region of interest. The use of a photomultiplier tube requires correction for its response to different wavelengths to improve the accuracy of the emission spectrum.

v) *Read-out:* The output is normally recorded on magnetic media, floppy disk, tape, meter or strip recorder. The data are corrected for irregularities in source lamp intensity, monochromator response and background, then plotted as intensity against wavelength.

CHAPTER IV

EXPERIMENTAL

Materials. All chemicals were reagent-grade materials used without further purification.

Synthesis of Monomeric Dihalogenocuprate(I) Complexes: $[CuX_2]L$ (L = quaternary ammonium, phosphonium & arsonium salts, etc.)

$[(P(C_6H_5)_4][CuCl_2]$:

$[P(C_6H_5)_4]Cl$ (0.94 g, 2.5 mmol) was dissolved in 40 mL of ethanol and 0.25 g (2.5 mmol) of CuCl was added to the solution. Ascorbic acid† was added to the solution to insure the presence of Cu(I). The mixture was allowed to react under reflux in a nitrogen atmosphere for 5 h, then cooled to room temperature and filtered. Colorless tetragonal crystals were noticed to form after the filtrate was cooled to -5°C for 48 h. The dry crystals did not emit at room temperature upon observation in a UV lamp box (254 and 300 nm)††. Liquid paraffin was used to coat the crystals to guard against decomposition. A

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† Ascorbic acid is added without being weighed. The amount needed varies depending upon the extent of oxidation of Cu(I) in CuX used. Normally, ascorbic acid is added until the color of solution is changed to colorless (indication of presence of Cu(I)). When the solution turns to green after it is exposed to the air for some time, additional ascorbic acid is then added.

†† When we say a compound does not emit, we mean that no emission is observed under either of two wavelengths of the UV box. When a compound emits, it is meant that emission is noticed under the wavelength given.

crystal with appropriate dimensions (<0.5x0.5x0.5 mm^3)††† was mounted on a glass fiber for use in X-ray diffraction studies.

[P(C_3H_7)(C_6H_5)$_3$][CuBr$_2$]:

[P(C_3H_7)(C_6H_5)$_3$]Br (0.97 g, 2.5 mmol) was dissolved in 40 mL of ethanol, to which 0.25 g (1.7 mmol) of CuBr and powdered Cu were added. The mixture was allowed to react under reflux in a nitrogen atmosphere for five hours, then cooled to room temperature and filtered. Colorless prismatic crystals formed after the filtrate was cooled to -5°C for 72 h. The crystals did not fluoresce when examined under UV light at room temperature. Crystals were coated with liquid paraffin to prevent them from decomposition. A crystal with appropriate dimensions was glued on a glass fiber for X-ray structural analysis.

[K(18-crown-6)][CuBr$_2$]:

18-crown-6 (0.26 g, 1 mmol) and CuBr (0.14 g, 1 mmol) were dissolved in 20 mL of acetone and 20 mL of saturated aqueous KBr solution, respectively. The two solutions were mixed and 10 mL of H_2O was added, followed by the addition of ascorbic acid to give a colorless solution. The solution was allowed to react under reflux for five hours, then cooled to room temperature and filtered. Colorless rhombohedron crystals formed after the filtrate had evaporated slowly at room temperature for about 72 h. Blue light was observed at room temperature when the crystals were examined in a UV lamp box (254 nm). With the use of liquid paraffin as coating to avoid decomposition, one crystal with appropriate dimensions was mounted on a glass fiber for structural determination using X-ray diffraction.

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††† This criterion will be used throughout the writing. When appropriate dimensions of a crystal are said, 0.5x0.5x0.5 mm^3 is assumed.

[K(18-crown-6)][$CuCl_2$]:

18-crown-6 (0.26 g, 1 mmol) and CuCl (0.10 g, 1 mmol) were dissolved in 20 mL of acetone and 20 mL of saturated aqueous KCl solution, respectively. H_2O (10 mL) was added to the mixture, followed by addition of ascorbic acid, forming a colorless solution with little solid (CuCl) left undissolved. The mixture was allowed to react under reflux for 5 h, then cooled to room temperature and filtered. Colorless needle crystals were noticed to form after evaporation of the filtrate at room temperature over a 72-h period. The dry crystals emitted blue light at room temperature when excited with a UV lamp (254 nm). Liquid paraffin was used as a coating on the crystals. A crystal of appropriate size was mounted on a glass fiber for X-ray diffraction studies.

[$N(C_4H_9)$][CuIBr]:

[$N(C_4H_9)_4$]Br (0.19 g, 1 mmol) was heated to melting. CuI (0.32 g, 1 mmol) was added and dissolved in the molten [$N(C_4H_9)_4$]Br, forming a yellow liquid. The liquid was kept warm for 5 min, then allowed to cool. Brown solid formed upon cooling of the liquid. The solid was recrystallized from 20 mL of ethyl acetate with ascorbic acid added, giving a light brown solution. Colorless cubic crystals precipitated after the solution was cooled to -5°C for 48 h. These crystals fluoresced blue-green at ambient temperature in a UV lamp box (254 nm). Liquid paraffin was coated on the crystals to help them resist decomposition. A crystal of suitable size was mounted on a glass fiber for X-ray diffraction work.

[$N(C_5H_{11})$][CuI_2]:

[$N(C_5H_{11})_4$]I (0.43 g, 1 mmol) was heated to melting. CuI (0.19 g, 1 mmol) was added and dissolved in the molten [$N(C_5H_{11})_4$]I, forming a brown-yellow liquid. The liquid was kept warm for 5 min, then allowed to cool. Brown-yellow solid formed upon cooling the liquid. The solid was recrystallized from 20 mL of ethyl acetate with addition of ascorbic acid, giving a brown-yellow solution. Light yellow cubic crystals were seen to form after the solution was cooled to -5°C for 48 h. Emission of blue light was observed when the dry crystals were examined in a UV lamp box (254 nm) at room temperature. Liquid paraffin coating was employed on the crystals to prevent decomposition. A crystal with appropriate dimensions was mounted on a glass fiber for structural analysis by X-ray diffraction.

$[As(C_6H_5)_4][CuBr_2]$:

$[As(C_6H_5)_4]Br$ (1.16 g, 2.5 mmol) was dissolved in 40 mL of ethanol to which 0.36 g (2.5 mmol) of CuBr and some copper powder were added. The resulting mixture was allowed to react under reflux in a nitrogen atmosphere for 5 h, then cooled to ambient temperature and filtered. Colorless tetragonal crystals were seen to form after the filtrate was cooled to -5°C for 72 h. The crystals did not emit when observed under UV light at room temperature. The crystal surfaces were coated with liquid paraffin to protect from decomposition. A crystal of appropriate size was glued on a glass fiber for use in structural determination by X-ray diffraction.

$[K(Dicyclohexano\text{-}18\text{-}crown\text{-}6)][CuCl_2]$:

Dicyclohexano-18-crown-6 (0.37 g, 1 mmol) was dissolved in 20 mL of acetone and 0.10 g (1 mmol) of CuCl dissolved in 20 mL of saturated aqueous KCl solution. H_2O (10 mL) was added to the mixture of two solutions, followed by addition of ascorbic acid, giving a colorless solution containing small amount of undissolved CuCl. The mixture was allowed to react under reflux for

5 h, then cooled to room temperature and filtered. Colorless irregular thin plate crystals were noticed to form after evaporation of the filtrate at ambient temperature for about 72 h. The crystalline material emitted blue light at ambient temperature upon excitation at 254 nm. A crystal of a suitable size, coated with liquid paraffin, was mounted on a glass fiber for use in X-ray diffraction studies.

[K(Dicyclohexano-18-crown-6)][CuBr$_2$]:

Dicyclohexano-18-crown-6 (0.37 g, 1 mmol) was dissolved in 20 mL of acetone and 0.14 g (1 mmol) of CuBr dissolved in 20 mL of saturated aqueous KBr solution. The two solutions were mixed, and 10 mL of H_2O and ascorbic acid were added to the resulting solution, giving a colorless solution. The solution was allowed to react under reflux for 5 h, then cooled to room temperature. Some white solid was precipitated from the solution. The solution was filtered and colorless thin plate crystals were noticed to form after evaporation of the filtrate at room temperature for 72 h. The crystals gave off blue light in a UV lamp box (254 nm) at ambient temperature. A crystal with appropriate dimensions was coated with liquid paraffin and mounted on a glass fiber for X-ray structure determination.

[N(C$_5$H$_{11}$)$_4$][CuBr$_2$]:

[N(C$_5$H$_{11}$)$_4$]Br (0.38 g, 1 mmol) was melted by heating. CuBr (0.14 g, 1 mmol), with some ascorbic acid, was dissolved in the molten [N(C$_5$H$_{11}$)$_4$]Br, giving a brown liquid. The liquid was kept warm for 5 min, then allowed to cool. Brown-red solid formed upon cooling of the liquid. The solid was recrystallized from 20 mL of ethyl acetate, forming a brown-red solution. Light yellow thick plates formed after the solution was cooled to -5°C for 48 h. The dry crystals emitted blue-green at room temperature upon observation under UV light (254 nm). Liquid paraffin was used on the crystals to guard against decomposition. A crystal with suitable dimenssions, was mounted on a glass fiber for molecular structural determination by X-ray diffraction.

$[P(C_6H_5)_3]_2N[CuCl_2]$:

$[P(C_6H_5)_3]_2NCl$ (0.57 g, 1 mmol) was dissolved in 25 mL of ethanol and 0.10 g (1 mmol) of CuCl and some ascorbic acid were added to the solution. The resulting mixture was allowed to react under reflux in a nitrogen atmosphere for 5 h, then cooled to room temperature and filtered. The filtrate gave colorless tetragonal crystals after being cooled to -5°C for 72 h. No emission was observed when the crystals were excited under UV radiation at ambient temperature. The crystals were coated with liquid paraffin to retard decomposition. A crystal, with appropriate dimensions, was glued on a glass fiber for use in X-ray diffraction analysis.

$[N(C_6H_{13})_4][CuBr_2]$:

$[N(C_6H_{13})_4]Br$ (0.43 g, 1 mmol) of was melted by heating. CuCl (0.14 g, 1 mmol) of CuBr, with some ascorbic acid, was dissolved in the molten $[N(C_6H_{13})_4]Br$, giving a colorless liquid. The liquid was then heating for 5 min, then allowed to cool. Light yellow solid formed upon cooling of the liquid. Acetone (30 mL) was used to recrystallize the solid, forming a colorless solution. Colorless plate crystals formed after the solution was cooled to -5°C for 48 h. Blue light was emitted at room temperature when the crystals were excited under UV light (254 nm). A crystal with appropriate dimensions, after being coated with liquid paraffin, was attached to a glass fiber for use in X-ray diffraction studies.

$[N(C_6H_{13})_4][CuCl_2]$:

$[N(C_6H_{13})_4]Cl$ (0.39 g, 1 mmol) of was melted by heating. CuCl (0.10 g, 1 mmol), with some ascorbic acid, was added and dissolved in the molten $[N(C_6H_{13})_4]C$, giving a light yellow liquid. The liquid was kept warm for 5 min, then allowed to cool. Light yellow solid formed upon cooling of the liquid. 30 mL of acetone was used to recrystallize the solid, forming a light yellow solution. Colorless rectangular plate crystals formed after the solution was cooled to -5°C for 48 h. The crystals emitted blue light at room temperature when examined under UV excitation (254 nm). A crystal coated with liquid paraffin to avoid decomposition, and with appropriate dimensions was mounted on a glass fiber for use in determination of molecular structure by X-ray diffraction.

$[P(C_4H_9)_4][CuBr_2]$:

$[P(C_4H_9)_4]Br$ (0.34 g, 1 mmol) was melted by heating. CuBr (0.14 g, 1 mmol), and some ascorbic acid, were dissolved in the molten $[P(C_4H_9)_4]Br$, giving a light brown liquid. The liquid was kept warm for five minutes, then allowed to cool to room temperature. Acetone (30 mL) was added, forming a dark brown-green solution. Colorless irregular plates formed after the solution was cooled to -5°C for 48 h. When excited under UV radiation (254 nm), the crystals emitted green light at room temperature. The crystals were coated with liquid paraffin for protection. A crystal with appropriate dimensions was chosen and glued on a glass fiber for use in X-ray diffraction analysis of the molecular structure.

Synthesis of Compounds with Non-Linear Structure

$[N(C_4H_9)_4][Cu_2I_4]$:

$[N(C_4H_9)_4]I$ (0.92 g, 2.5 mmol) was dissolved in 35 mL of ethanol and 0.48 g (2.5 mmol) of CuI, with ascorbic acid, added to the solution. The mixture was allowed to react under reflux in a nitrogen atmosphere for 5 h, then cooled to room temperature and filtered. Colorless prisms formed after the filtrate cooled to -5°C for 72 h. The crystalline solid fluoresced light blue at ambient temperature upon observation in under UV light (254 nm). Liquid paraffin was employed on the crystals to stop them from decomposing. A coated crystal with appropriate dimensions was mounted on a glass fiber for X-ray diffraction studies.

$[P(C_6H_5)_4]_2[Cu_2I_4]$:

$[P(C_6H_5)_4]I$ (0.58 g, 1.25 mmol) was dissolved in a mixture of 20 mL of acetone and 20 mL of H_2O. CuI (0.24 g, 1.25 mmol) was added to the solution. Some ascorbic acid was added to the solution to insure the presence of Cu(I). The mixture was allowed to react under reflux in for 3 h, then cooled to room temperature and filtered. Colorless needles formed after the filtrate was cooled to -5°C for 120 h. Yellow light was given off when the dry crystals were examined in a UV lamp box (254 nm) at room temperature. A liquid paraffin coated crystal, with appropriate dimensions, was mounted on a glass fiber for structural determination by X-ray diffraction.

[K(Dicyclohexano-18-crown-6)]$_2$[Cu_4I_6]:

Dicyclohexano-18-crown-6 (0.48 g, 1.3 mmol) was dissolved in 10 mL of ethanol. CuI (0.25 g, 1.3 mmol) was dissolved in 20 mL of saturated aqueous KI solution, followed by addition of 10 mL of H_2O and ascorbic acid. The two solutions were mixed, forming a colorless solution, which was allowed to react under reflux for 5 h, then cooled to room temperature and filtered. Yellow irregular plates were noticed to form after evaporation of the filtrate at -5 °C for about 72 h. The crystals emitted yellow at ambient temperature upon observation in a UV lamp box (254 nm). A crystal of appropriate size, after being coated with liquid paraffin to prevent decomposition, was mounted on a glass fiber for use in X-ray diffraction studies.

[K(Dicyclohexano-18-crown-6)(acetone)]$_2$[Cu$_2$I$_4$]:

CuI (0.38 g, 2 mmol) was dissolved in 20 mL of saturated aqueous KI solution, with addition of 20 mL of acetone. Dicyclohexano-18-crown-6 (0.75 g, 2 mmol) in 20 mL of acetone was added to the resulting solution. The solution was allowed to react under reflux for 3 h, then cooled slowly to room temperature and filtered. Yellow prisms were noticed to form after evaporation of the filtrate at -5 °C for about 72 h. Emission of yellow light was observed at room temperature when the crystals were subjected to excitation under UV light (254 nm). Liquid paraffin coating was used on the crystals to avoid decomposition. A crystal with appropriate dimensionsn was chosen and mounted on a glass fiber for X-ray diffraction work.

[K(18-Crown-6)][Cu$_2$I$_3$]:

CuI (0.38 g, 2 mmol) was dissolved in 20 mL of saturated aqueous KI solution to which 20 mL of acetone was added, followed by addition of 0.72 g (2.7 mmol) of 18-crown-6 in 20 mL of acetone. The resulting solution was allowed to react under reflux for 3 h, then cooled slowly to room temperature and filtered. Colorless needles formed after evaporation of the filtrate at -5°C for about 120 h. The crystals did not give emission at ambient temperature when examined under a UV radiation source. A crystal with a suitable size, after being coated with liquid paraffin, was glued on a glass fiber for use in structural determination studies.

[K(Dicyclohexano-18-Crown-6)]$_2$[Cu$_2$Cl$_4$]:

Dicyclohexano-18-crown-6 (0.37 g, 1 mmol) and CuCl (0.10 g, 1 mmol) were dissolved, respectively, in 20 mL of acetone and 20 mL of saturated aqueous KCl solution. To the mixture of the two solutions, 15 mL of H_2O was added, followed by addition of ascorbic acid, forming a clear solution containing small amount of undissolved CuCl. The mixture was heated under reflux for 5 h, then allowed to cool to room temperature. Colorless tetragonal crystals were noticed to form after evaporation of the filtrate at room temperature for about 72 h. When excited under UV radiation (254 nm) at room temperature, the dry crystals emitted light yellow. One of crystals coated with liquid paraffin was chosen and affixed on a glass fiber for use in X-ray diffraction analysis.

[K(Benzo-15-crown-5)$_2$]$_2$[Cu$_2$I$_4$]:

CuI (0.38 g, 2 mmol) was dissolved in 20 mL of saturated aqueous KI solution to which 10 mL of ethanol was added. The resulting solution was mixed with benzo-15-crown-5 (0.53 g, 2 mmol) in 25 mL of ethanol, giving a colorless solution, which was allowed to react under reflux for 5 h, then cooled slowly to room temperature and filtered. Light brown needle crystals were noticed to form after evaporation of the filtrate at room temperature for about 72 h. The crystalline compound emitted blue light when observed in a UV lamp box

(254 nm) at room temperature. Liquid paraffin was employed on the crystals to prevent them from decomposition. A crystal with appropriate dimensions was mounted on a glass fiber for X-ray diffraction experiments.

$[K(12\text{-crown-}4)\text{-}H_2O]_2[Cu_4I_6]$:

CuI (0.38 g, 2 mmol) was dissolved in 20 mL of saturated aqueous LiI solution, giving a suspension to which 1 mL (6 mmol) of 12-crown-4 and 20 mL of acetone were added, followed by addition of ascorbic acid, resulting in a light yellow solution. The resulting solution was allowed to react under reflux for 4 h, then cooled slowly to room temperature and filtered. Colorless hexagonal plates were observed to form after evaporation of the filtrate at room temperature for about five days. No emission from the crystals was observed in a UV lamp box at room temperature. With the use of liquid paraffin as coating on the crystal surface, a crystal with appropriate dimensions was mounted on a glass fiber for use in structural studies by X-ray diffraction.

$[K(\text{Dicyclohexano-}18\text{-crown-}6)]_2[Cu_2Br_4]$:

Dicyclohexano-18-crown-6 (0.37 g, 1 mmol) was dissolved in 20 mL of acetone and 0.14 g (1 mmol) of CuBr in 20 mL of saturated aqueous KBr solution. When the two solutions were mixed, a light pink solution with some white solid formed. To the pink solution, 10 mL of H_2O was added, followed by addition of ascorbic acid, giving a colorless solution. The solution was heated under reflux to allow reaction to proceed for 5 h, then cooled to room temperature. Some white solid precipitated from the solution upon cooling to room temperature. The solution was filtered and the filtrate gave colorless tetragonal crystals after evaporation at room temperature for about 72 h. Yellow light was emitted by the crystals under excitation of UV radiation (254 nm) at ambient temperature. Liquid paraffin was put onto a crystal of suitable size, which was mounted on a glass fiber for X-ray diffraction determination of the structure.

[1, 4, 8, 11-Tetraazacyclotetradecane][CuI]:

1, 4, 8, 11-Tetraazacyclo-tetradecane (0.20 g, 1 mmol) and CuI (0.19 g, 1 mmol) were dissolved, respectively, in 20 mL of acetone and 20 mL of saturated aqueous NaI solution. A black-purple solution formed when the two colorless solutions were mixed. The resulting solution was allowed to react under reflux for 3 h, then cooled to room temperature and filtered. Purple rectangular crystals precipitated upon evaporation of the filtrate slowly at room temperature over a 72-h period. When excited under UV light (254 nm) at ambient temperature, the dry crystals did not emit. The crystal surfaces were coated with liquid paraffin to guard against decomposition. A crystal with appropriate dimensions was mounted on a glass fiber for use in structural analysis by X-ray diffraction.

$[N(C_6H_5)(CH_3)_3]_4[Cu_6Br_{10}]$:

$[N(C_6H_5)(CH_3)_3]Cl$ (0.34 g, 2 mmol) and CuBr (0.29 g, 2 mmol) were individually dissolved in two portions of 20 mL of ethanol. Mixing the two solutions gave a colorless solution containing small amount of undissolved CuBr. Some copper powder was added to the solution to insure the presence of Cu(I). The mixture was allowed to react under reflux in a nitrogen atmosphere for 5 h, then cooled to room temperature and filtered. Light yellow needle crystals formed after the filtrate cooled to -5°C for 120 h. No emission was oberved when the crystals were examined in a UV lamp box at room temperature. Liquid paraffin was employed on the crystals to keep them from decomposition. A crystal with appropriate dimensions was mounted on a glass fiber for X-ray diffraction experiments.

$[N(C_3H_7)_4]_2[Cu(II)_2Cl_6]$:

$[N(C_3H_7)_4]Cl$ (2.0 g, 9 mmol) was dissolved in 40 mL ethanol. To the resulting solution, 0.25 g (2.5 mmol) of CuCl were added, followed by the addition of some ascorbic acid, resulting in a clear solution. The solution was allowed to react under reflux in a nitrogen atmosphere for 5 h, then cooled to room temperature and filtered. Light brown rhombohedral crystals formed after the filtrate evaporated slowly at room temperature for 1 month. The crystals did not emit when excited by UV radiation at ambient temperature. A crystal of an appropriate size, coated with liquid paraffin to avoid decomposition, was mounted on a glass fiber for use in the structural deterrmination.

$[Na(15\text{-crwon-}5)]_2[Na(15\text{-crwon-}5)\text{-}H_2O]_2[Cu_2I_4][Cu_2I_3]$:

CuI (0.76 g, 4 mmol) was dissolved in 20 mL of saturated aqueous NaI. To the resulting solution, 2 mL (10 mmol) of 15-crown-5 was added, followed by addition of 30 mL of acetone, giving a colorless solution containing small amount of undissolved CuI. The mixture was allowed to react under reflux for five hours, then cooled to room temperature, filtered. Colorless needles were noticed to form after the filtrate cooled to -5°C for about 72 h. The crystalline compound did not give emission at room temperature upon observation in a UV lamp box. With the use of liquid paraffin as a coating on exterior surfaces, a crystal with appropriate dimensions was mounted on a glass fiber for use in X-ray investigation.

$[N(C_6H_5)(CH_3)_3]_3[Cu_3I_6]$:

$[N(C_6H_5)(CH_3)_3]I$ (0.26 g, 1 mmol) and CuI (0.19 g, 1 mmol) were added to 10 mL of diethylene glycol. The resulting mixture was heated until the solid material dissolved. The liquid was allowed to cool to room temperature, and 30 mL of acetone were added. The resulting solution was heated under reflux for 4 h, then cooled to room temperature, and filtered. Light yellow rhombic crystals were seen to form after evaporation of the filtrate at 5°C for 48 h. Emission of orange was observed when the crystals were examined at room temperature in a UV lamp box (254 nm). Liquid paraffin coating was employed on the crystals to guard against decomposition. A crystal with appropriate dimensions was glued on a glass fiber for X-ray structure determination.

CRYSTALLOGRAPHY

Crystals with appropriate dimensions ($\leq$0.5 mm in all dimensions) of each compound were chosen for X-ray diffraction. A single crystal of good quality was mounted on a Siemens P4 automated four-circle diffractometer equipped with a PC-486DX computer, and molybdenum radiation ($\lambda = 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.[84] The intensity data were collected at room temperature using a variable scan rate, a θ - 2θ scan mode and a scan range of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value (normally 50.0°). 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 reflections. The raw intensity data collected were corrected for Lorentz, polarization, decomposi tion, centering, and background effects, after the redundant and space group forbidden data were removed. Observed reflections ($I>4.0\ F(I)$) were used to search for a solution of the non-hydrogen atom positions by direct methods.[95-97] Refinement of the scale factor, positional and anisotropic thermal parameters for all atoms was carried out by either XLS[83] or SHELXL[98] to convergence. Scattering factors were taken from the International Tables for Crystallography.[99] Hydrogen atom positions were calculated by using idealized geometry. The profile fitting technique for data reduction was employed when necessary. Furthermore, an empirical absorption correction was applied in the final stages to improve the refinement. A weighting scheme ($w = (\sigma^2(F)+\mathrm{abs}(g)F^2)^{-1}$)* and extinction correction were employed at the last stages of refinement. Final refinement led to the agreement factor R ($R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$).

FLUORESCENCE

Emission spectra of all compounds were measured using an Oriel modular spectrofluorometer. The sample was prepared as a finely ground powder spread on double-sided tape attached to a 0.5 × 1.5 inch glass plate. A Xe lamp was used as the light source. Measurements were made from 350-700 nm at 0.2 nm intervals with a scan speed of 1 nm/sec at temperatures: 10, 25, 50, 75, 125, 175, 225, and 275K (some samples were measured at 10K and room temperature).

The emission spectrum was obtained by irradiating the sample at the wavelength of maximum absorption and observing the emitted fluorescence

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* If $g<0$, its absolute value is refined. Positive or zero g gives a fixed weighting scheme.

with a scanning monochromator which gave a plot of intensity versus wavelength. The absorption spectrum was obtained by plotting the intensity of the maximum fluorescence emission as the wavelength of the exciting radiation was changed.

Data were corrected for inhomogeneities of monochromator performance and window transmission before plotting. Intensity scales are reported in arbitrary units due to lack of standardization of sample preparation.

CHAPTER V

RESULTS AND DISCUSSION

This study has focused on the solid state anionic linear Cu(I) complexes, $[CuX_2]^-$, and their emission. Correlation of crystallographic symmetry and emission of $[CuX_2]^-$ was sought. During the course of this study, twenty-six new anionic cuprous complexes have been synthesized and structurally characterized by single crystal X-ray diffraction. Of the complexes prepared, thirteen are linear dicoordinate $[CuX_2^-][L^+]$ species, (where L^+ = quaternary or other cation). The other complexes are non $[CuX_2]^-$ Compounds and of the following types: $[Cu_2X_4]^{-2}$, $[Cu_2X_3]^-$, $[Cu_3X_6]^{-3}$, $[Cu_4X_6]^{-2}$, $[Cu_6X_{10}]^{-4}$, etc. Four of these have been submitted for publication.[100-103] Complete crystallographic data and results for all complexes prepared in this study are presented in Tables 8-136. Emission study was carried out for $[CuX_2]^-$ complexes only.

Among non $[CuX_2]^-$ complexes, $[(Bu_4N)_2][Cu_2I_4]$, $[(Ph_4N)_2][Cu_2I_4]$, [K(DC18-Crown-6)-acetone]$_2$$[Cu_2I_4]$, [K(Benzo-15-Crown-5)$_2$]$_2$$[Cu_2I_4]$, [K(DC-18-Crown-6)]$_2$$[Cu_2Br_4]$, [K(DC18-Crown-6)]$_2$$[Cu_2Cl_4]$, [(Propyl)$_4$N]$_2$[Cu(II)$_2Cl_6$] are observed to have a planar rhombohedron in which two trigonal planar copper atoms, each of which is bonded to a terminal halogen atom, are bridged by two halogen atoms. [K(DC18-Crown-6)]$_2$$[Cu_4I_6]$ shows octahedral geometry within Cu_4I_6 cluster, but the Cu atoms are disordered. The disorder takes the form of eight half occupancy positions to account for the four copper atoms. These disordered positions form the corners of a cube which then shows each of the six iodine atoms centered above one cage of the cube. However, at any one time, only alternate copper atoms are present. [Li(12-

Crown-4-H_2O)]$_2$[Cu_4I_6] possesses a polymeric chain of edge-sharing rhombohedra in which the tetrahedral copper atoms of every second rhomb are bridged by an additional iodine atom. [Na(15-Crown-5)]$_2$[Na(15-Crown-5)-H_2O]$_2$[Cu_2I_4][Cu_2I_3]$_2$ crystallizes with two different copper(I) halide motifs in the unit cell: a polymer of edge-sharing rhombohedra and a discrete planar rhombohedron. In [1,4,8,11-Tetraazacyclotetradecane][CuI], Cu is bonded to four N atoms of the 1,4,8,11-Tetraazacyclotetradecane ring to form a cation, which has iodine atom as its counterion. [$PhMe_3N$][Cu_6Br_{10}] has been found to contain a centrosymmetric eight membered ring of alternating copper(I) and bromine atoms fused to two six membered rings of alternating Cu and Br atoms. A terminal bromide atom is attached to one copper atom of each of the six membered rings. [$PhMe_3N$][Cu_3I_6] exists as an isosceles triangle of three copper atoms each bound to a terminal iodide atom. Copper atoms at the unique edge are bridged by an iodide atom and the triangle is capped on both faces by two additional iodine atoms.

The linear complexes, [CuX_2^-][L^+], were found to crystallize with two different internal symmetry elements: a center of symmetry or a 2-fold rotation axis symmetry and without internal symmetry (internal mirror symmetry is also possible in [CuX_2]$^-$ cluster[50], but no complex of this type was obtained in this study). The large number of [CuX_2^-][L^+] compounds with different symmetry elements provide an opportunity to examine the effect of an internal symmetry element on the emission spectra of the cuprous halide in a systematic way.

A tabulation of Cu-X bond distances, X-Cu-X angles for the linear complexes is shown in Table 4. The copper atoms in the [CuX_2^-][L^+] complexes are dicoordinate with each copper atom bound to two halogen atoms. X-Cu-X is nearly linear in all compounds, and is constrained to be exactly linear in the presence of a center of symmetry. The average Cu-X distances for I, Br and Cl are 2.372(1) Å, 2.213 Å and 2.063 Å, respectively. The average Cl-Cu-Cl angle for the compounds without center of symmetry is 175.6(2)°, whereas that of Br-Cu-Br is 175.1(1)°.

The presence or absence of two-fold axes or inversion centers seems not to influence the Cu-X distances and X-Cu-X angles appreciably. In the complexes, [K-(18-crown-6)][$CuBr_2$], [K-(dicyclohexano-18-crown-6)][$CuBr_2$], [K-(18-crown-6)][$CuCl_2$] and [K-(dicyclohexano-18-crown-6)][$CuCl_2$], the halogen atoms of $[CuX_2]^-$ are possibly within interactive distance of positively

TABLE 4

THE Cu-X BOND DISTANCES AND X-Cu-X ANGLES
IN [CuX_2^-][L^+] COMPLEXES

Compound	Cu-X distance(Å)	X-Cu-X angle(°)	Cu-X ave.(Å)	X-Cu-X ave.(°)
center of symmetry				
[$(Pentyl)_4N$][CuI_2]	2.371(1)	180		
	2.374(1)	180		
			2.372(1)	180
[$(Butyl)_4N$][CuIBr]	2.277(6),2.254(10)	180		
[$(Pentyl)_4N$][$CuBr_2$]	2.207(1)	180		
[K-(18-crown-6)][$CuBr_2$]	2.224(1)	180		
[K-(DC-18-crown-6)][$CuBr_2$]	2.218(3)	180		
			2.236(4)	180
[K-(18-crown-6)][$CuCl_2$]	2.093(3)	180		
[K-(DC-18-crown-6)][$CuCl_2$]	2.085(2)	180		
			2.089(2)	180
2-fold axis symmetry				
[$(Ph_3P)_2N$][$CuCl_2$]	2.025(4)	175.8(3)	2.025(4)	175.8(3)
no internal symmetry				
[Ph_4As][$CuBr_2$]	2.199(2),2.209(2)	173.6(1)		
[$(Propyl)Ph_3P$][$CuBr_2$]	2.220(7),2.207(8)	177.1(4)		
[He_4N][$CuBr_2$]	2.195(2),2.210(2)	174.7(1)		
			2.190(4)	175.1(2)
[$(Hexyl)_4N$][$CuCl_2$]	2.084(3),2.073(4)	176.0(2)		
[Ph_4P][$CuCl_2$]	2.079(4),2.068(4)	174.7(1)		
			2.076(4)	175.4(2)

charged potassium atoms, X···K distances being 3.420(2) and 3.295(2) Å for K···Br and K···Cl, respectively. The interaction between X and K is weak and does not affect the linearity of $[CuX_2]^-$ in these compounds.

Fifteen previously known $[CuX_2]^-$ were remade according to methods described in the literature[13,16,50,58] to increase the numbers of complexes included in the emission study. A comparison of the cell dimensions of these crystalline compounds prepared in this laboratory with those values in the literature was made to verify the identities of the compounds. Table 5 shows these comparisons. Complete crystal structure determinations were not carried out for these compounds. Structural information from the literature was used to identify the presence of absence of symmetry elements.

Emission spectra for all $[CuX_2^-][L^+]$ complexes, including those resynthesized from the literature, were measured over the temperature range 10K to 298K with excitation at 250 (some other wavelengths are used for few compounds) and 300 nm. Emission spectra were recorded in the visible range from 350-700 nm using a long pass filter to screen out radiation at the wavelengths lower than 345 nm including excitation beam scattered by the sample. Data were corrected for monochromator response, and inhomogeneities of transmission of the emitted beam at various wavelengths. It has been shown from the emission spectra that those compounds containing benzene rings in the cation do not emit, while those without benzene rings emit at the range of 465-515 nm. The presence or absence of a specific symmetry element seemed not to affect the maximum emission wavelength noticeably. The summary of emission of the compounds, along with their space groups and internal symmetry is tabulated in Table 6.

A representative compound was chosen from each category of linear complexes, X=Cl, Br, I and with or without specific symmetry elements, was

TABLE 5

COMPARISON OF CELL DIMENSIONS FOUND WITH LITERATURE VALUES

Compound	a (Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)
$[K(18C6)][CuI_2]$	8.886(5)	8.789(4)	14.135(5)	90.0	104.03(4)	90.0
	8.906(5)	**8.791(4)**	**14.120(5)**	**90.0**	**104.04(3)**	**90.0**
$[K(DC18C6)][CuI_2]$	9.094(3)	9.150(4)	10.810(4)	103.10(3)	93.36(3)	126.92(2)
	9.126(8)	**9.211(6)**	**10.877(5)**	**103.37(5)**	**93.40(6)**	**126.86(4)**
$[(Propyl)_4N][CuBr_2]$	13.000(7)	7.573(4)	8.919(4)	90.0	91.01(4)	90.0
	13.01(2)	**7.577(5)**	**8.858(4)**	**90.0**	**91.01(4)**	**90.0**
$[EtPh_3P][CuBr_2]$	9.753(5)	12.257(3)	9.750(3)	90.0	118.71(3)	90.0
	9.758(2)	**12.220(4)**	**9.767(4)**	**90.0**	**118.70(3)**	**90.0**
$[Bu_4N][CuBr_2]$	13.080(5)	10.222(6)	15.978(7)	90.0	92.67(3)	90.0
	13.059(8)	**10.060(5)**	**15.920(7)**	**90.0**	**92.56(4)**	**90.0**
$[Ph_4P][CuBr_2]$	9.341(1)	18.287(2)	13.577(1)	90.0	102.26(1)	90.0
	9.337(4)	**18.292(6)**	**13.573(4)**	**90.0**	**102.25(3)**	**90.0**
$[Rb(15C5)_2][CuBr_2]$	36.802(8)	13.135(5)	12.317(5)	90.0	95.44(3)	90.0
	36.708(3)	**13.151(3)**	**12.360(7)**	**90.0**	**95.57(5)**	**90.0**
$[Ph_3p_3BrPhP][CuBr_2]$	12.430(7)	21.843(12)	9.702(2)	90.0	104.40(3)	90.0
	12.516(6)	**21.96(2)**	**9.722(2)**	**90.0**	**104.66(3)**	**90.0**
$[Bu_4N][CuBrCl]$	13.068(6)	10.089(5)	15.873(8)	90.0	92.29(4)	90.0
	13.051(5)	**9.942(8)**	**15.859(9)**	**90.0**	**92.72(4)**	**90.0**
$[Bu_4N][CuCl_2]$	13.056(5)	9.979(3)	15.794(8)	90.0	91.87(4)	90.0
	13.055(1)	**9.844(1)**	**15.776(2)**	**90.0**	**92.39(1)**	**90.0**
$[Ph_4As][CuCl_2]$	17.490(6)	17.509(7)	14.577(4)	90.0	90.0	90.0
	17.47(1)	**17.47(1)**	**14.522(7)**	**90.0**	**90.0**	**90.0**
$[(Propyl)_4N]CuCl_2]$	12.570(4)	7.565(4)	8.854(7)	90.0	91.26(5)	90.0
	12.628(3)	**7.587(2)**	**8.869(2)**	**90.0**	**91.39(2)**	**90.0**
$[PhMe_3N][CuCl_2]$	10.012(2)	7.326(1)	8.360(6)	90.0	108.50(4)	90.0
	10.040(4)	**7.360(3)**	**8.378(5)**	**90.0**	**108.32(4)**	**90.0**
$[Rb(15C5)_2][CuCl_2]$	9.095(6)	9.564(4)	8.890(5)	91.60(4)	99.66(5)	73.33(4)
	9.120(3)	**9.520(5)**	**8.889(4)**	**91.44(4)**	**99.68(3)**	**73.18(3)**
$[(Benzyl)Ph_3P][CuCl_2]$	9.539(3)	14.024(3)	17.137(6)	90.0	93.25(3)	90.0
	9.571(2)	**14.000(3)**	**17.093(4)**	**90.0**	**93.29(2)**	**90.0**

Note: plain text ----- experimental values; bold ----- literature values.

TABLE 6

SYMMETRY AND EMISSION OF COMPOUNDS WITH [CuX$_2$]$^-$

Compound	Space Group	Symmetry	λ_{em}
[(Pentyl)$_4$N][CuI$_2$]	P1bar	center	494 nm
[K(18C6)][CuI$_2$]	P1bar	center	483 nm
[K(DC18C6)][CuI$_2$]	P1bar	center	466 nm
[Bu$_4$N][CuIBr]	A2/a	center	492 nm
[K(18C6)][CuBr$_2$]	$P2_1/n$	center	467 nm
[K(DC18C6)][CuBr$_2$]	A2/a	center	466 nm
[Bu$_4$N][CuBr$_2$]	C2/c	center	478 nm
[Bu$_4$N][CuBrCl]	C2/c	center	494 nm
[K(18C6)][CuCl$_2$]	$P2_1/n$	center	493 nm
[Rb(15C5)$_2$][CuCl$_2$]	P1bar	center	514 nm
[Bu$_4$N][CuCl$_2$]	C2/c	center	506 nm
[Pr$_4$N][CuBr$_2$]	P2/n	2-fold axis	470 nm
[Pr$_4$N][CuCl$_2$]	P2/n	2-fold axis	490 nm
[(Ph$_3$P)$_2$N][CuCl$_2$]	Pbcn	2-fold axis	no emission
[Ph$_3$MeN][CuCl$_2$]	$P2_1/m$	mirror symmetry	no emission
[Rb(15C5)$_2$][CuBr$_2$]	C2/c	no symmetry	488 nm
[Ph$_3$EtP][CuBr$_2$]	$P2_1$	no symmetry	no emission
[Ph$_3$PrP][CuBr$_2$]	$P2_1$	no symmetry	no emission
[Ph$_3$p-BrPhP][CuBr$_2$]	$P2_1/n$	no symmetry	no emission
[Ph$_4$P][CuBr$_2$]	$P2_1/c$	no symmetry	no emission
[Ph$_4$As][CuBr$_2$]	$P2_1/a$	no symmetry	no emission
[Ph$_4$P][CuCl$_2$]	I4bar	no symmetry	no emission
[Ph$_4$As][CuCl$_2$]	I4bar	no symmetry	no emission
[BzPh$_3$P][CuCl$_2$]	$P2_1/n$	no symmetry	no emission

used as a model for *ab initio* calculations, using Gaussian 90 and the LANL1NMB basis set.[104] The crystallographic coordinates for the $[CuX_2]^-$ group were converted to orthogonal coordinates and used as the input positional values. Valence electrons for Cu and X atoms were included in the calculation (10 electrons for Cu and 2x8 electrons for X used) with inner core electrons represented by pseudopotentials. Thus a total of 26 electrons were included for the $[CuX_2]^-$ group and the HOMO orbital is number 13. The energy levels of the HOMO, LUMO orbitals as determined by the *ab initio* calculations and their differences are shown in Table 7.

TABLE 7

AB INITIO CALCULATIONS OF $[CuX_2]^-$

Orbitals	No symmetry	1bar	2-fold axis	2-fold axis*	Mirror
		X=I			
LUMO		$0.23301(\pi_u)$ P_xCu**			
HOMO		$-0.17080(\pi_g)$ P_xI			
ΔE		0.40381			
		X=Br			
LUMO	0.24407 P_yCu	$0.24352(\pi_u)$ P_xCu	0.24553 PzCu	0.24417 P_yCu	
HOMO	-0.18021 P_yBr	$-0.18034(\pi_g)$ P_xBr	-0.17998 P_zBr	-0.18023 P_yBr	
ΔE	0.42428	0.42386	0.42551	0.42440	
		X=Cl			
LUMO	0.25226 P_yCu	$0.25036(\pi_u)$ P_xCu	0.25261 P_xCu		0.25006 P_yCu
HOMO	-0.18995 P_yCl	$-0.19029(\pi_g)$ P_xCl	-0.18990 P_xCl		-0.19032 P_yCl
ΔE	0.44221	0.44065	0.44251		0.44038

* Both Cu and Br are on a 2-fold axis

** The molecular orbital is dominated by P_x of Cu

According to the selection rules, there is no restriction on a transition between orbitals for the $[CuX_2]^-$ molecule with an internal 2-fold axis , mirror or lacking internal symmetry elements. A center of symmetry leads to two possible states associated with an orbital, g (even), or u (uneven). Only transitions between orbitals with different symmetries are allowed; g→u, u→g, according to the selection rules. Normally excitation and emission involve transitions between the HOMO and LUMO. When the HOMO and LUMO have the same symmetry, transitions between the HOMO and LUMO are impossible. In order for a transition to occur, emission must occur from an orbital of higher energy than the LUMO leading to emission of a different energy. *Ab initio* calculations on centrosymmetric $[CuX_2]^-$ complexes show that the HOMO has g symmetry, while the LUMO has u symmetry. Thus, the transition between the HOMO and LUMO is allowed although other transitions are forbidden (Figure 8). Therefore, the selection rules do not alter the observed emission in this situation. Since transitions involving the HOMO and LUMO for all $[CuX_2]^-$ complexes are possible, the energy involved in a transition is, thus, dependent only on the difference between the HOMO and LUMO.

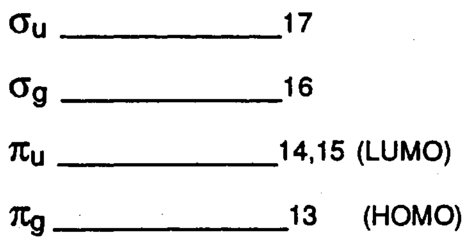

Figure 8. Energy Diagram of Molecular Orbitals for CuX_2^- with Center of Symmetry.

ab initio calculations in this study show that the HOMO orbital is dominated by p orbitals of halogen atoms, whereas the LUMO has a major contribution from the p orbitals of the Cu atoms. This observation suggests that the excitation of a compound occurs by the donor-acceptor pair mechanism, i.e. promotion of an electron from a p orbital of halogen atom of a ligand to a p orbital of the Cu atom.

Several points concerning the experimental results and *ab initio* calculations should be addressed:

1) The differences between the HOMO and the LUMO are similar for all compounds, suggesting that these compounds should emit at about the same wavelengths. This is consistent with the experimental observation, which shows that all compounds which do not contain benzene rings emit at the wavelengths of 465-515 nm.

2) The influence having different halogen atoms was minimal, if not absent. The compounds with I or Br or Cl emit at about same wavelengths. However, there appears to be a trend, according to the *ab initio* calculations, that the energy gap between HOMO and LUMO orbitals becomes smaller when changing a halogen atom from Cl to Br to I, suggesting a compound should emit at longer wavelength when replacing Cl by Br or by I. The differences in maximum emission wavelengths for X=I, Br and Cl were not reliably detected by this study.

3) Compounds containing benzene rings do not emit, regardless of what halide or symmetry element is present in the compounds. The benzene ring seems to serve as a quencher of emission of $[CuX_2]^-$. The absence of emission from these compounds is likely to result from the optical characteristics of the benzene ring systems. However, the presence of a benzene ring in a fluorescent compound does not always keep the compound from emitting. It is interesting to notice that some cuprous halide compounds (in other studies) with motifs other than $[CuX_2]^-$ and possessing benzene rings do emit in the range of 565-630 nm.[15,16] The presence of benzene rings does not quench emission in this case. In order to examine the emission behavior of the ligands containing benzene rings alone, their spectra were measured under the same conditions as those used for the cuprous compounds themselves. The spectra

obtained for the ligands alone did not show profound emission within the detecting ranges (350-700 nm). These experimental results led to the following expalnation.

In the compounds having benzene rings, there exist two competitive absorption sites during the excitation process, $[CuX_2]^-$, the primary center and the benzene-ring, the secondary center. They both will absorb light individually when excited. According to the emission theory, the emission properties of a molecule or a fluorescent center may be greatly affected by the presence of other fluorescent centers present in the same molecule or in the same sample. The quenching of emission from the primary fluorescent center by the secondary one present in the same molecule may be through one of the following three means: i) absorbing the exciting light, thus preventing it from exciting the primary fluorescent center; ii) absorbing the emitted fluorescent light given off by the primary fluorescent center and returning to its own ground state in a radiationless manner; iii) interacting with the excited primary center by means of the energy transfer which leads to loss of energy (not by emitting a photon) from the primary center to the secondary one.

The first way appears not present. If benzene rings absorb exciting light, then there should be no emission observed for the compounds with or without $[CuX_2]^-$.

The second way is possible. Benzene usually shows four principal absorption bands: 185, 207, 259 and 340 nm. The higher energy excitations cause emission in the range of 250-340 nm,[105,106] which is not within the detection range of the fluorometer used in this study. This explains why no emission was observed for ligands containing benzene rings although they are supposed to emit. Besides the four common bands known, benzene and some its derivatives are expected to show a weak, but distinct, absorption band (5th band) at about 520 nm, which is believed to result from the singlet-triplet transitions.[107] The emitted light from the primary center ($[CuX_2]^-$) corresponds to the wavelength of the 5th absorption band of benzene and might therefore be absorbed by benzene rings. The excited benzene system may return to the ground state by emission or by radiationlessly producing heat. The compounds with motifs other than $[CuX_2]^-$ and possessing benzene rings show emission because their emission is in the range of 565-630 nm, which is not within the range of absorption of a benzene ring. Thus, the compounds show normal emission behavior as if no benzene rings are present. The explanation using absorption of 5th band of a benzene ring is, however, not so convincing because this absorption is so weak that the emitted light is not likely to be absorbed within the band.

The third possible way is to transfer energy between the excited molecule of $[CuX_2]^-$ and benzene rings. If there is energy transfer between benzene rings and the excited $[CuX_2]^-$ prior to a photon being given out, the excited $[CuX_2]^-$ would give excess energy by non-emission means to the benzene rings and return to the ground state.

$$([CuX_2]^-)^* + C_6H_6 \rightarrow [CuX_2]^- + (C_6H_6)^*$$

excited state excited state

This energy transfer process would, therefore, quench emission of $[CuX_2]^-$. However, emission from the compounds with motifs other than $[CuX_2]^-$ is not quenched although the same energy transfer process might be still present. The explanation to this is that the energy transfer process is competing with emission process, if the energy transfer process is not efficient enough or not prior to the emission process (it is assumed that it is the case for compounds with motifs other than $[CuX_2]^-$), then the excited molecule would return to the ground state by giving out a photon rather than by other means. This explains why some compounds containing benzene rings emit.

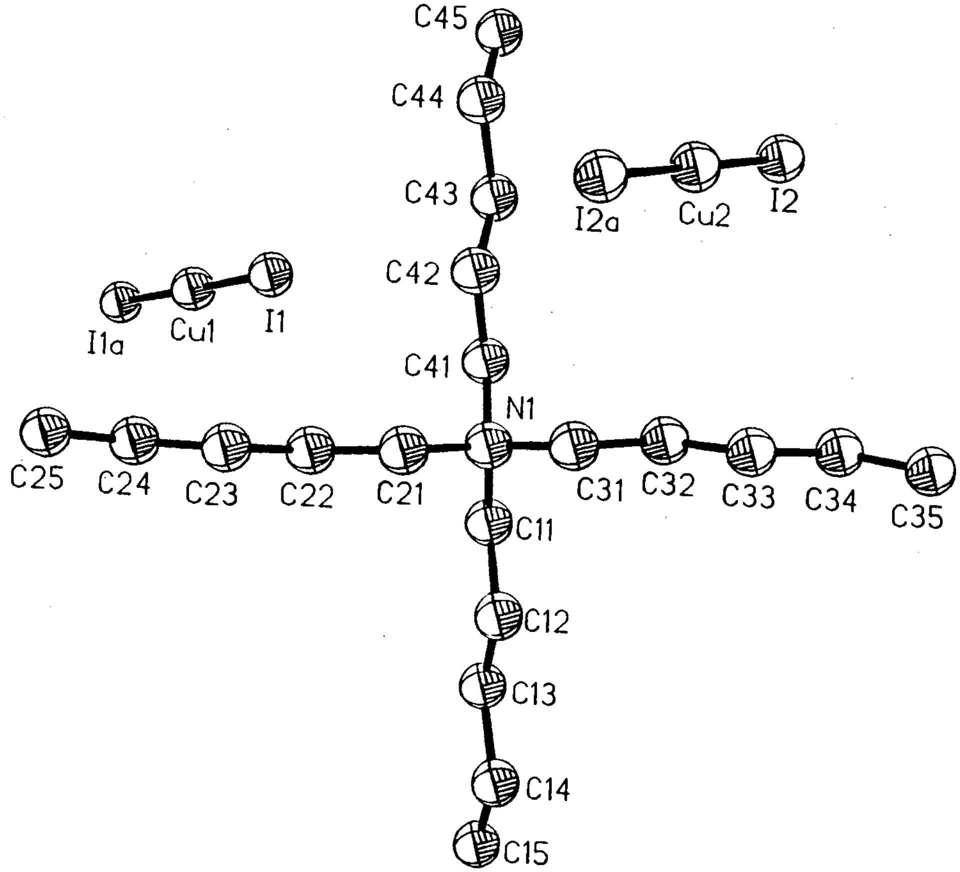

Figure 9. Projection View of [(*n*-Pentyl)$_4$N][CuI$_2$].

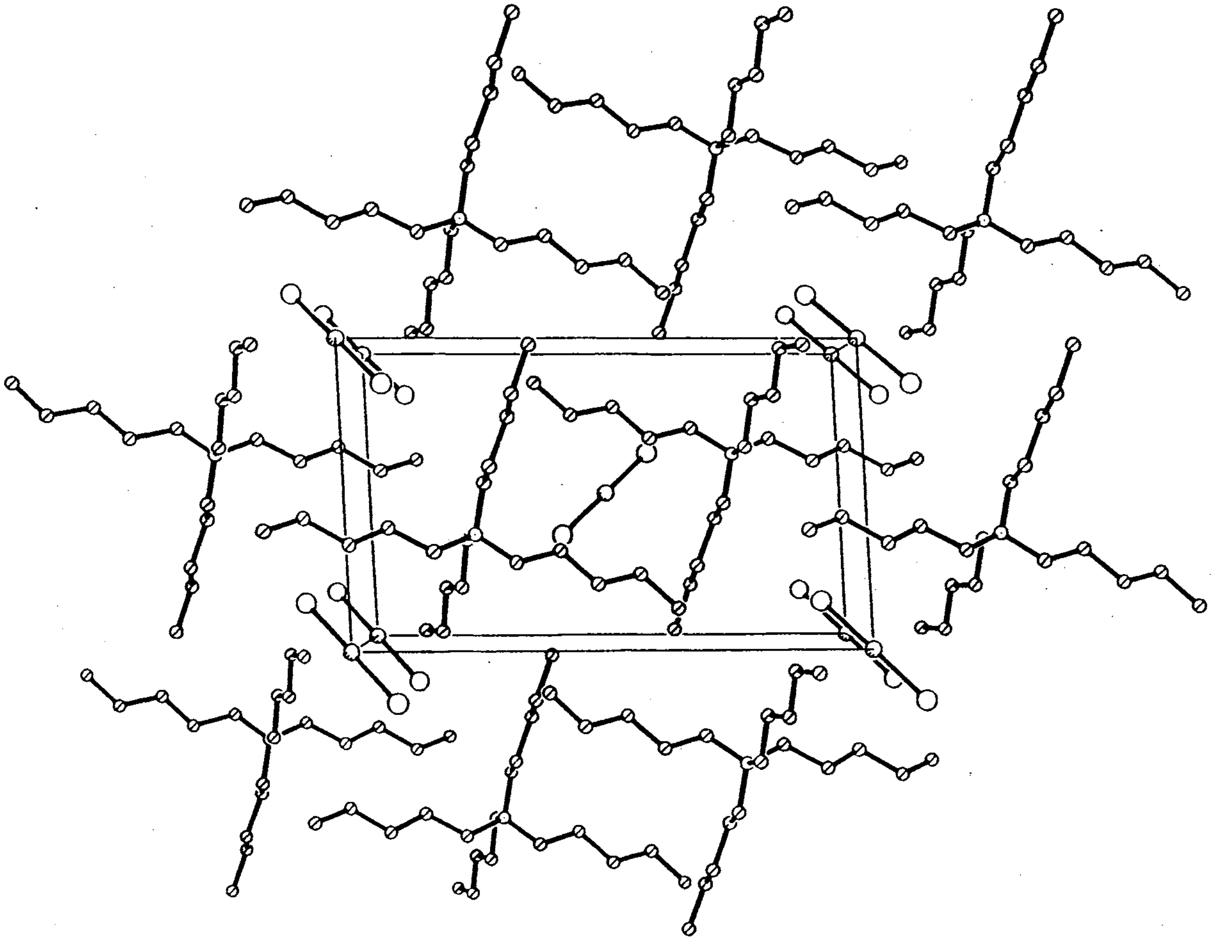

Figure 10. Packing Diagram for [(*n*-Pentyl)$_4$N][CuI$_2$].

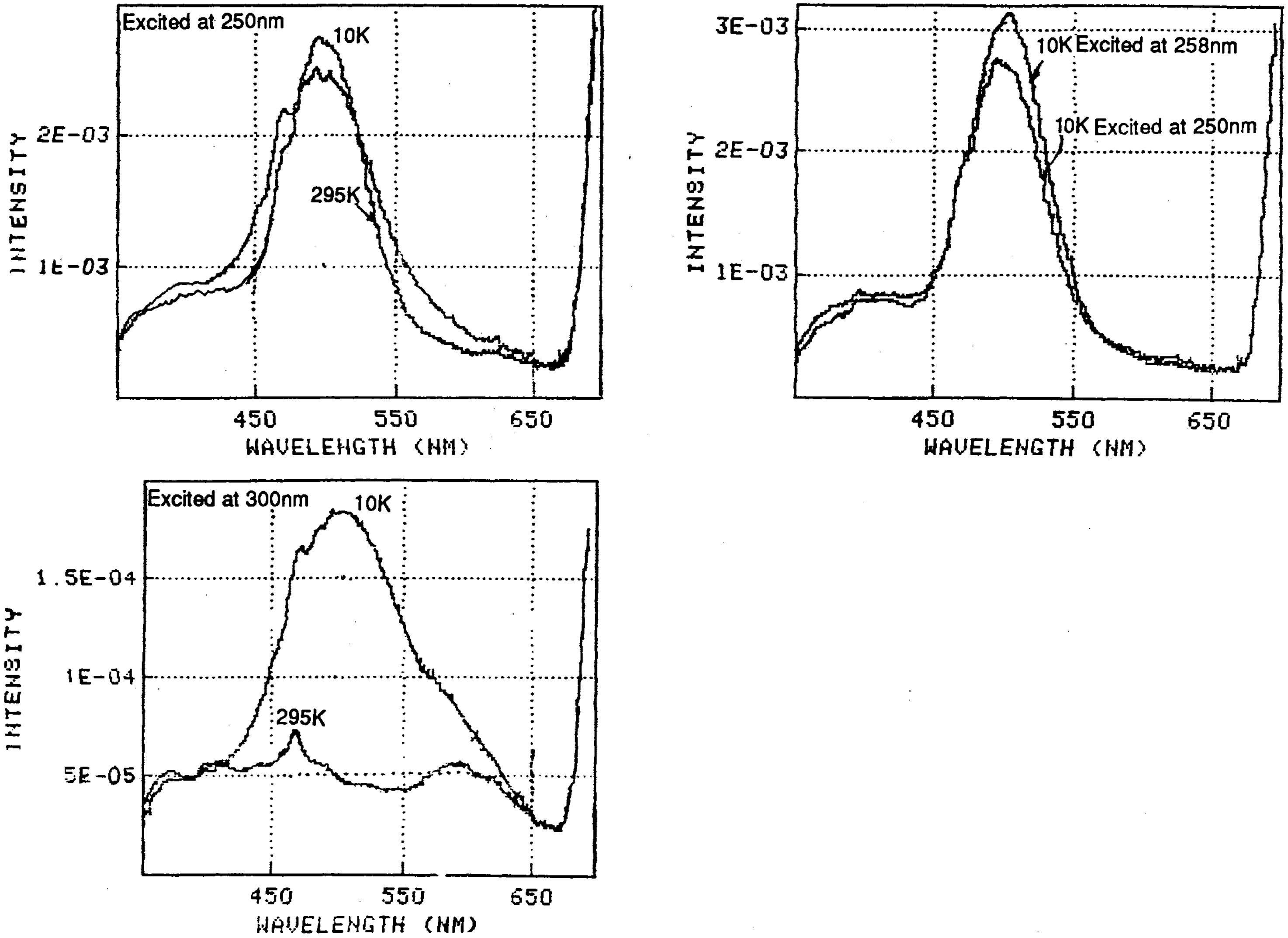

Figure 11. Emission Spectra of [(*n*-Pentyl)$_4$N][CuI$_2$].

TABLE 8

CRYSTAL DATA FOR $[(n\text{-Pentyl})_4N][CuI_2]$

Formula	$CuI_2NC_{20}H_{44}$
MWT	615.93
a	9.332(2) Å
b	15.492(7)
c	9.274(6)
α	93.24(5)°
β	89.75(4)
γ	86.85(3)
V	1336.6(11) $Å^3$
F (000)	612
μMoK_α	31.08 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.530 g cm^{-3}
Z	4
Obs. Refl.	7631
Contribut. Refl.	2484
Variab.	220
R/R_w	5.8/7.2%
Space Group	P1bar
Octants Meas.	±h, +k, ±l

TABLE 9

POSITIONAL PARAMETERS FOR $[(n\text{-Pentyl})_4N][CuI_2]$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	0.1518 (1)	0.0901 (1)	0.1382 (1)
I2	0.3618 (1)	0.5901 (1)	0.3480 (1)
Cu1	0.0000	0.0000	0.0000
Cu2	0.5000	0.5000	0.5000
N1	0.6277 (1)	0.2503 (1)	0.1269 (1)
C11	0.648 (1)	0.229 (1)	-0.032 (1)
C12	0.798 (1)	0.213 (1)	-0.084 (1)
C13	0.806 (1)	0.178 (1)	-0.240 (1)
C14	0.951 (1)	0.164 (1)	-0.304 (1)
C15	0.954 (2)	0.127 (1)	-0.454 (2)
C21	0.679 (1)	0.175 (1)	0.214 (1)
C22	0.606 (1)	0.091 (1)	0.180 (1)
C23	0.656 (1)	0.022 (1)	0.281 (1)
C24	0.576 (1)	-0.061 (1)	0.255 (2)
C25	0.613 (2)	-0.128 (1)	0.354 (2)
C31	0.714 (1)	0.326 (1)	0.179 (1)
C32	0.680 (1)	0.409 (1)	0.108 (1)
C33	0.782 (1)	0.478 (1)	0.155 (1)
C34	0.754 (2)	0.560 (1)	0.077 (1)
C35	0.860 (2)	0.628 (1)	0.113 (2)
C41	0.467 (1)	0.271 (1)	0.149 (1)
C42	0.416 (1)	0.286 (1)	0.302 (1)
C43	0.262 (1)	0.324 (1)	0.305 (1)
C44	0.196 (1)	0.337 (1)	0.454 (1)
C45	0.045 (2)	0.374 (1)	0.454 (2)

TABLE 10

HYDROGEN POSITIONAL PARAMETERS FOR $[(n\text{-Pentyl})_4N][CuI_2]$

ATOM	x	y	z
H111	0.5967	0.1782	-0.0589
H112	0.6070	0.2780	-0.0838
H121	0.8467	0.2635	-0.0736
H122	0.8455	0.1739	-0.0244
H131	0.7595	0.1223	-0.2444
H132	0.7512	0.2179	-0.2969
H141	1.0021	0.2181	-0.2985
H142	1.0119	0.1232	-0.2428
H151	0.9097	0.0709	-0.4586
H152	0.9000	0.1658	-0.5142
H153	1.0513	0.1169	-0.4953
H211	0.7824	0.1630	0.1943
H212	0.6657	0.1904	0.3152
H221	0.5079	0.1011	0.1883
H222	0.6249	0.0714	0.0849
H231	0.7597	0.0083	0.2663
H232	0.6418	0.0442	0.3811
H241	0.4735	-0.0452	0.2635
H242	0.5970	-0.0839	0.1571
H251	0.7196	-0.1429	0.3521
H252	0.5961	-0.1042	0.4585
H253	0.5653	-0.1800	0.3437
H311	0.6999	0.3352	0.2825
H312	0.8157	0.3095	0.1599
H321	0.6812	0.4007	0.0094
H322	0.5855	0.4195	0.1333
H331	0.7743	0.4899	0.2607
H332	0.8811	0.4549	0.1349

TABLE 10 (Continued)

H341	0.7545	0.5464	-0.0258
H342	0.6558	0.5841	0.1049
H351	0.8584	0.6419	0.2198
H352	-0.9570	0.6042	0.0891
H353	0.8410	0.6803	0.0660
H411	0.4412	0.3235	0.0988
H412	0.4159	0.2236	0.1062
H421	0.4221	0.2359	0.3490
H422	0.4748	0.3248	0.3518
H431	0.2613	0.3805	0.2633
H432	0.2054	0.2858	0.2474
H441	0.1985	0.2803	0.4997
H442	0.2563	0.3745	0.5165
H451	0.0434	0.4315	0.4122
H452	-0.0145	0.3372	0.3955
H453	0.0025	0.3829	0.5507

TABLE 11

ANISOTROPIC THERMAL PARAMETERS FOR $[(n\text{-Pentyl})_4N][CuI_2]$

ATOM	U11	U22	U33	U12	U13	U23
I1	820 (7)	763 (6)	1130 (8)	-177 (5)	-165 (6)	-133 (6)
I2	1128 (8)	755 (6)	828 (7)	126 (5)	-165 (6)	159 (5)
Cu1	64 (1)	57 (1)	94 (2)	-4 (1)	-6 (1)	-7 (1)
Cu2	93 (2)	57 (1)	64 (1)	8 (1)	-7 (1)	2 (1)
N1	52 (6)	36 (4)	41 (5)	-2 (4)	-11 (4)	5 (4)
C11	44 (6)	36 (5)	56 (7)	-10 (4)	-3 (5)	6 (5)
C12	69 (8)	58 (7)	47 (7)	-15 (6)	-9 (6)	0 (5)
C13	55 (7)	40 (6)	67 (8)	7 (5)	7 (6)	5 (5)
C14	74 (9)	81 (9)	54 (8)	-8 (7)	0 (7)	-6 (6)
C15	106 (12)	118 (14)	99 (12)	-12 (10)	20 (10)	-41 (10)
C21	43 (6)	38 (5)	49 (6)	4 (4)	0 (5)	10 (4)
C22	63 (7)	45 (6)	67 (7)	0 (5)	-16 (6)	15 (5)
C23	62 (7)	51 (7)	62 (7)	0 (6)	-12 (6)	18 (6)
C24	68 (8)	52 (8)	117 (11)	-8 (6)	-8 (8)	25 (7)
C25	88 (11)	66 (9)	146 (14)	-14 (8)	-8 (10)	41 (9)
C31	49 (6)	54 (6)	45 (6)	-23 (5)	-5 (5)	-2 (5)
C32	62 (7)	53 (7)	63 (7)	-13 (6)	-16 (6)	3 (6)
C33	69 (8)	50 (7)	70 (8)	-19 (6)	-3 (6)	2 (6)
C34	122 (12)	53 (8)	77 (9)	-26 (8)	-20 (8)	16 (7)
C35	156 (15)	65 (9)	81 (10)	-37 (9)	-32 (10)	20 (7)
C41	45 (6)	39 (6)	54 (7)	-8 (5)	0 (5)	6 (5)
C42	60 (8)	59 (7)	55 (7)	2 (6)	-1 (6)	7 (6)
C43	73 (8)	38 (6)	57 (7)	-5 (5)	-11 (6)	-3 (5)
C44	69 (9)	71 (8)	75 (9)	-4 (7)	-3 (7)	14 (7)
C45	87 (11)	131 (15)	100 (12)	39 (10)	12 (9)	22 (10)

The anisotropic displacement exponent takes the form:

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

$\times 10^4$ for I, and $\times 10^3$ for Cu, N and C.

TABLE 12

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[(n\text{-Pentyl})_4N][CuI_2]$

Cu1 - I1	2.371 (1)	I1 - Cu1 - I1'	180
Cu2 - I2	2.374 (1)	I2 - Cu2 - I2"	180
Cu1 - I1'	2.371 (1)	N1 - C11 - C12	116.2 (8)
Cu2 - I2"	2.374 (1)	C11 - C12 - C13	111.7 (9)
N1 - C11	1.50 (1)	C12 - C13 - C14	116 (1)
N1 - C21	1.51 (1)	C13 - C14 - C15	114 (1)
N1 - C31	1.51 (1)	N1 - C21 - C22	115.4 (8)
N1 - C41	1.52 (1)	C21 - C22 - C23	111.1 (9)
C11 - C12	1.48 (2)	C22 - C23 - C24	112 (1)
C12 - C13	1.52 (2)	C23 - C24 - C25	115 (1)
C13 - C14	1.48 (2)	N1 - C31 - C32	115.5 (8)
C14 - C15	1.47 (2)	C31 - C32 - C33	111.9 (9)
C21 - C22	1.53 (1)	C32 - C33 -C34	112 (1)
C22 - C23	1.52 (2)	C33 - C34 - C35	114 (1)
C23 - C24	1.52 (2)	N1 - C41 - C42	116.6 (8)
C24 - C25	1.45 (2)	C41 - C42 - C43	109.6 (9)
C31 - C32	1.50 (2)	C42 - C43 - C44	114 (1)
C32 - C33	1.52 (2)	C43 - C44 - C45	113 (1)
C33 - C34	1.50 (2)		
C34 - C35	1.51 (2)		
C41 - C42	1.50 (2)		
C42 - C43	1.52 (2)		
C43 - C44	1.51 (2)		
C44 - C45	1.50 (2)		

Symmetry operations:

' = -x, -y, -z.
" = 1.0-x, 1.0-y, 1.0-z.

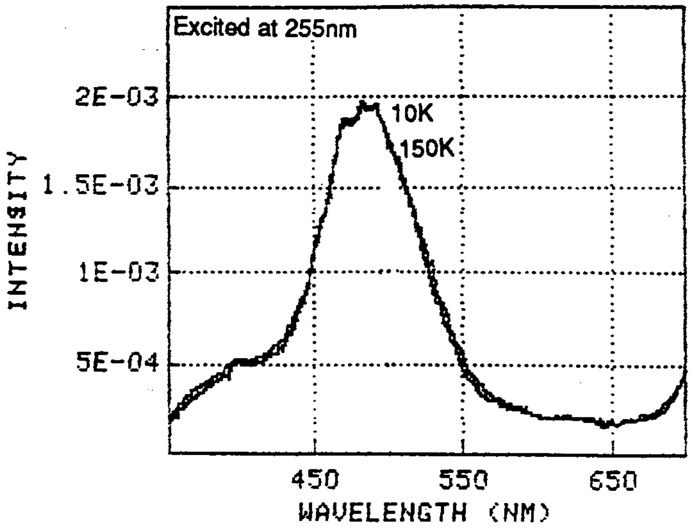

Figure 12. Emission Spectra of [K-(18-Crown-6)][CuI$_2$].

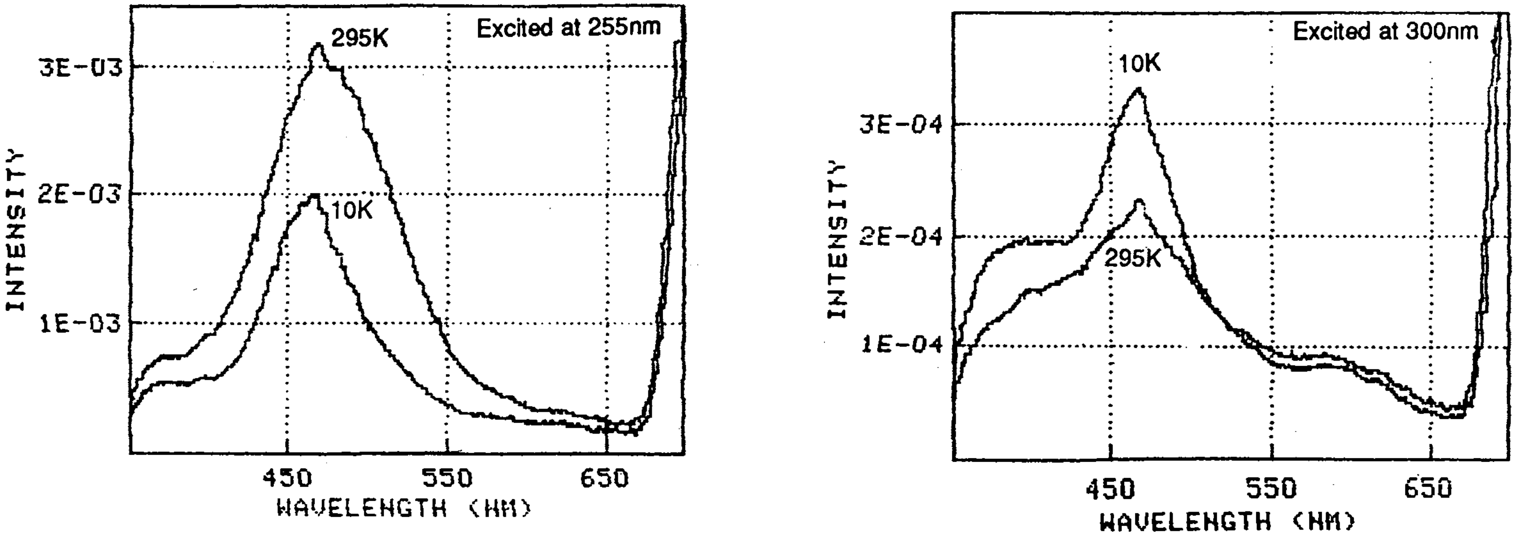

Figure 13. Emission Spectra of [K-(DC18-Crown-6)][CuI_2].

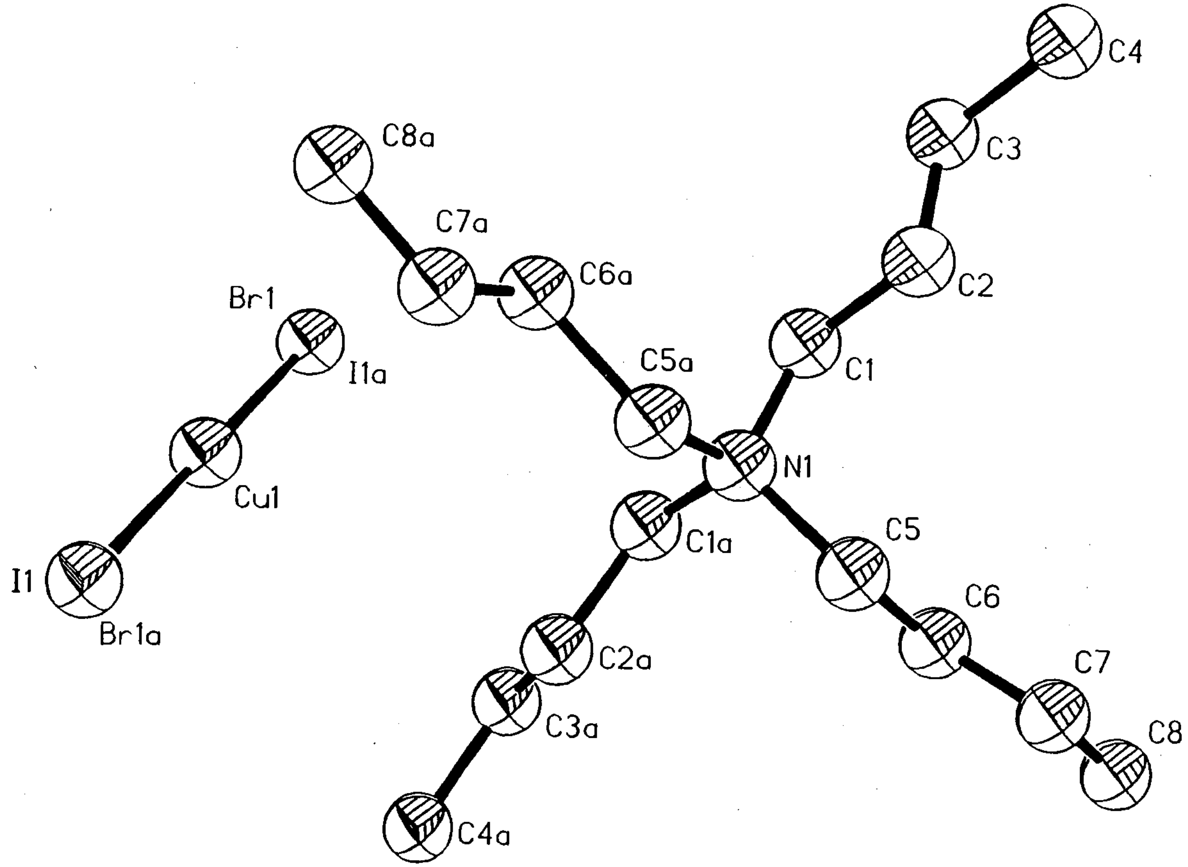

Figure 14. Projection View of [(Butyl)$_4$N][CuIBr].

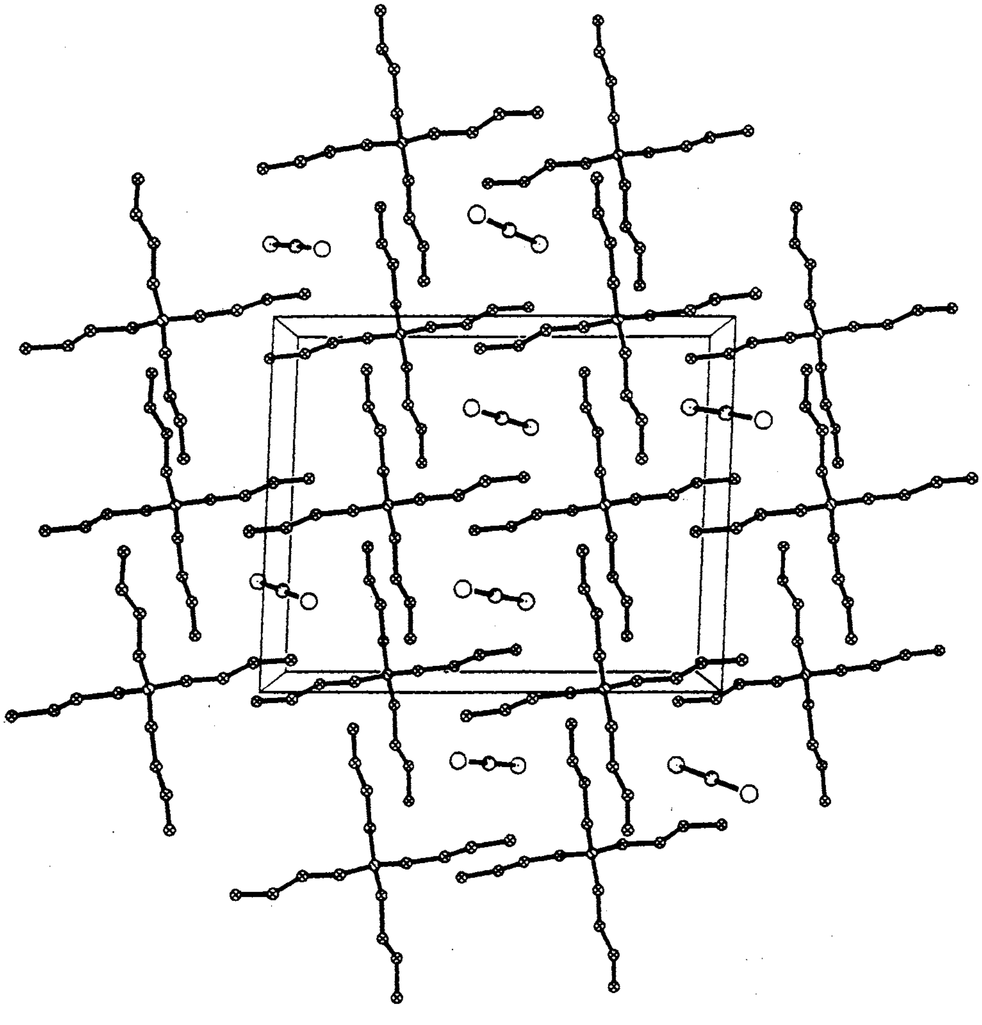

Figure 15. Packing Diagram for [(Butyl)$_4$N][CuIBr].

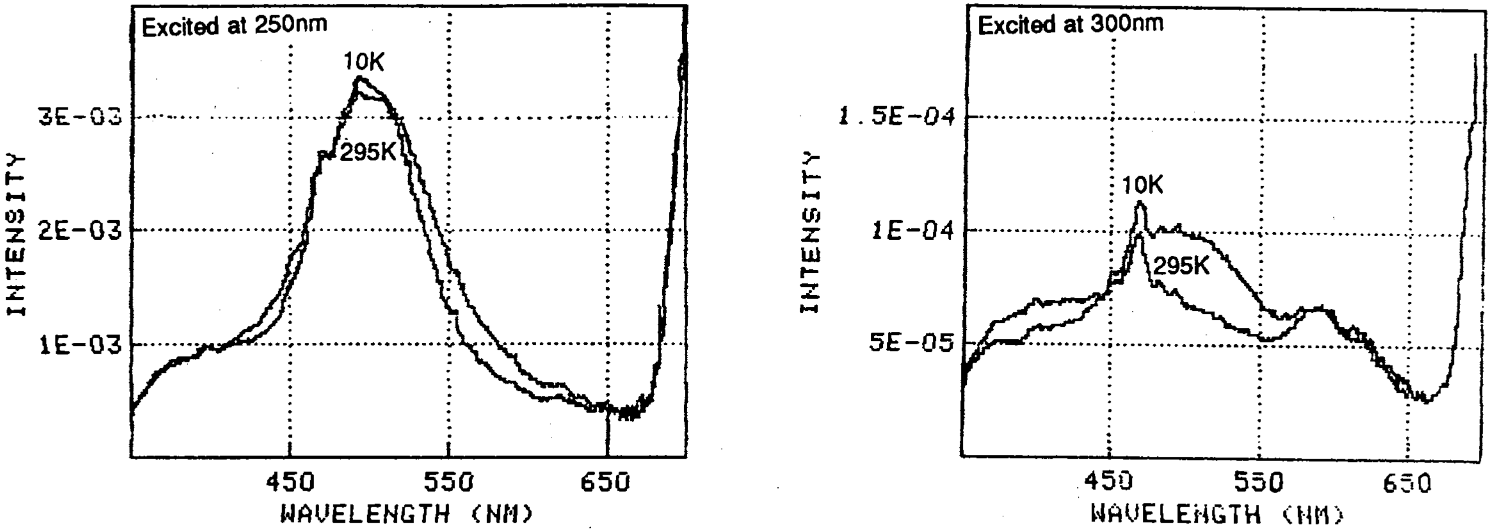

Figure 16. Emission Spectra of [(Butyl)$_4$N][CuIBr].

TABLE 13

CRYSTAL DATA FOR TETRABUTYLAMMONIUM IODOBROMOCUPRATE(I)

Formula	$CuIBrNC_{16}H_{36}$
MWT	512.82
a	16.060(6) Å
b	10.326(4)
c	13.064(3)
α	90.0°
β	92.56(2)
γ	90.0
V	2164.3(13) $Å^3$
F (000)	1024
μMoK_{α}	42.47 cm^{-1}
λMoK_{α}	0.71069 Å
D_{calc}	1.574 g cm^{-3}
Z	4
Obs. Refl.	2882
Contribut. Refl.	588
Variab.	103
R/R_w	5.8/6.6%
Space Group	A2/a
Octants Meas.	±h, +k, +l

TABLE 14

POSITIONAL PARAMETERS FOR TETRABUTYLAMMONIUM IODOBROMOCUPRATE(I)

ATOM	x (SIG (x))	y (SIG (y))	(SIG (z))
Cu1	0.5000	0.2500	0.2500
I1	0.4288 (4)	0.4391 (6)	0.2255 (6)
Br1	0.5708 (6)	0.0628 (10)	0.2719 (8)
N1	0.7500	0.353 (2)	0.5000
C1	0.824 (1)	0.265 (1)	0.484 (1)
C2	0.909 (1)	0.329 (1)	0.473 (1)
C3	0.968 (1)	0.231 (2)	0.436 (1)
C4	1.054 (1)	0.297 (2)	0.425 (1)
C5	0.766 (1)	0.441 (2)	0.594 (1)
C6	0.774 (1)	0.372 (1)	0.706 (1)
C7	0.806 (1)	0.467 (2)	0.775 (1)
C8	0.811 (1)	0.405 (2)	0.875 (2)

TABLE 15

HYDROGEN POSITIONAL PARAMETERS FOR TETRABUTYLAMMONIUM IODOBROMOCUPRATE(I)

ATOM	x	y	z
H11	0.8306	0.2036	0.5414
H12	0.8137	0.2130	0.4213
H21	0.9044	0.4061	0.4246
H22	0.9304	0.3694	0.5394
H31	0.9734	0.1583	0.4836
H32	0.9483	0.1963	0.3689
H41	1.0513	0.3684	0.3762
H42	1.0764	0.3304	0.4909
H43	1.0927	0.2309	0.4007
H51	0.8149	0.4941	0.5837
H52	0.7173	0.5045	0.5945
H61	0.7182	0.3377	0.7165
H62	0.8105	0.2974	0.6926
H71	0.8607	0.5004	0.7556
H72	0.7685	0.5439	0.7768
H81	0.7582	0.3730	0.8987
H82	0.8505	0.3295	0.8774
H83	0.3420	0.4666	0.9285

TABLE 16

ANISOTROPIC THERMAL PARAMETERS FOR TETRABUTYLAMMONIUM IODOBROMOCUPRATE(I)

ATOM	U11	U22	U33	U12	U13	U23
I1	53 (4)	44 (2)	106 (6)	15 (3)	29 (3)	-22 (4)
Br1	117 (7)	198 (11)	109 (7)	-27 (6)	-39 (4)	-18 (7)
Cu1	61 (2)	99 (3)	81 (2)	-7 (2)	-3 (2)	-21 (2)
N1	4 (1)	6 (1)	4 (1)	0	0 (1)	0
C1	8 (1)	5 (1)	4 (1)	2 (1)	1 (1)	-2 (1)
C2	4 (1)	7 (1)	5 (1)	2 (1)	0 (1)	0 (1)
C3	7 (1)	9 (1)	6 (1)	0 (1)	2 (1)	1 (1)
C4	4 (1)	11 (2)	9 (1)	1 (1)	0 (1)	3 (1)
C5	4 (1)	6 (1)	8 (1)	0 (1)	0 (1)	-3 (1)
C6	7 (1)	5 (1)	3 (1)	1 (1)	-1 (1)	0 (1)
C7	8 (1)	8 (1)	3 (1)	2 (1)	-1 (1)	0 (1)
C8	9 (1)	22 (3)	7 (1)	-1 (2)	-1 (1)	-5 (2)

The anisotropic displacement exponent takes the form:

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

x 10^3 for I, Br and Cu, and x 10^2 for N and C.

TABLE 17

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR TETRABUTYLAMMONIUM IODOBROMOCUPRATE(I)

Cu1 - I1	2.277 (6)	I1 - Cu1 - I1'	179.9 (4)
Cu1 - Br1	2.254 (10)	Br1 - Cu1 - Br1'	179.8 (7)
I1 - Br1'	0.040 (12)	I1 - Cu1 - Br1	179.2 (1)
Br1 - I1'	0.040 (12)	I1' - Cu1 - Br1'	179.2 (1)
N1 - C1	1.52 (2)	I1 - Cu1 - Br1'	0.8 (3)
N1 - C5	1.53 (2)	Br1 - Cu1 - I1'	0.8 (3)
C1 - C2	1.52 (2)	C1 - N1 - C5	111 (1)
C2 - C3	1.48 (2)	C1 - N1 - C1"	107 (1)
C3 - C4	1.55 (2)	C1 - N1 - C5"	110 (1)
C5 - C6	1.52 (2)	C5 - N1 - C5"	107 (1)
C6 - C7	1.49 (2)	C5 - N1 - C1"	110 (1)
C7 - C8	1.45 (3)	C1" - N1 - C5"	111 (1)
		N1 - C1 - C2	118 (1)
		C1 - C2 - C3	109 (1)
		C2 - C3 - C4	109 (1)
		N1 - C5 - C6	116 (1)
		C5 - C6 - C7	109 (1)
		C6 - C7 - C8	110 (1)

Symmetry operations:

' = 1.0-x, 0.5-y, 0.5-z.
" = 1.5-x, y, 1.0-z.

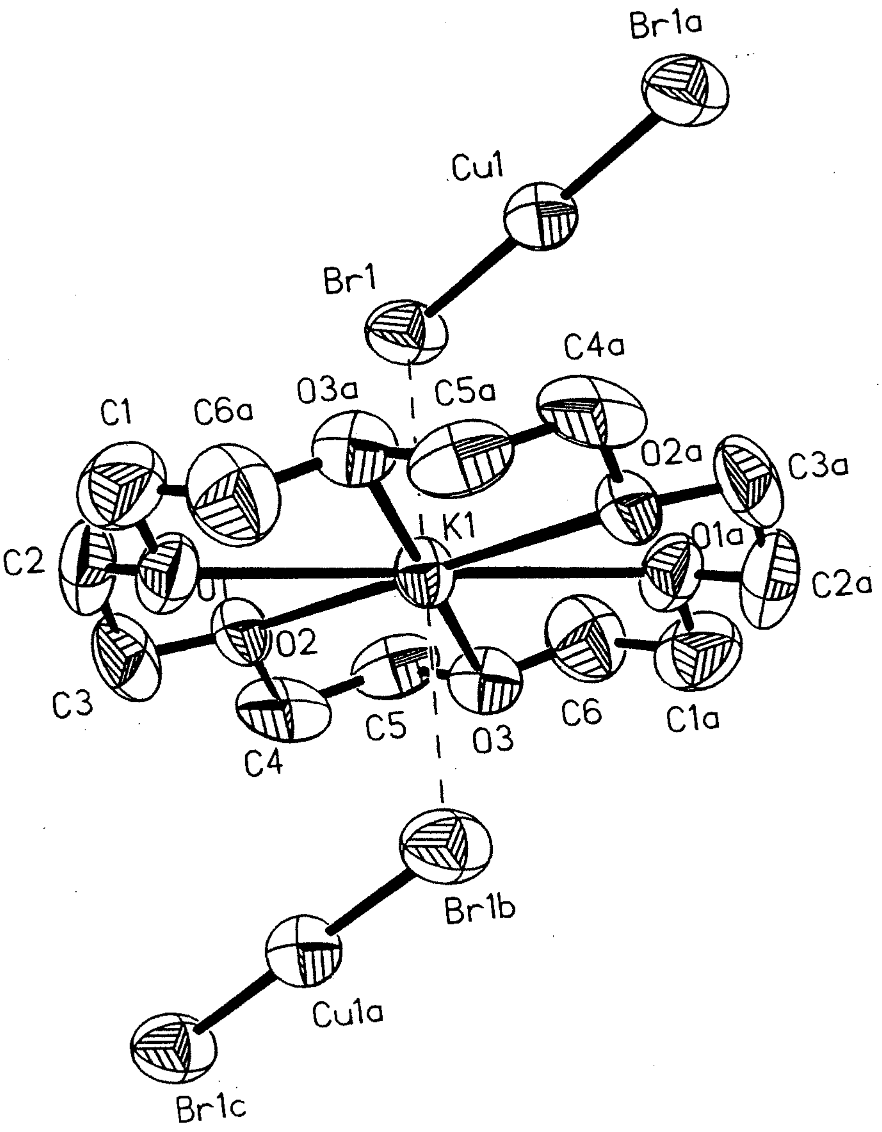

Figure 17. Projection View of [K-(18-Crown-6)][$CuBr_2$].

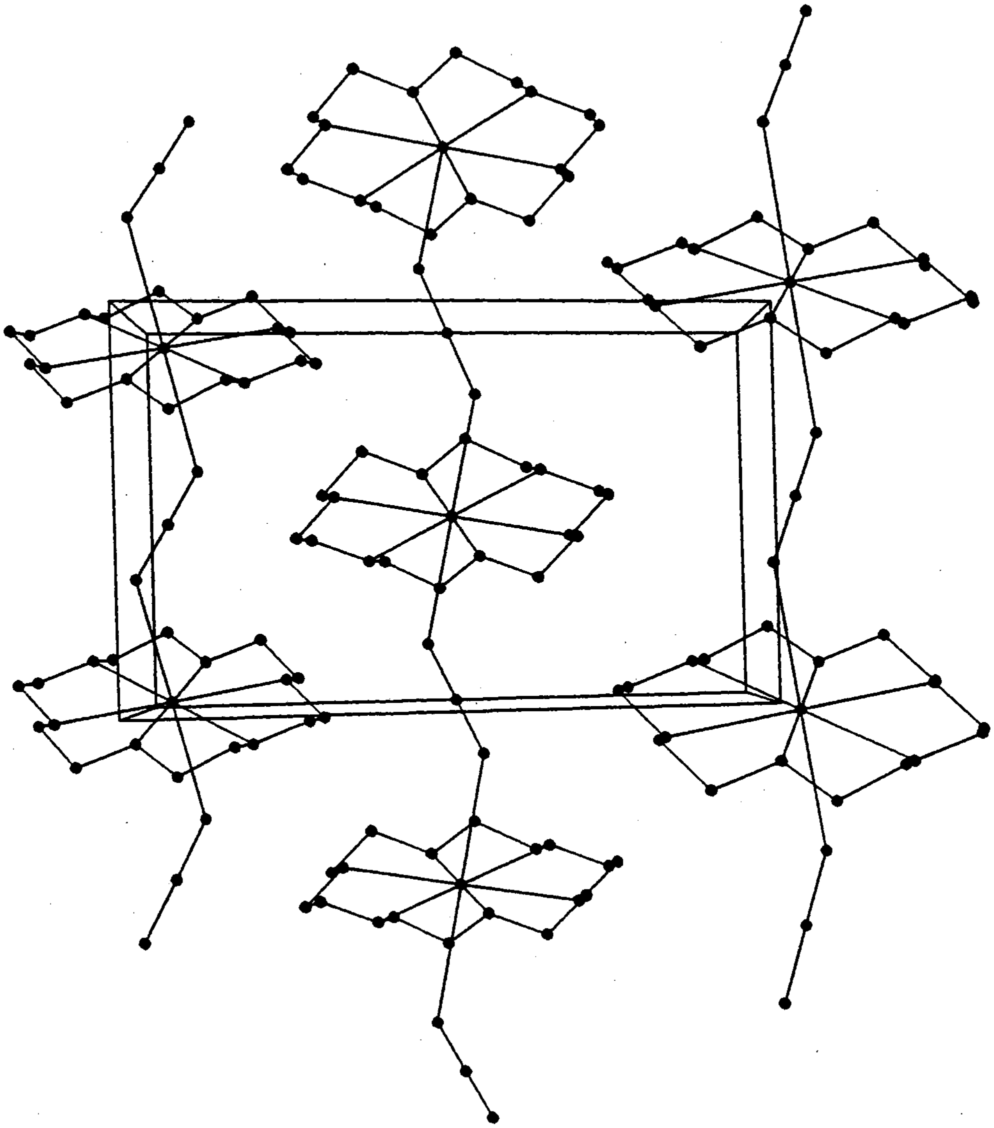

Figure 18. Packing Diagram for [K-(18-Crown-6)][$CuBr_2$].

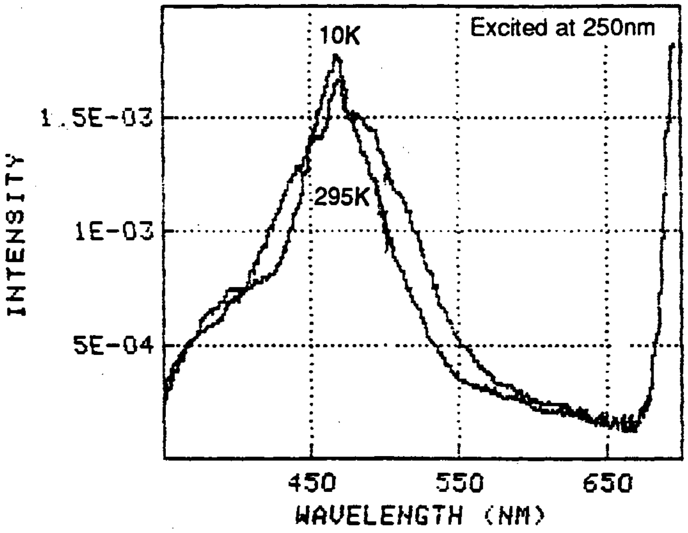

Figure 19. Emission Spectra of [K-(18-Crown-6)][$CuBr_2$].

TABLE 18

CRYSTAL DATA FOR [K-(18-Crown-6)][$CuBr_2$]

Formula	$CuBr_2KC_{12}O_6H_{24}$
MWT	526.8
a	8.769(2) Å
b	8.397(2)
c	13.880(3)
α	90.0°
β	103.04(3)
γ	90.0
V	995.5(4) Å^3
F (000)	524
μMoK_α	53.39 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	1.757 g cm^{-3}
Z	2
Independent Refl.	2275
Obs. Refl. ($F > 4.0\sigma(F)$)	675
Variab.	104
R/R_w	4.2/3.6%
Space Group	$P2_1/n$
Octants Meas.	+h, +k, ±l

TABLE 19

POSITIONAL PARAMETERS FOR [K-(18-Crown-6)][$CuBr_2$]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Br1	0.8236 (1)	0.1562 (2)	0.5453 (1)
Cu1	1.0000	0.0000	0.5000
K1	1.0000	0.5000	0.5000
O1	0.7541 (8)	0.6154 (9)	0.3525 (6)
O2	0.7232 (8)	0.6049 (8)	0.5468 (6)
O3	0.9968 (10)	0.5557 (9)	0.6999 (5)
C1	0.737 (2)	0.555 (2)	0.255 (1)
C2	0.607 (1)	0.617 (2)	0.378 (1)
C3	0.622 (1)	0.693 (1)	0.475 (1)
C4	0.745 (1)	0.667 (2)	0.647 (1)
C5	0.845 (2)	0.555 (2)	0.715 (1)
C6	1.084 (2)	0.448 (2)	0.765 (1)

TABLE 20

HYDROGEN POSITIONAL PARAMETERS FOR $[K\text{-}(18\text{-Crown-}6)][CuBr_2]$

ATOM	x	y	z
H1A	0.8334	0.5796	0.2360
H1B	0.7261	0.4414	0.2583
H2A	0.5761	0.5087	0.3859
H2B	0.5292	0.6670	0.3278
H3A	0.6673	0.7960	0.4701
H3B	0.5226	0.7075	0.4923
H4A	0.6465	0.6835	0.6645
H4B	0.7998	0.7667	0.6513
H5A	0.8451	0.5789	0.7827
H5B	0.7997	0.4514	0.6998
H6A	1.0450	0.3433	0.7469
H6B	1.1904	0.4559	0.7574

TABLE 21

ANISOTROPIC THERMAL PARAMETERS FOR [K-(18-Crown-6)][$CuBr_2$]

ATOM	U11	U22	U33	U12	U13	U23
Br1	74 (1)	61 (1)	88 (1)	-5 (1)	33 (1)	-13 (1)
Cu1	64 (1)	58 (2)	57 (1)	-3 (1)	16 (1)	-1 (1)
K1	44 (2)	58 (3)	41 (2)	8 (2)	12 (2)	2 (2)
O1	53 (5)	75 (7)	58 (6)	-4 (4)	-6 (4)	11 (5)
O2	47 (5)	55 (6)	78 (6)	12 (4)	14 (4)	-2 (5)
O3	73 (6)	62 (6)	51 (5)	-2 (5)	20 (5)	-1 (4)
C1	11 (1)	9 (1)	7 (1)	-1 (1)	-1 (1)	0 (1)
C2	4 (1)	10 (1)	10 (1)	-1 (1)	0 (1)	5 (1)
C3	6 (1)	8 (1)	11 (1)	3 (1)	3 (1)	0 (1)
C4	9 (1)	7 (1)	10 (1)	0 (1)	7 (1)	-4 (1)
C5	10 (1)	8 (1)	4 (1)	-2 (1)	3 (1)	-1 (1)
C6	10 (1)	10 (1)	9 (1)	1 (1)	2 (1)	1 (1)

The anisotropic displacement exponent takes the form:

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

$\times 10^3$ for Br, Cu, K and O, $\times 10^2$ for C.

TABLE 22

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
[K-(18-Crown-6)][$CuBr_2$]

Br1 - Cu1	2.224 (1)	Cu1 - Br1 - K1	94.3 (1)
Br1' - Cu1	2.224 (1)	Br1 - Cu1 - Br1'	180.0 (1)
K1 ···Br1	3.400 (2)	Br1 - K1 - O1	97.0 (2)
K1 - O1	2.791 (7)	Br1 - K1 - O2	76.7 (1)
K1 - O2	2.793 (8)	Br1 - K1 - O3	81.5 (2)
K1 - O3	2.821 (8)	O1 - K1 - O2	59.5 (2)
K1 - O1"	2.791 (7)	O1 - K1 - O3	119.1 (2)
K1 - O2"	2.793 (8)	O2 - K1 - O3	61.1 (2)
K1 - O3"	2.821 (8)	O1 - K1 - O1"	180.0 (1)
O1 - C1	1.42 (2)	O2 - K1 - O1"	120.5 (2)
O1 - C2	1.41 (2)	O3 - K1 - O1"	60.9 (2)
O2 - C3	1.39 (1)	O1 - K1 - O2"	120.5 (2)
O2 - C4	1.46 (2)	O2 - K1 - O2"	180.0 (1)
O3 - C5	1.40 (2)	O3 - K1 - O2"	118.9 (2)
O3 - C6	1.38 (2)	O1" - K1 - O2"	59.5 (2)
C1 - C6"	1.65 (2)	O1 - K1 - O3"	60.9 (2)
C2 - C3	1.47 (2)	O2 - K1 - O3"	118.9 (2)
C4 - C5	1.47 (2)	O3 - K1 - O3"	180.0 (1)
C6 - C1"	1.65 (2)	O1" - K1 - O3"	119.1 (2)
		O2" - K1 - O3"	61.1 (2)
		K1 - O1 - C1	118.2 (6)
		K1 - O1 - C2	114.4 (7)
		C1 - O1 - C2	109.9 (9)
		K1 - O2 - C3	116.8 (8)
		K1 - O2 - C4	113.5 (6)
		C3 - O2 - C4	114.8 (9)
		K1 - O3 - C5	111.6 (6)
		K1 - O3 - C6	114.0 (7)

TABLE 22 (Continued)

C5 - O3 - C6	108.1 (10)
O1 - C1 - C6"	105.4 (9)
O1 - C2 - C3	109.9 (9)
O2 - C3 - C2	109.4 (10)
O2 - C4 - C5	108.4 (10)
O3 - C5 - C4	110.6 (10)
O3 - C6 - C1"	108.1 (11)

Symmetry operations:

' = 2.0-x, -y, 1.0-z.
" = 2.0-x, 1.0-y, 1.0-z.

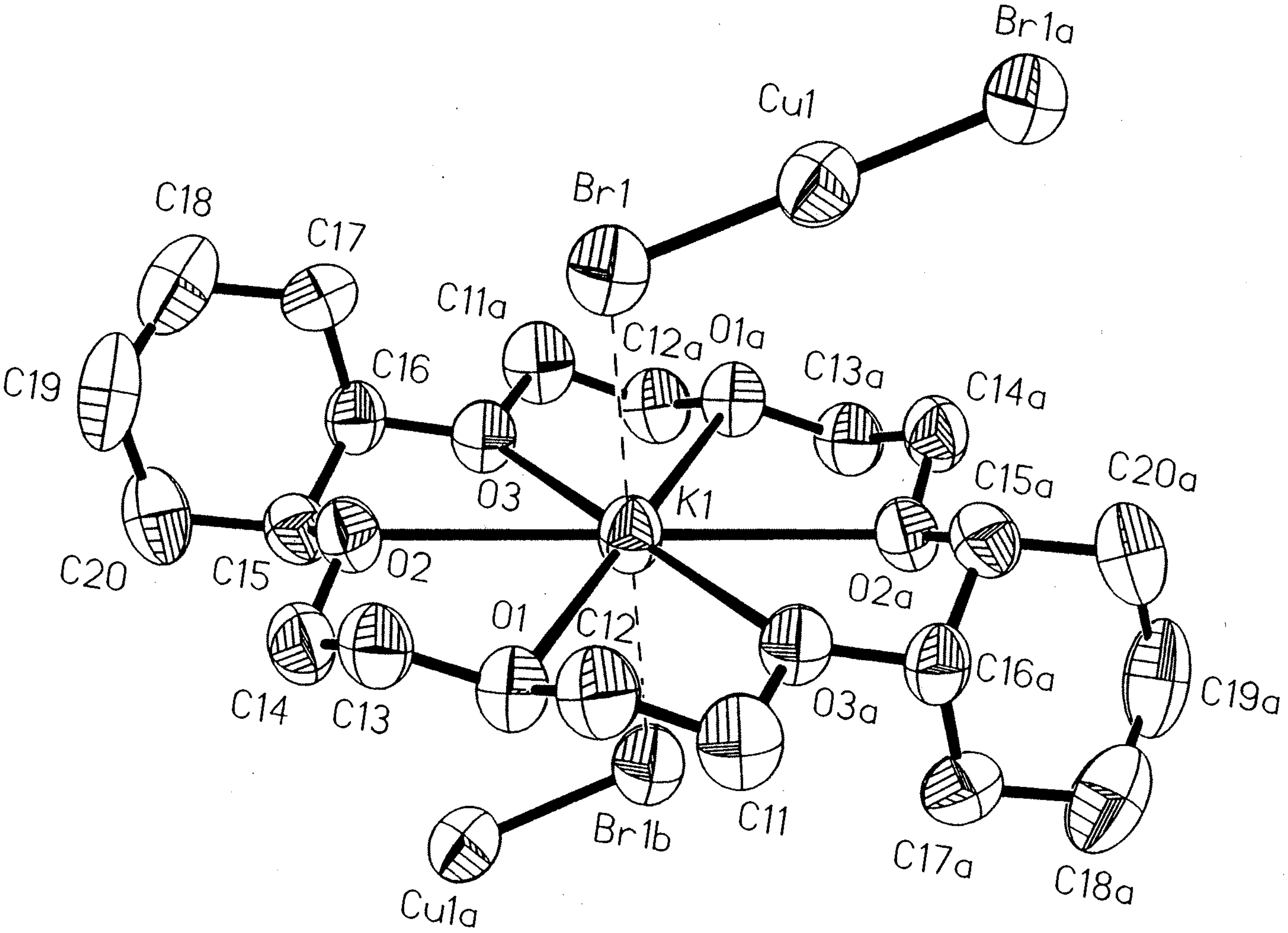

Figure 20. Projection View of [K-(DC18-Crown-6)][$CuBr_2$].

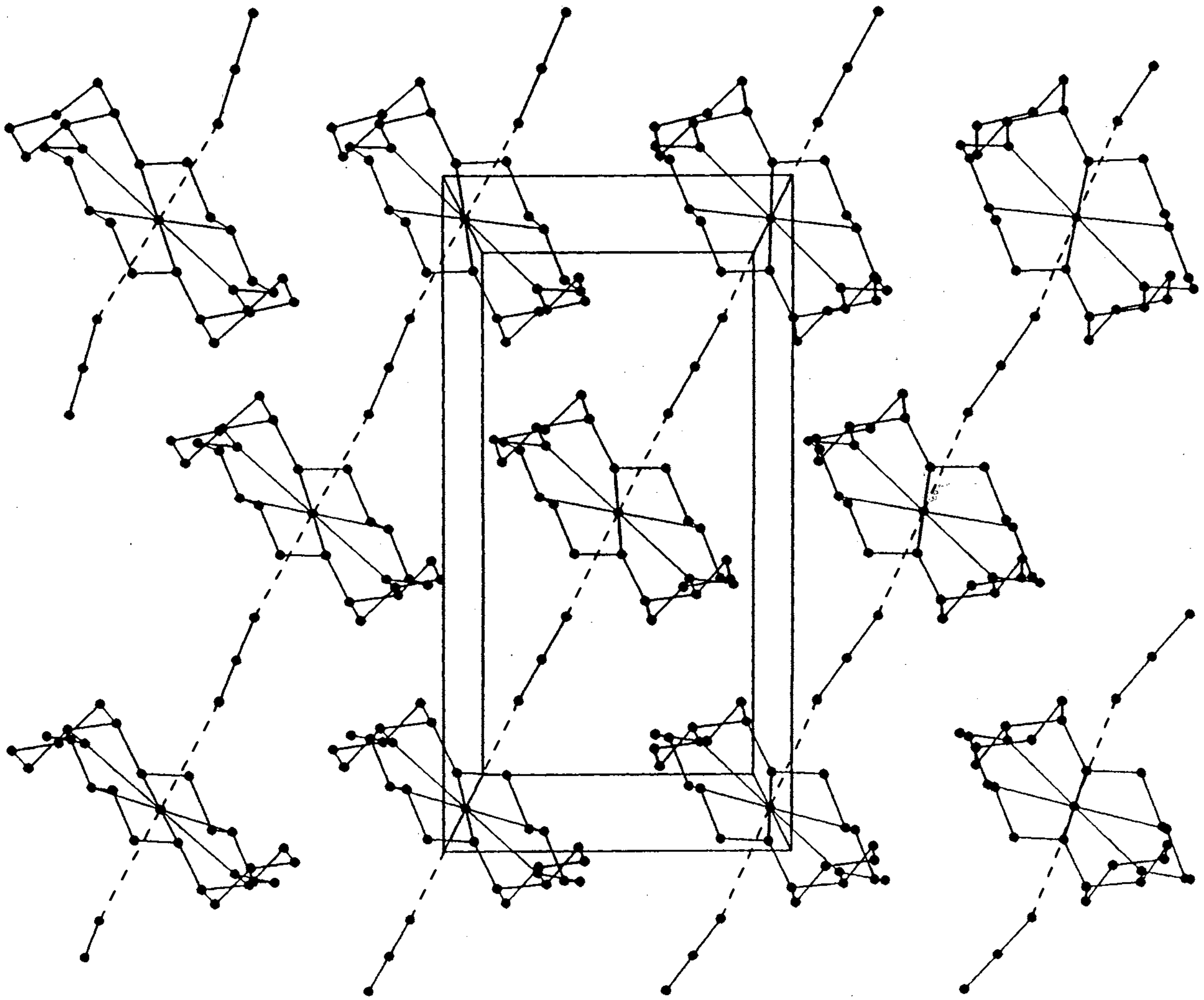

Figure 21. Packing Diagram for [K-(DC18-Crown-6)][CuBr$_2$].

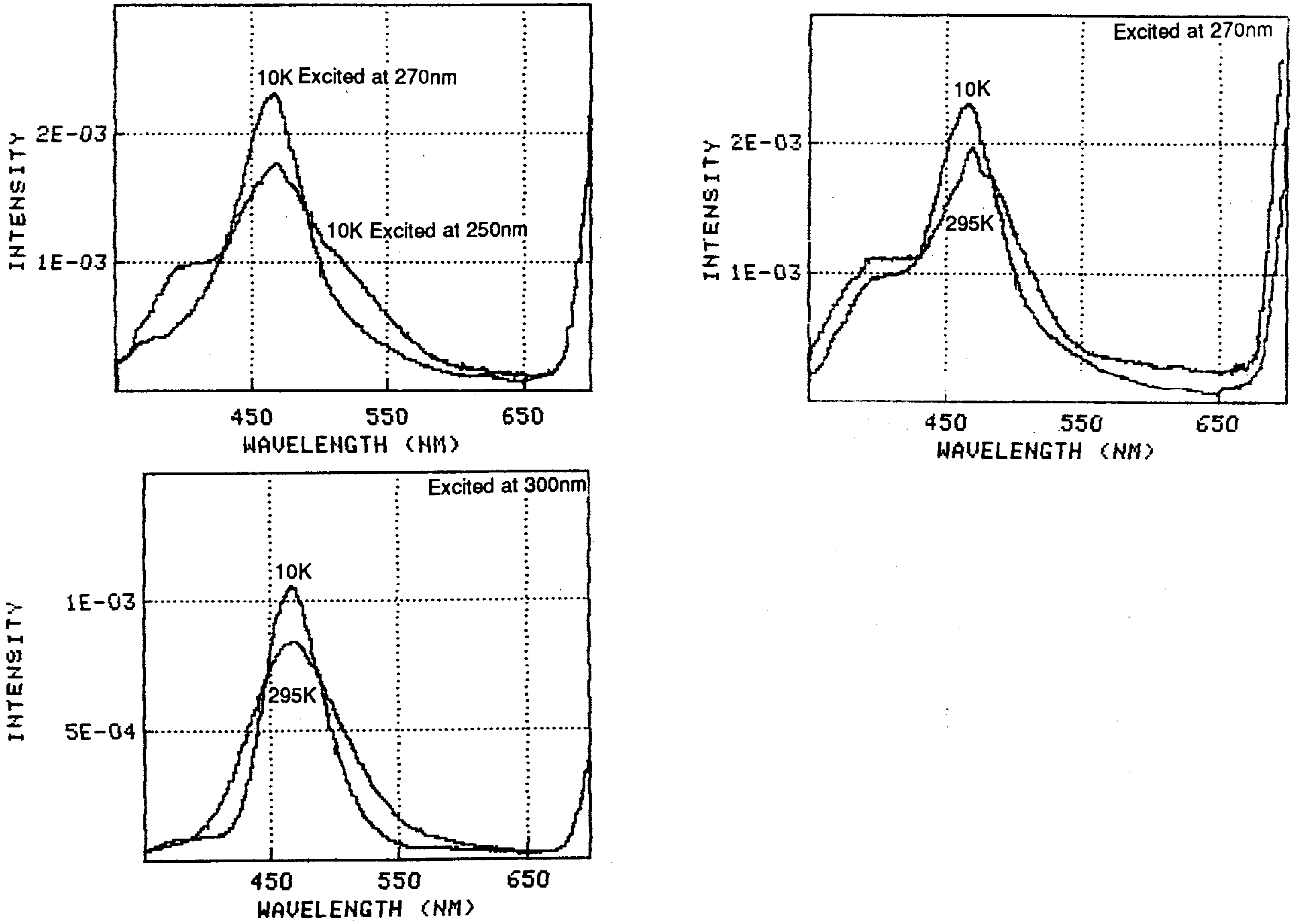

Figure 22. Emission Spectra of [K-(DC18-Crown-6)][$CuBr_2$].

TABLE 23

CRYSTAL DATA FOR [K-(Dicyclohexano-18-Crown-6)][$CuBr_2$]

Formula	$CuBr_2KC_{20}O_6H_{36}$
MWT	634.9
a	15.670(3) Å
b	8.080(2)
c	20.714(4)
α	90.0°
β	91.71(3)
γ	90.0
V	2621.4(10) $Å^3$
F (000)	1288
μMoK_α	40.71 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	1.609 g cm^{-3}
Z	4
Independent Refl.	3019
Obs. Refl. ($F > 4.0\sigma(F)$)	1024
Variab.	140
R/R_W	4.1/4.6%
Space Group	C2/c
Octants Meas.	+h, +k, ±l

TABLE 24

POSITIONAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)][$CuBr_2$]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Br1	0.3264 (1)	0.6665 (1)	0.4177 (1)
Cu1	0.2500	0.7500	0.5000
K1	0.5000	0.5000	0.5000
O1	0.4730 (3)	0.2370 (6)	0.4160 (2)
O2	0.5739 (3)	0.5113 (7)	0.3713 (2)
O3	0.6142 (3)	0.7346 (3)	0.4680 (2)
C11	0.3775 (5)	0.1226 (9)	0.4915 (4)
C12	0.3897 (5)	0.1712 (10)	0.4240 (3)
C13	0.4856 (5)	0.2803 (10)	0.3504 (3)
C14	0.5732 (5)	0.3509 (10)	0.3441 (4)
C15	0.6559 (5)	0.5912 (10)	0.3729 (3)
C16	0.6434 (5)	0.7610 (10)	0.4039 (3)
C17	0.5846 (6)	0.8674 (10)	0.3636 (4)
C18	0.6198 (7)	0.8871 (14)	0.2964 (4)
C19	0.6347 (7)	0.7253 (14)	0.2636 (4)
C20	0.6924 (6)	0.6151 (12)	0.3067 (4)

TABLE 25

HYDROGEN POSITIONAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)][$CuBr_2$]

ATOM	x	y	z
H11A	0.3451	0.0218	0.4918
H11B	0.4322	0.1044	0.5124
H12A	0.3798	0.0789	0.3956
H12B	0.3484	0.2556	0.4135
H13A	0.4445	0.3623	0.3368
H13B	0.4785	0.1848	0.3232
H14A	0.6132	0.2813	0.3673
H14B	0.5894	0.3561	0.2998
H15A	0.6952	0.5276	0.3992
H16A	0.6977	0.8159	0.4069
H17A	0.5780	0.9730	0.3841
H17B	0.5297	0.8148	0.3603
H18A	0.6733	0.9446	0.2999
H18B	0.5810	0.9525	0.2703
H19A	0.6584	0.7410	0.2218
H19B	0.5806	0.6709	0.2577
H20A	0.6987	0.5092	0.2863
H20B	0.7477	0.6659	0.3102

TABLE 26

ANISOTROPIC THERMAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)][$CuBr_2$]

ATOM	U11	U22	U33	U12	U13	U23
Cl1	89 (1)	91 (1)	73 (1)	11 (1)	12 (1)	8 (1)
Cu1	73 (1)	71 (1)	70 (1)	-5 (2)	4 (1)	8 (1)
K1	66 (2)	57 (2)	48 (1)	-14 (1)	9 (1)	-7 (1)
O1	53 (4)	64 (3)	50 (3)	-11 (3)	-1 (2)	-6 (3)
O2	55 (4)	59 (3)	57 (3)	-5 (3)	12 (3)	-7 (3)
O3	62 (3)	55 (3)	53 (3)	-12 (3)	5 (3)	-6 (3)
C11	75 (6)	58 (6)	70 (6)	-31 (5)	4 (5)	-20 (5)
C12	66 (6)	72 (5)	58 (5)	-8 (5)	-3 (4)	-10 (5)
C13	77 (7)	68 (6)	41 (5)	2 (5)	-7 (4)	-13 (4)
C14	77 (6)	62 (6)	56 (5)	-4 (5)	15 (4)	-8 (5)
C15	48 (5)	66 (5)	59 (5)	4 (5)	4 (4)	-3 (5)
C16	51 (5)	61 (5)	53 (5)	-13 (5)	8 (4)	-1 (5)
C17	84 (7)	62 (6)	69 (6)	11 (5)	2 (5)	14 (5)
C18	130 (10)	120 (10)	75 (7)	-10 (8)	10 (7)	35 (7)
C19	110 (9)	149 (11)	49 (6)	-28 (8)	18 (6)	5 (7)
C20	62 (6)	111 (8)	69 (6)	-10 (6)	17 (5)	-14 (6)

The anisotropic displacement exponent takes the form:

$\exp(-2\pi (U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$
x 10^3 for Br, Cu, K, O, and C.

TABLE 27

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR [K-(Dicyclohexano-18-Crown-6)][CuBr$_2$]

Br1 - Cu1	2.218 (1)	Cu1 - Br1 - K1	100.1 (1)
Br1' - Cu1	2.218 (1)	Br1 - Cu1 - Br1'	180.0 (1)
K1···Br1	3.440 (1)	Br1 - K1 - O1	83.4 (1)
K1 - O1	2.771 (5)	Br1 - K1 - O2	82.3 (1)
K1 - O2	2.938 (5)	Br1 - K1 - O3	97.1 (1)
K1 - O3	2.703 (5)	O1 - K1 - O2	60.7 (1)
O1 - C12	1.42 (1)	O1 - K1 - O3	118.3 (1)
O1 - C13	1.42 (1)	O2 - K1 - O3	58.3 (1)
O2 - C14	1.41 (1)	K1 - O1 - C12	109.6 (4)
O2 - C15	1.44 (1)	K1 - O1 - C13	112.9 (4)
O3 - C16	1.43 (1)	C12 - O1 - C13	110.9 (5)
O3 - C11"	1.43 (1)	K1 - O2 - C14	109.6 (4)
C11 - C12	1.47 (1)	K1 - O2 - C15	111.8 (4)
C11 - O3"	1.43 (1)	C14 - O2 - C15	114.6 (6)
C13 - C14	1.50 (1)	K1 - O3 - C16	124.3 (4)
C15 - C16	1.53 (1)	K1 - C12 - O1	47.9 (3)
C15 - C20	1.51 (1)	K1 - C12 - C11	81.5 (4)
C16 - C17	1.50 (1)	O1 - C12 - C11	110.9 (6)
C17 - C18	1.52 (1)	O1 - C13 - C14	109.3 (6)
C18 - C19	1.50 (2)	O2 - C14 - C13	108.1 (6)
C19 - C20	1.54 (1)	O2 - C15 - C16	106.6 (6)
K1 - O1"	2.771 (5)	O2 - C15 - C20	113.6 (6)
K1 - O2"	2.938 (5)	C16 - C15 - C20	108.8 (7)
K1 - O3"	2.703 (5)	O3 - C16 - C15	107.7 (6)
		O3 - C16 - C17	113.2 (6)
		C15 - C16 - C17	111.4 (6)
		C16 - C17 - C18	109.7 (7)
		C17 - C18 - C19	113.0 (8)

TABLE 27 (Continued)

	C18 - C19 - C20	109.9 (7)
	C15 - C20 - C19	111.6 (7)

Symmetry operations:

' = 0.5-x, 1.5-y, 1.0-z.
" = 1.0-x, 1.0-y, 1.0-z.

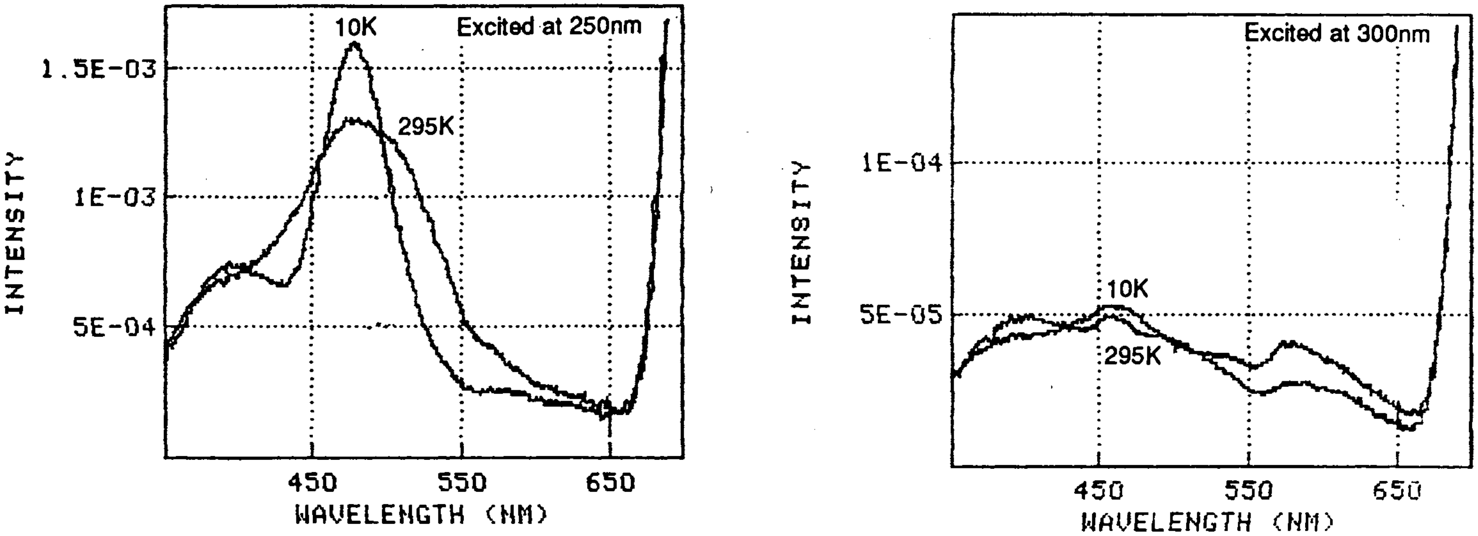

Figure 23. Emission Spectra of [(Butyl)$_4$N][CuBr$_2$].

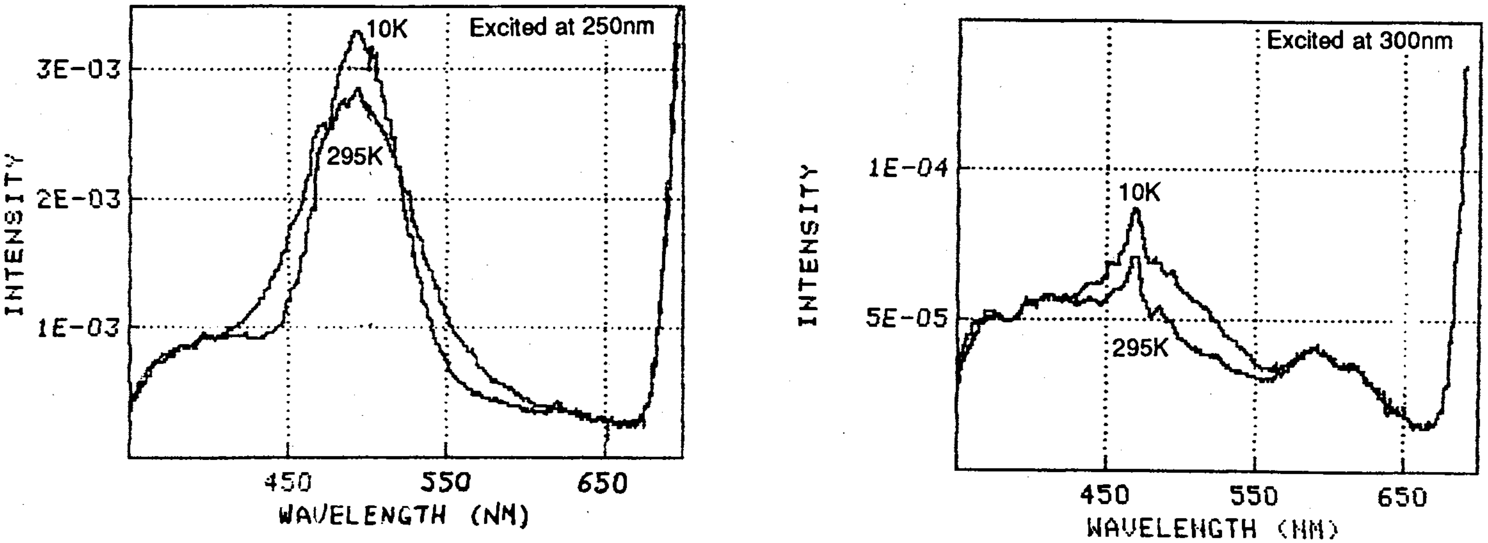

Figure 24. Emission Spectra of $[(Butyl)_4N][CuBrCl]$.

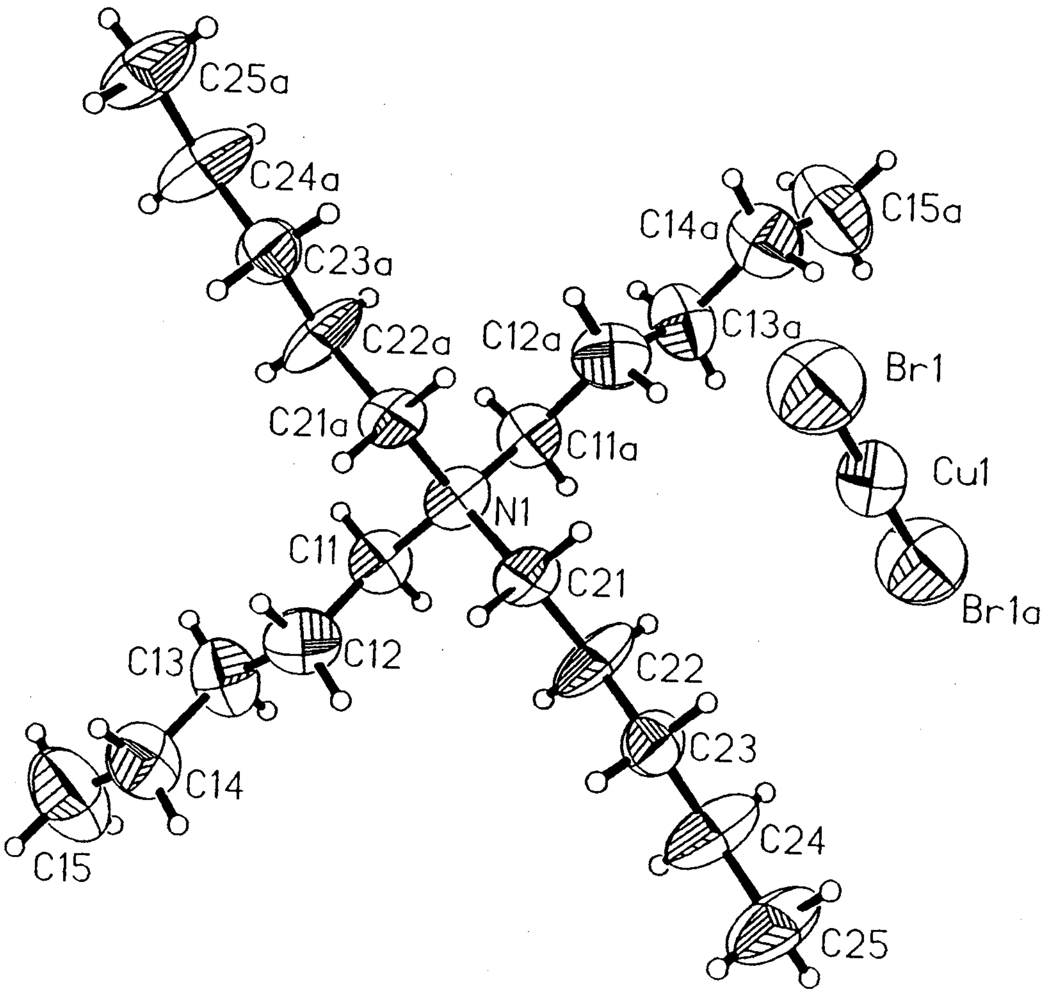

Figure 25. Projection View of [$(n\text{-Pentyl})_4N$][$CuBr_2$].

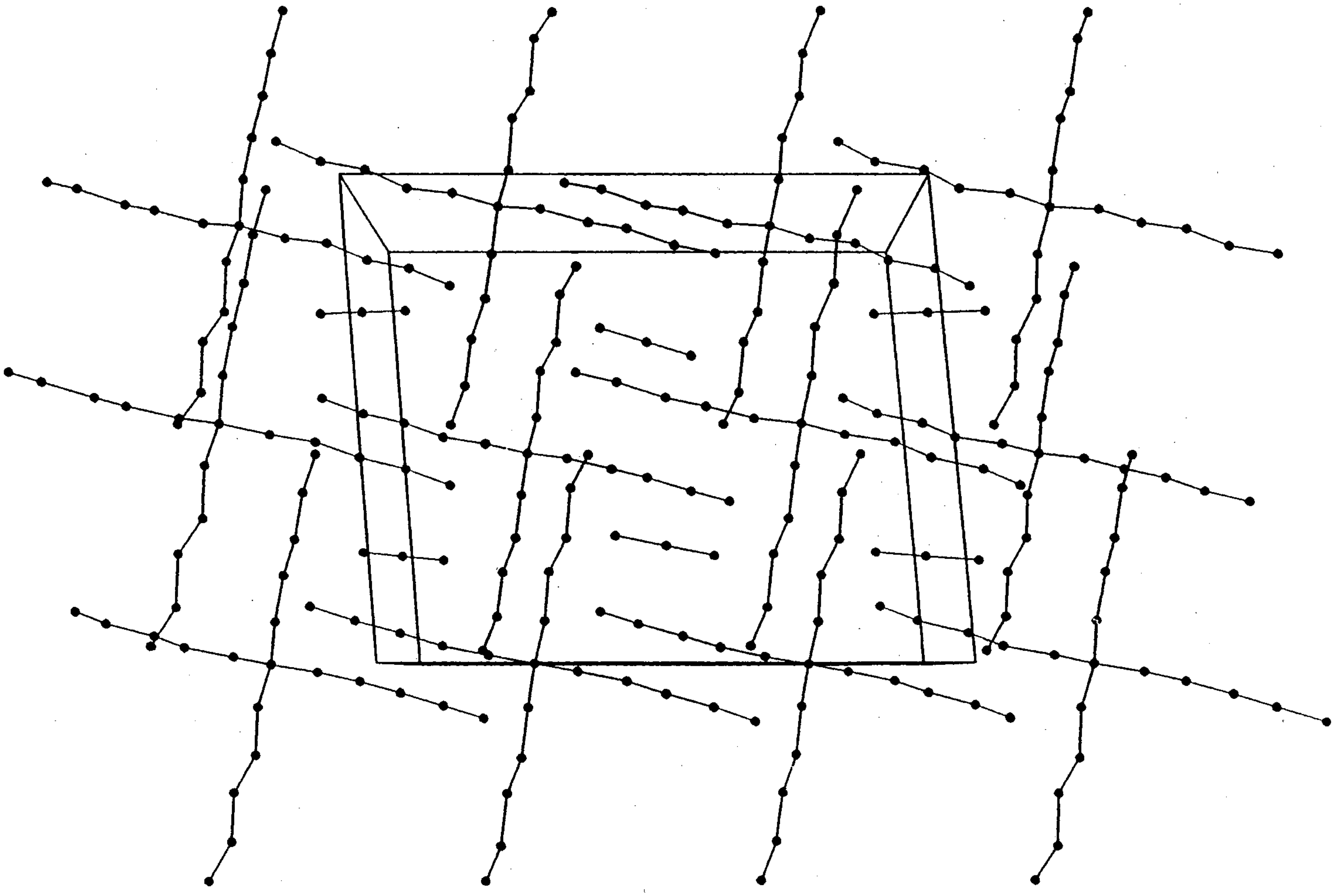

Figure 26. Packing Diagram for $[(n\text{-Pentyl})_4\text{N}][\text{CuBr}_2]$.

TABLE 28

CRYSTAL DATA FOR $[(n\text{-Pentyl})_4N][CuBr_2]$

Formula	$CuBr_2NC_{20}H_{44}$
MWT	521.92
a	12.836(1) Å
b	13.090(2)
c	15.422(1)
α	90°
β	95.07(1)
γ	90
V	2581.1(5) $Å^3$
F (000)	1080
μMoK_α	39.45 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	1.343 g cm^{-3}
Z	4
Independent Refl.	2276
Refl. Used	2276
Variab.	112
R/R_w	3.7/5.3%
Space Group	C2/c
Octants Meas.	+h, +k, ±l

TABLE 29

POSITIONAL PARAMETERS FOR [(*n*-Pentyl)$_4$N][CuBr$_2$]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cu1	0.2500	0.2500	0.0000
Br1	0.2351 (1)	0.3833 (1)	0.0857 (1)
N1	0.5000	0.1239 (5)	0.2500
C11	0.5940 (4)	0.0543 (4)	0.2712 (3)
C12	0.6999 (4)	0.1049 (4)	0.2876 (4)
C13	0.7787 (4)	0.0254 (4)	0.3216 (4)
C14	0.8873 (4)	0.0701 (4)	0.3385 (4)
C15	0.9670 (4)	-0.0077 (4)	0.3741 (4)
C21	0.5169 (4)	0.1933 (4)	0.1731 (3)
C22	0.5373 (5)	0.1398 (4)	0.0893 (3)
C23	0.5635 (4)	0.2169 (4)	0.0215 (3)
C24	0.5917 (5)	0.1640 (4)	-0.0604 (3)
C25	0.6208 (5)	0.2365 (4)	-0.1308 (3)

TABLE 30

HYDROGEN POSITIONAL PARAMETERS FOR $[(n\text{-Pentyl})_4N][CuBr_2]$

ATOM	x	y	z
H11A	0.5989	0.0078	0.2235
H11B	0.5811	0.0143	0.3213
H12A	0.6952	0.1561	0.3316
H12B	0.7189	0.1379	0.2357
H13A	0.7816	-0.0261	0.2776
H13B	0.7586	-0.0073	0.3733
H14A	0.8852	0.1225	0.3818
H14B	0.9095	0.1005	0.2866
H15A	1.0353	0.0216	0.3861
H15B	0.9449	-0.0375	0.4263
H15C	0.9694	-0.0596	0.3303
H21A	0.5744	0.2386	0.1887
H21B	0.4552	0.2340	0.1608
H22A	0.4773	0.1007	0.0676
H22B	0.5959	0.0947	0.1008
H23A	0.6223	0.2570	0.0443
H23B	0.5043	0.2611	0.0095
H24A	0.5315	0.1259	-0.0833
H24B	0.6480	0.1169	-0.0466
H25A	0.6364	0.2008	-0.1824
H25B	0.5640	0.2830	-0.1448
H25C	0.6813	0.2739	-0.1078

TABLE 31

ANISOTROPIC THERMAL PARAMETERS FOR [(*n*-Pentyl)$_4$N][CuBr$_2$]

ATOM	U11	U22	U33	U12	U13	U23
Cu1	84 (1)	96 (1)	77 (1)	2 (1)	0 (1)	4 (1)
Br1	129 (1)	112 (1)	122 (1)	-26 (1)	14 (1)	4 (1)
N1	76 (7)	34 (5)	53 (5)	0	14 (5)	0
C11	72 (5)	44 (5)	59 (4)	6 (4)	12 (4)	6 (5)
C12	85 (6)	60 (5)	83 (5)	6 (5)	22 (5)	-5 (5)
C13	74 (6)	57 (5)	89 (5)	15 (4)	-5 (5)	-14 (5)
C14	76 (6)	71 (6)	99 (5)	10 (4)	4 (5)	2 (5)
C15	99 (7)	135 (8)	154 (7)	52 (6)	-22 (6)	-15 (7)
C21	70 (5)	54 (5)	53 (4)	20 (4)	17 (4)	-4 (4)
C22	124 (7)	62 (5)	46 (4)	4 (4)	22 (4)	18 (5)
C23	69 (5)	67 (5)	55 (4)	4 (4)	11 (4)	17 (4)
C24	146 (8)	83 (6)	71 (5)	9 (5)	46 (5)	12 (6)
C25	138 (7)	110 (6)	72 (4)	-3 (5)	46 (5)	32 (6)

The anisotropic displacement exponent takes the form:
$\exp(-2\pi(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$
x 10^3 for Cu, Br, N and C.

TABLE 32

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR [(*n*-Pentyl)$_4$N][CuBr$_2$]

Cu1 - Br1	2.2074 (8)	Br1 - Cu1 - Br1'	180.0
Cu2 - Br1'	2.2074 (8)	C21 - N1 - C21"	106.8 (5)
N1 - C11	1.525 (3)	C11" - N1 - C21"	111.0 (3)
N1 - C11"	1.525 (3)	C21 - N1 - C11"	110.7 (3)
N1 - C21	1.525 (3)	C21" - N1 - C11	110.7 (3)
N1 - C21"	1.525 (3)	C21 - N1 - C11	111.0 (3)
C11 - C12	1.513 (2)	C11" - N1 - C11	106.6 (5)
C12 - C13	1.513 (2)	C12 - C11 - N1	117.2 (4)
C13 - C14	1.512 (2)	C13 - C12 - C11	108.7 (5)
C14 - C15	1.512 (2)	C14 - C13 - C12	111.8 (4)
C21 - C22	1.513 (2)	C15 - C14 - C13	112.7 (5)
C22 - C23	1.513 (2)	C22 - C21 - N1	115.8 (4)
C23 - C24	1.512 (2)	C23 - C22 - C21	110.3 (4)
C24 - C25	1.512 (2)	C24 - C23 - C22	110.9 (4)
		C25 - C24 - C23	113.9 (4)

Symmetry operations:

' = -x+1/2, -y+1/2, -z.
" = -x+1.0, y, -z+1/2.

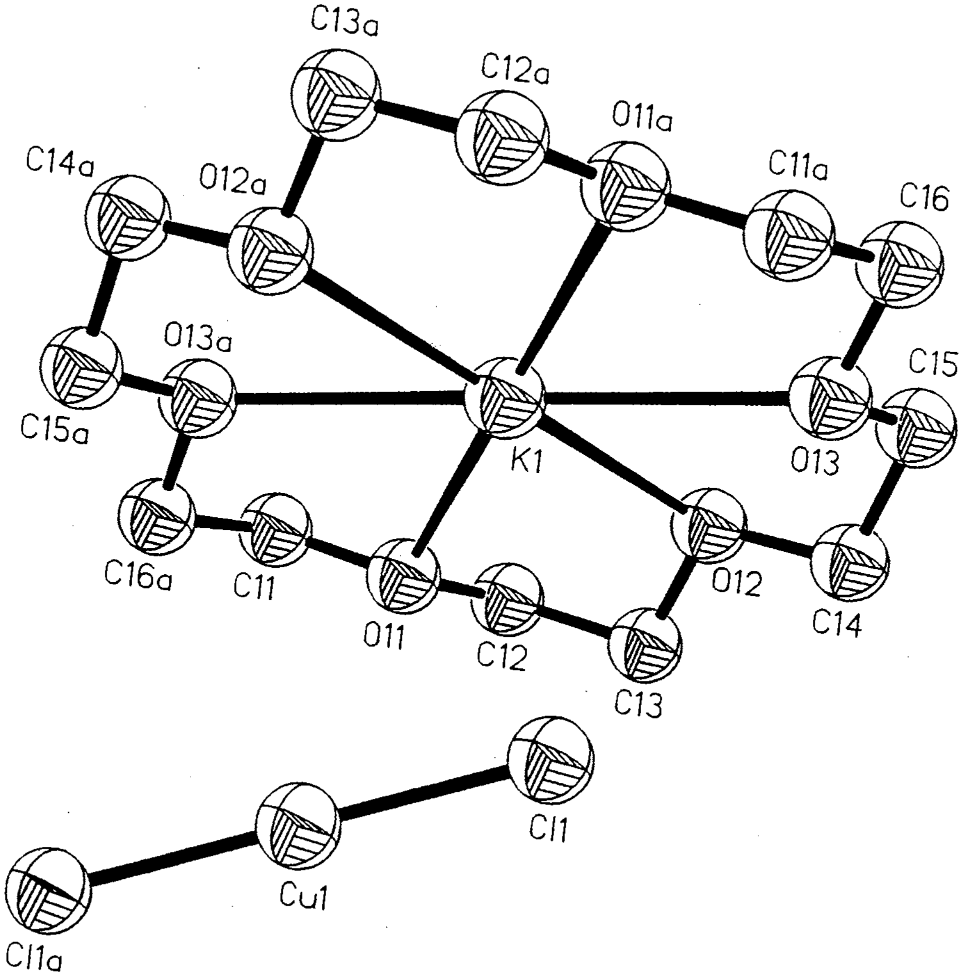

Figure 27. Projection View of [K-(18-Crown-6)][$CuCl_2$].

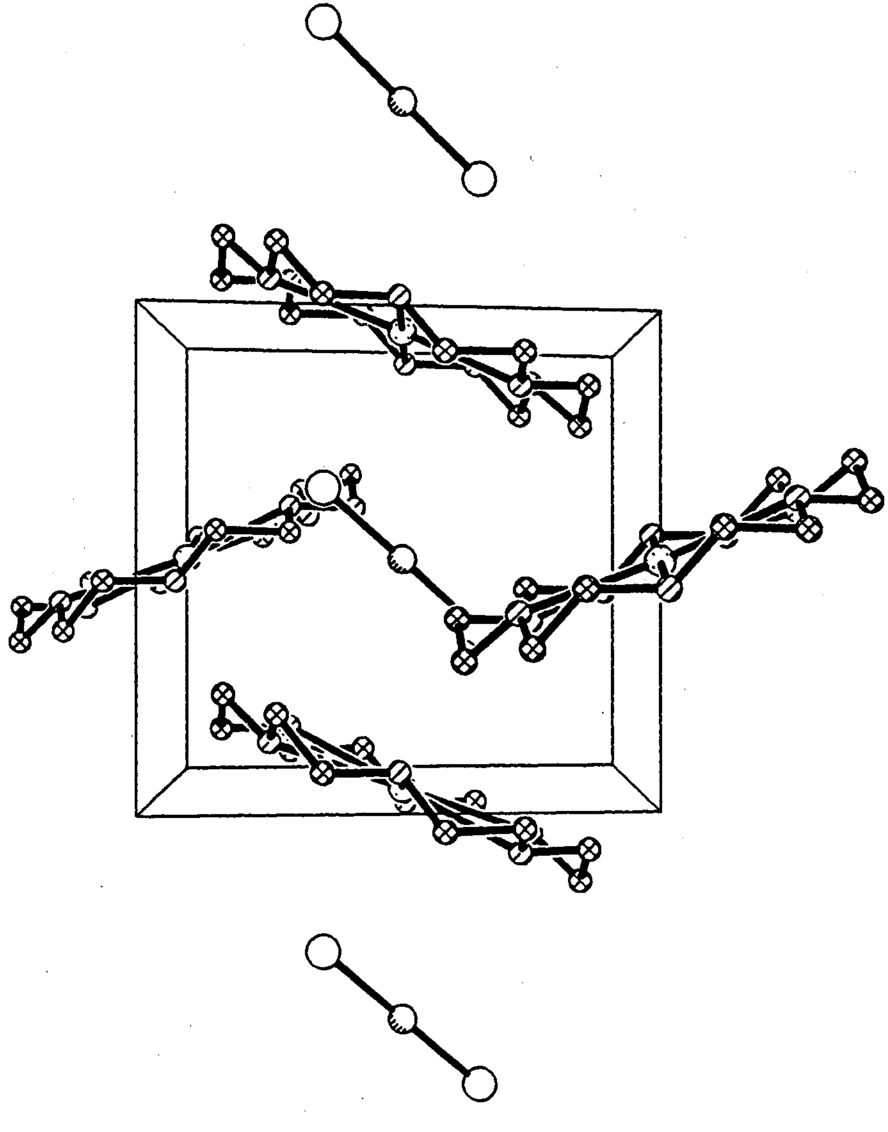

Figure 28. Packing Diagram for [K-(18-Crown-6)][$CuCl_2$].

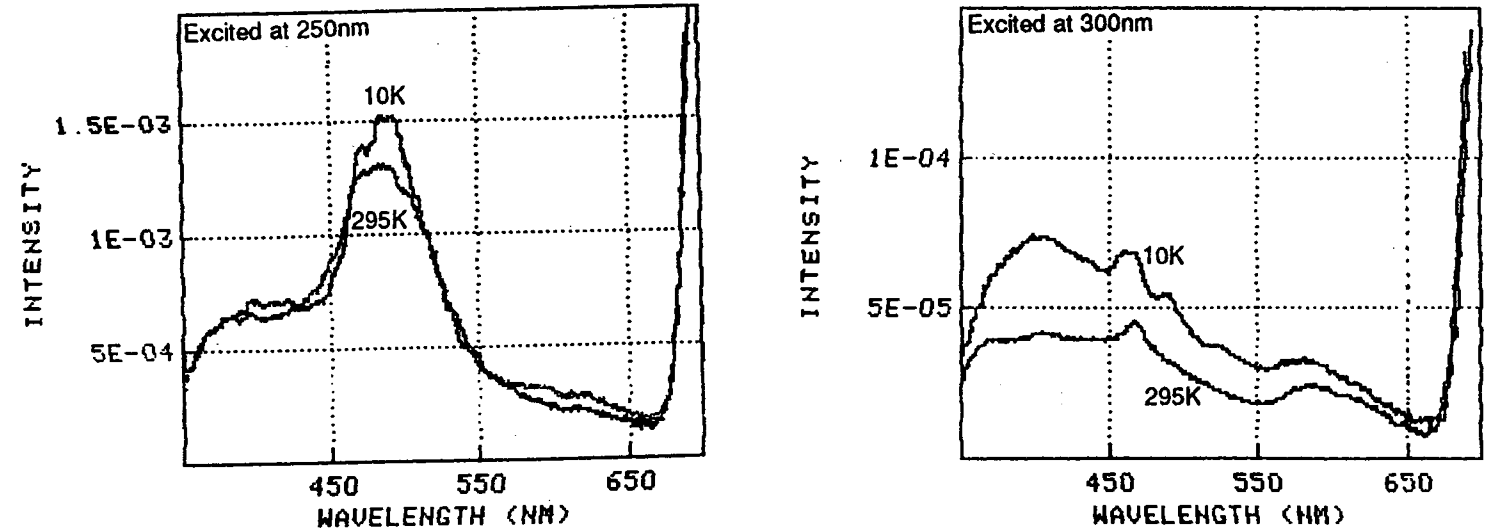

Figure 29. Emission Spectra of [K-(18-Crown-6)][$CuCl_2$].

TABLE 33

CRYSTAL DATA FOR [K-(18-Crown-6)][$CuCl_2$]

Formula	$CuCl_2KC_{12}O_6H_{24}$
MWT	437.87
a	13.790(6) Å
b	8.163(2)
c	8.672(3)
α	90.0°
β	102.95(3)
γ	90.0
V	951.4(5) $Å^3$
F (000)	452
μMoK_α	16.72 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.528 g cm^{-3}
Z	2
Obs. Refl.	2767
Contribut. Refl.	865
Variab.	103
R/R_w	5.7/7.1%
Space Group	$P2_1/n$
Octants Meas.	±h, +k, +l

TABLE 34

POSITIONAL PARAMETERS FOR [K-(18-Crown-6)][$CuCl_2$]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cl1	0.5414 (2)	0.3453 (4)	0.3333 (3)
Cu1	0.5000	0.5000	0.5000
K1	0.5000	0.0000	0.5000
O11	0.6502 (4)	0.1240 (8)	0.7454 (7)
O12	0.7017 (4)	-0.0528 (7)	0.4934 (7)
O13	0.5460 (4)	-0.1057 (8)	0.2217 (7)
C11	0.624 (1)	0.122 (1)	0.891 (1)
C12	0.745 (1)	0.062 (1)	0.749 (1)
C13	0.764 (1)	0.065 (1)	0.588 (1)
C14	0.714 (1)	-0.054 (1)	0.338 (1)
C15	0.643 (1)	-0.171 (1)	0.242 (1)
C16	0.474 (1)	-0.203 (1)	0.120 (1)

TABLE 35

HYDROGEN POSITIONAL PARAMETERS FOR [K-(18-Crown-6)][$CuCl_2$]

ATOM	x	y	z
H111	0.6754	0.1752	0.9729
H112	0.6190	0.0069	0.9276
H121	0.7964	0.1274	0.8235
H122	0.7523	-0.0513	0.7886
H131	0.7472	0.1786	0.5404
H132	0.8342	0.0486	0.5863
H141	0.6995	0.0578	0.2882
H142	0.7828	-0.0786	0.3320
H151	0.6594	-0.1952	0.1394
H152	0.6481	-0.2774	0.2998
H161	0.4896	-0.2145	0.0157
H162	0.4716	-0.3135	0.1639

TABLE 36

ANISOTROPIC THERMAL PARAMETERS FOR $[K\text{-}(18\text{-}Crown\text{-}6)][CuCl_2]$

ATOM	U11	U22	U33	U12	U13	U23
Cl1	96 (2)	62 (2)	74 (2)	-13 (2)	25 (2)	-7 (2)
Cu1	58 (1)	55 (1)	67 (1)	0 (1)	7 (1)	-8 (1)
K1	40 (1)	56 (2)	38 (1)	0 (2)	8 (1)	-4 (2)
O11	57 (4)	59 (4)	46 (4)	1 (3)	-4 (3)	4 (3)
O12	44 (3)	51 (4)	67 (4)	5 (3)	14 (3)	6 (3)
O13	61 (4)	54 (4)	58 (4)	5 (3)	12 (3)	-15 (3)
C11	90 (8)	63 (7)	41 (5)	-26 (6)	-13 (5)	-7 (5)
C12	53 (5)	60 (6)	72 (6)	2 (6)	-10 (4)	-2 (6)
C13	30 (5)	61 (6)	119 (9)	-2 (5)	9 (5)	-2 (7)
C14	48 (5)	67 (7)	90 (7)	10 (5)	35 (5)	4 (6)
C15	83 (7)	55 (6)	56 (6)	20 (6)	38 (5)	10 (5)
C16	104 (9)	60 (6)	45 (5)	-15 (6)	24 (6)	-8 (5)

The anisotropic displacement exponent takes the form:
$\exp(-2\pi(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$
x 10^3 for Cl, Cu, K, O and C.

TABLE 37

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR [K-(18-Crown-6)][CuCl$_2$]

Cl1 - Cu1	2.093 (3)	Cl1 - Cu1 - Cl1'	180
Cl1' - Cu1	2.093 (3)	Cu1 - Cl1 - K1	96.5 (1)
K1 - O11	2.805 (6)	O11 - K1 - O12	60.5 (2)
K1 - O12	2.828 (6)	O11 - K1 - O13	120.0 (2)
K1 - O13	2.767 (7)	O12 - K1 - O13	61.0 (2)
O11 - C11	1.39 (1)	O13 - K1 - O11"	60.0 (2)
C11 - C16"	1.48 (2)	O11 - K1 - O13"	60.0 (2)
C16 - O13	1.42 (1)	O12 - K1 - O13"	119.0 (2)
O13 - C15	1.42 (1)	O12 - K1 - O11"	119.5 (2)
C15 - C14	1.48 (1)	O11 - K1 - O11"	180
C14 - O12	1.40 (1)	O12 - K1 - O12"	180
O12 - C13	1.43 (1)	O13 - K1 - O13"	180
C13 - C12	1.47 (2)	K1 - O11 - C11	112.7 (5)
C12 - O11	1.40 (1)	K1 - O11 - C12	114.6 (5)
O11 - C11	1.39 (1)	O11 - C11 - C16"	110.6 (7)
C16 - C11"	1.48 (2)	C11 - O11 - C12	114.2 (7)
K1 ··· Cl1	3.275 (3)	O11 - C12 - C13	109.9 (8)
		C12 - C13 - O12	108.8 (8)
		C13 - O12 - C14	111.7 (8)
		K1 - O12 - C13	110.8 (5)
		K1 - O12 - C14	111.0 (5)
		O12 - C14 - C15	109.3 (8)
		C14 - C15 - O13	108.3 (8)
		C15 - O13 - C16	112.4 (8)
		K1 - O13 - C15	113.7 (5)
		K1 - O13 - C16	116.8 (6)

TABLE 37 (continued)

	O11 - C11 - C16"	110.6 (7)
	O13 - C16 - C11"	107.0 (8)

Symmetry operations:

' = 1.0-x, 1.0-y, 1.0-z.
" = 1.0-x, -y, 1.0-z.

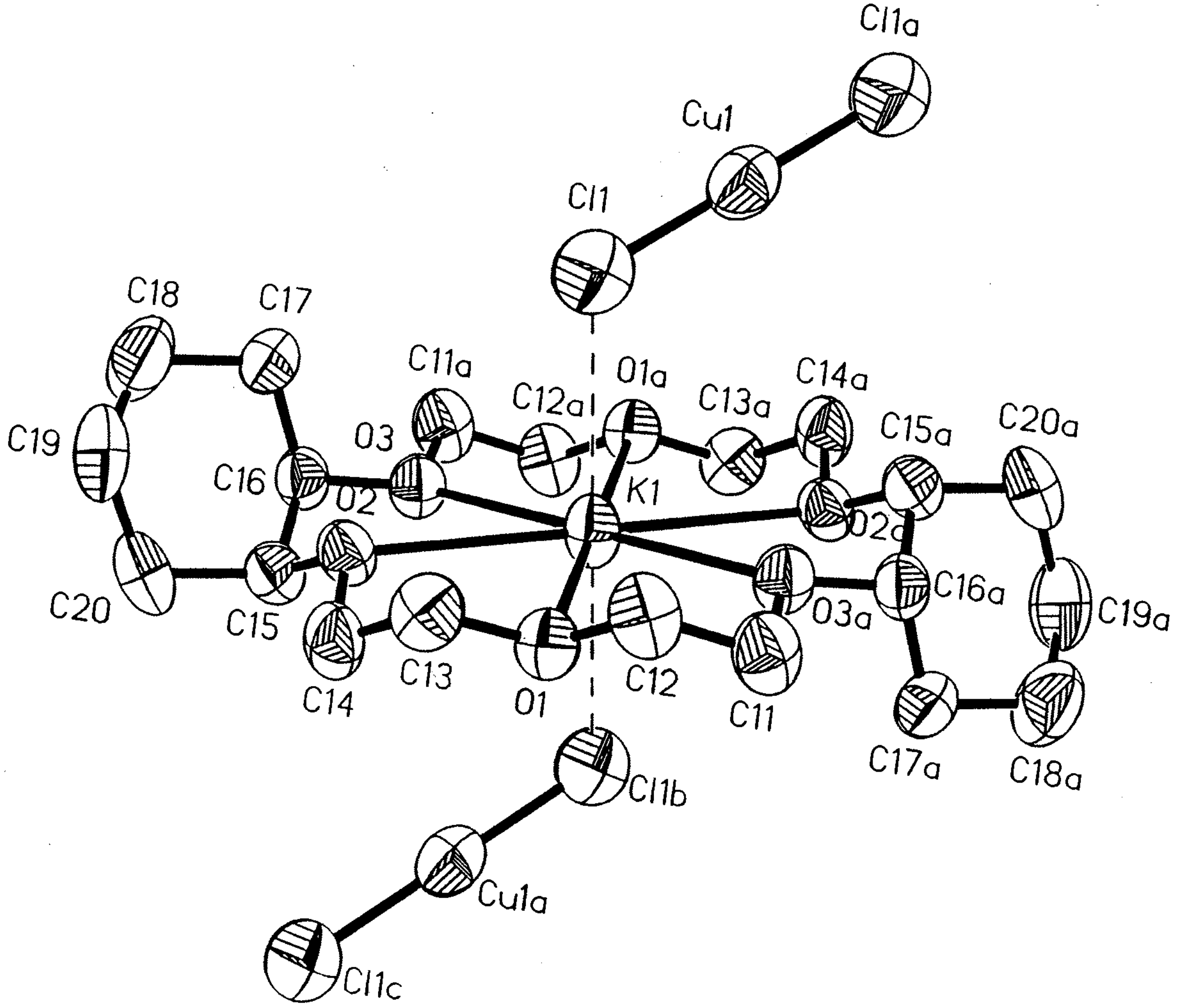

Figure 30. Projection View of [K-(DC18-Crown-6)][$CuCl_2$].

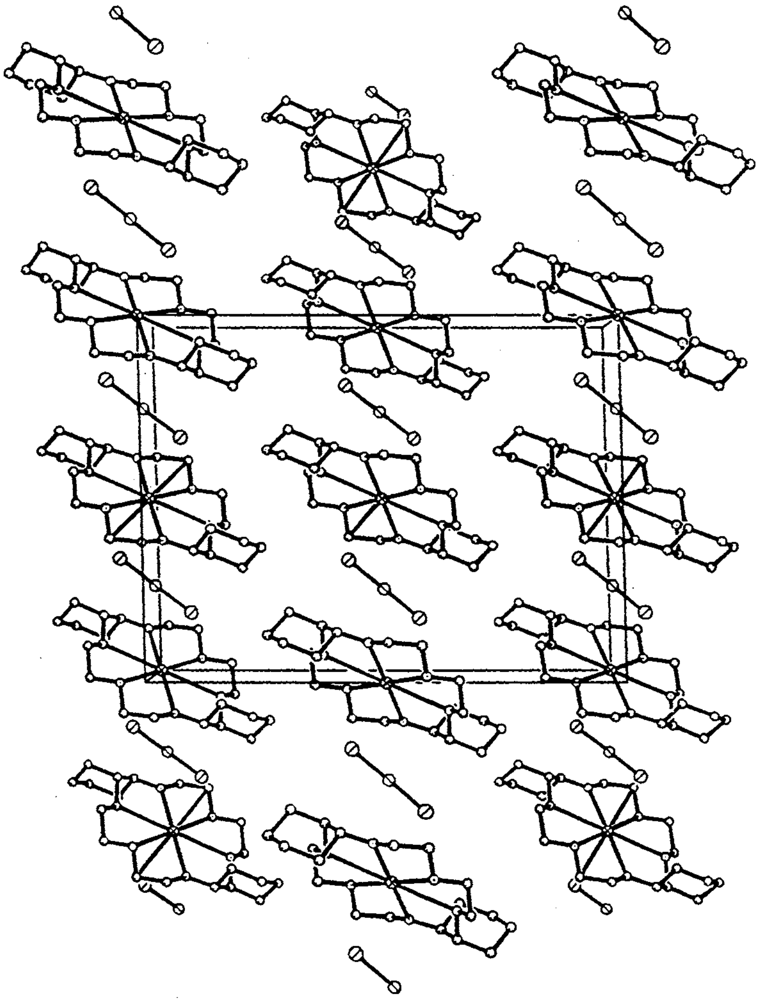

Figure 31. Packing Diagram for [K-(DC18-Crown-6)][$CuCl_2$].

TABLE 38

CRYSTAL DATA FOR [K-(Dicyclohexano-18-Crown-6)][$CuCl_2$]

Formula	$CuCl_2KC_{20}O_6H_{36}$
MWT	546.0
a	15.540(1) Å
b	8.060(1)
c	20.409(2)
α	90.0°
β	91.300(5)
γ	90.0
V	2555.4(4) $Å^3$
F (000)	1144
μMoK_α	12.57 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	1.419 g cm^{-3}
Z	4
Independent Refl.	2269
Obs. Refl. ($F > 4.0\sigma(F)$)	1178
Variab.	140
R/R_w	4.1/4.3%
Space Group	C2/c
Octants Meas.	+h, +k, ±l

TABLE 39

POSITIONAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)][$CuCl_2$]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cl1	0.3283 (1)	0.6641 (2)	0.4256 (1)
Cu1	0.2500	0.7500	0.5000
K1	0.5000	0.5000	0.5000
O1	0.4734 (2)	0.2335 (3)	0.4157 (1)
O2	0.5753 (2)	0.5107 (4)	0.3696 (1)
O3	0.6157 (2)	0.7348 (3)	0.4662 (1)
C11	0.3794 (3)	0.1202 (6)	0.4943 (2)
C12	0.3897 (3)	0.1684 (6)	0.4244 (2)
C13	0.4864 (3)	0.2781 (6)	0.3493 (2)
C14	0.5748 (3)	0.3493 (6)	0.3428 (2)
C15	0.6577 (3)	0.5915 (6)	0.3701 (2)
C16	0.6443 (3)	0.7601 (6)	0.4010 (2)
C17	0.5833 (3)	0.8657 (6)	0.3600 (2)
C18	0.6191 (4)	0.8877 (8)	0.2917 (2)
C19	0.6353 (4)	0.7219 (8)	0.2587 (2)
C20	0.6941 (3)	0.6138 (7)	0.3022 (2)

TABLE 40

HYDROGEN POSITIONAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)][$CuCl_2$]

ATOM	x	y	z
H11A	0.3231	0.0745	0.5006
H11B	0.4222	0.0382	0.5051
H12A	0.3815	0.0742	0.3961
H12B	0.3470	0.2501	0.4130
H13A	0.4452	0.3609	0.3360
H13B	0.4787	0.1826	0.3216
H14A	0.6150	0.2805	0.3667
H14B	0.5911	0.3524	0.2977
H15A	0.6971	0.5282	0.3969
H16A	0.6984	0.8175	0.4033
H17A	0.5743	0.9712	0.3806
H17B	0.5290	0.8092	0.3562
H18A	0.6738	0.9427	0.2962
H18B	0.5818	0.9556	0.2649
H19A	0.6589	0.7358	0.2159
H19B	0.5808	0.6668	0.2538
H20A	0.7020	0.5069	0.2825
H20B	0.7492	0.6675	0.3053

TABLE 41

ANISOTROPIC THERMAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)][$CuCl_2$]

ATOM	U11	U22	U33	U12	U13	U23
Cl1	105 (1)	103 (1)	86 (1)	14 (1)	11 (1)	12 (1)
Cu1	75 (1)	63 (1)	75 (1)	-7 (2)	-3 (1)	13 (1)
K1	65 (1)	51 (1)	46 (1)	-16 (1)	12 (1)	-10 (1)
O1	55 (2)	55 (2)	42 (2)	-6 (2)	-2 (1)	-6 (2)
O2	53 (2)	49 (2)	50 (2)	-2 (2)	12 (1)	-8 (2)
O3	62 (2)	43 (2)	50 (2)	-8 (2)	9 (1)	-5 (2)
C11	67 (3)	57 (3)	73 (4)	-20 (3)	15 (3)	-11 (3)
C12	59 (3)	67 (3)	59 (3)	-19 (3)	2 (3)	-17 (3)
C13	77 (3)	58 (3)	43 (3)	-5 (3)	-6 (2)	-11 (3)
C14	81 (4)	59 (3)	45 (3)	-4 (3)	18 (3)	-9 (3)
C15	49 (3)	63 (3)	56 (3)	3 (3)	6 (2)	2 (3)
C16	49 (3)	52 (3)	51 (3)	-5 (3)	10 (2)	2 (3)
C17	77 (3)	57 (3)	57 (3)	6 (3)	11 (3)	13 (3)
C18	110 (5)	101 (5)	66 (4)	-2 (4)	7 (3)	31 (4)
C19	107 (5)	119 (6)	48 (3)	-7 (4)	27 (3)	7 (4)
C20	58 (3)	92 (4)	66 (3)	-9 (3)	25 (3)	-16 (3)

The anisotropic displacement exponent takes the form:

$\exp(-2\pi(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$ x 10^3 for Cl, Cu, K, O, and C.

TABLE 42

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR [K-(Dicyclohexano-18-Crown-6)][CuCl$_2$]

Cl1 - Cu1	2.085 (2)	Cu1 - Cl1 - K1	106.0 (1)
Cl1' - Cu1	2.085 (2)	Cl1 - Cu1 - Cl1'	180.0 (1)
K1···Cl1	3.315 (2)	Cl1 - K1 - O1	85.3 (1)
K1 - O1	2.777 (3)	Cl1 - K1 - O2	84.6 (1)
K1 - O2	2.933 (3)	Cl1 - K1 - O3	97.9 (1)
K1 - O3	2.710 (3)	O1 - K1 - O2	61.2 (1)
O1 - C12	1.416 (5)	O1 - K1 - O3	118.2 (1)
O1 - C13	1.421 (5)	O2 - K1 - O3	57.9 (1)
O2 - C14	1.412 (6)	K1 - O1 - C12	109.5 (2)
O2 - C15	1.436 (5)	K1 - O1 - C13	111.9 (2)
O3 - C16	1.427 (5)	C12 - O1 - C13	111.3 (3)
O3 - C11"	1.421 (6)	K1 - O2 - C14	109.9 (2)
C11 - C12	1.491 (6)	K1 - O2 - C15	112.4 (2)
C11 - O3"	1.421 (6)	C14 - O2 - C15	114.7 (3)
C13 - C14	1.497 (7)	K1 - O2 - C15	112.4 (2)
C15 - C16	1.515 (7)	C14 - O2 - C15	114.7 (3)
C15 - C20	1.520 (6)	K1 - O3 - C16	124.0 (2)
C16 - C17	1.513 (6)	K1 - O3 - C11"	117.2 (2)
C17 - C18	1.523 (7)	C16 - O3 - C11"	113.4 (3)
C18 - C19	1.521 (9)	C12 - C11 - O3"	108.9 (4)
C19 - C20	1.531 (8)	K1 - C12 - O1	48.2 (2)
		K1 - C12 - C11	80.8 (3)
		O1 - C12 - C11	109.6 (4)
		O1 - C13 - C14	109.4 (3)
		O2 - C14 - C13	108.4 (4)
		O2 - C15 - C16	106.2 (3)
		O2 - C15 - C20	113.5 (4)
		C16 - C15 - C20	109.4 (4)

TABLE 42 (Continued)

O3 - C16 - C15	108.0 (4)
O3 - C16 - C17	113.0 (3)
C15 - C16 - C17	111.3 (4)
C16 - C17 - C18	109.5 (4)
C17 - C18 - C19	111.8 (5)
C18 - C19 - C20	110.2 (4)
C15 - C20 - C19	111.5 (4)

Symmetry operations:

' = 0.5-x, 1.5-y, 1.0-z.
" = 1.0-x, 1.0-y, 1.0-z.

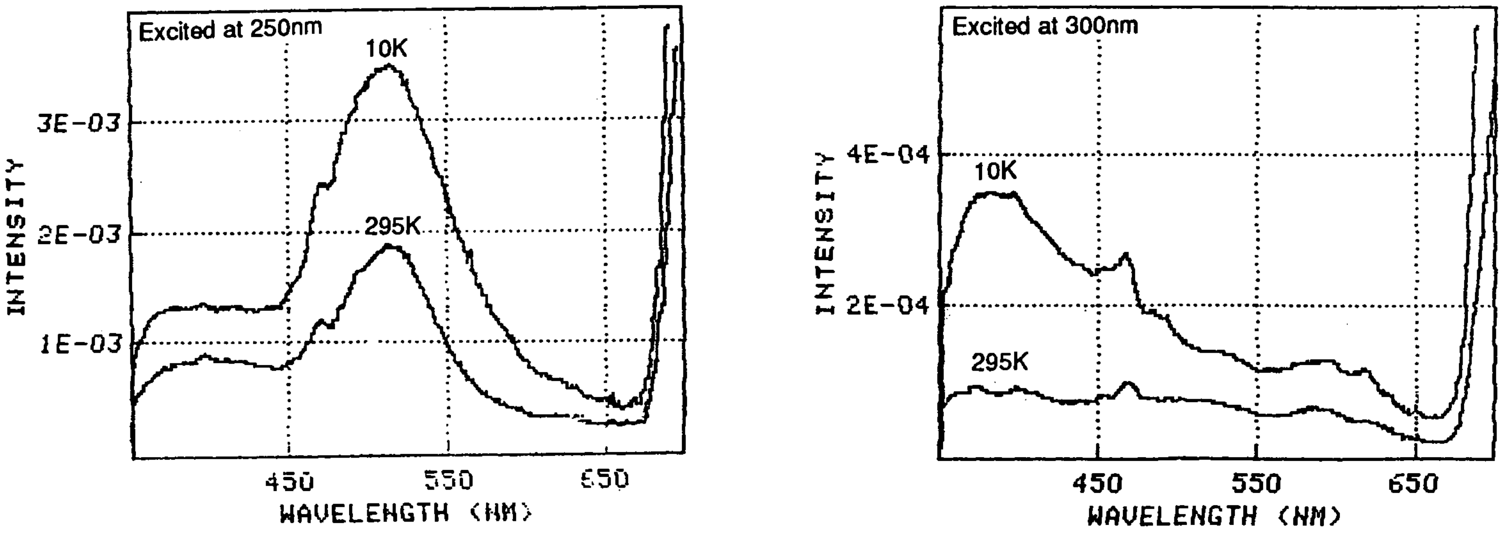

Figure 32. Emission Spectra of [Rb-(15-Crown-5)$_2$][CuCl$_2$].

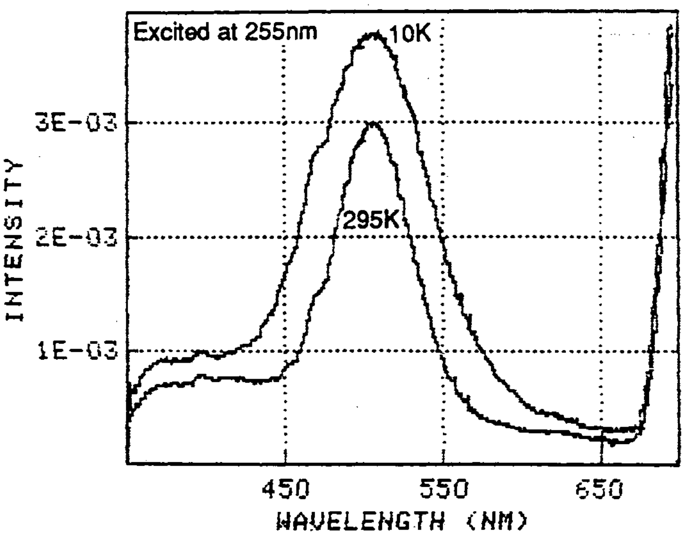

Figure 33. Emission Spectra of $[(Butyl)_4N][CuCl_2]$.

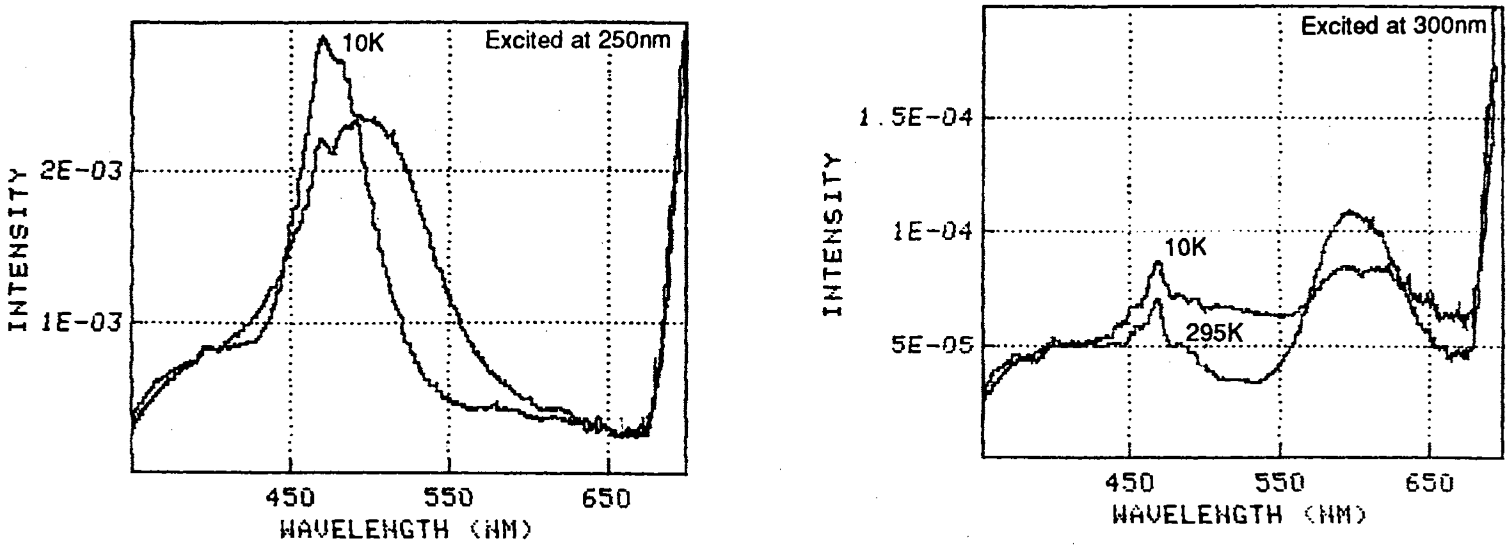

Figure 34. Emission Spectra of [(n-Propyl)$_4$N][CuBr$_2$].

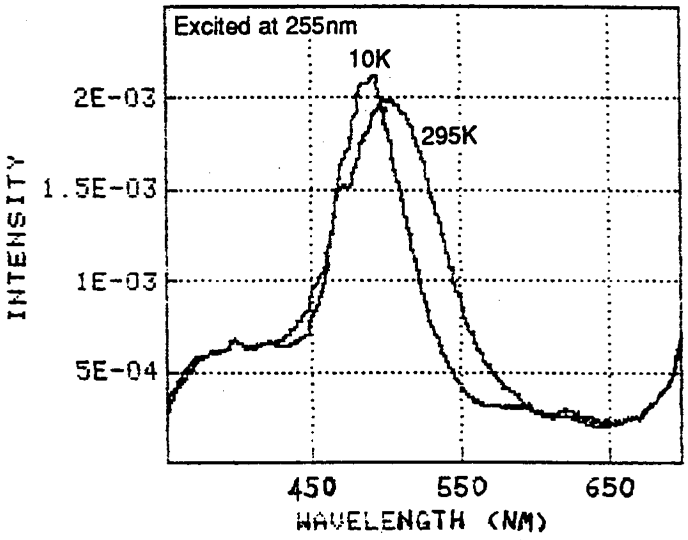

Figure 35. Emission Spectra of [(*n*-Propyl)$_4$N][CuCl$_2$].

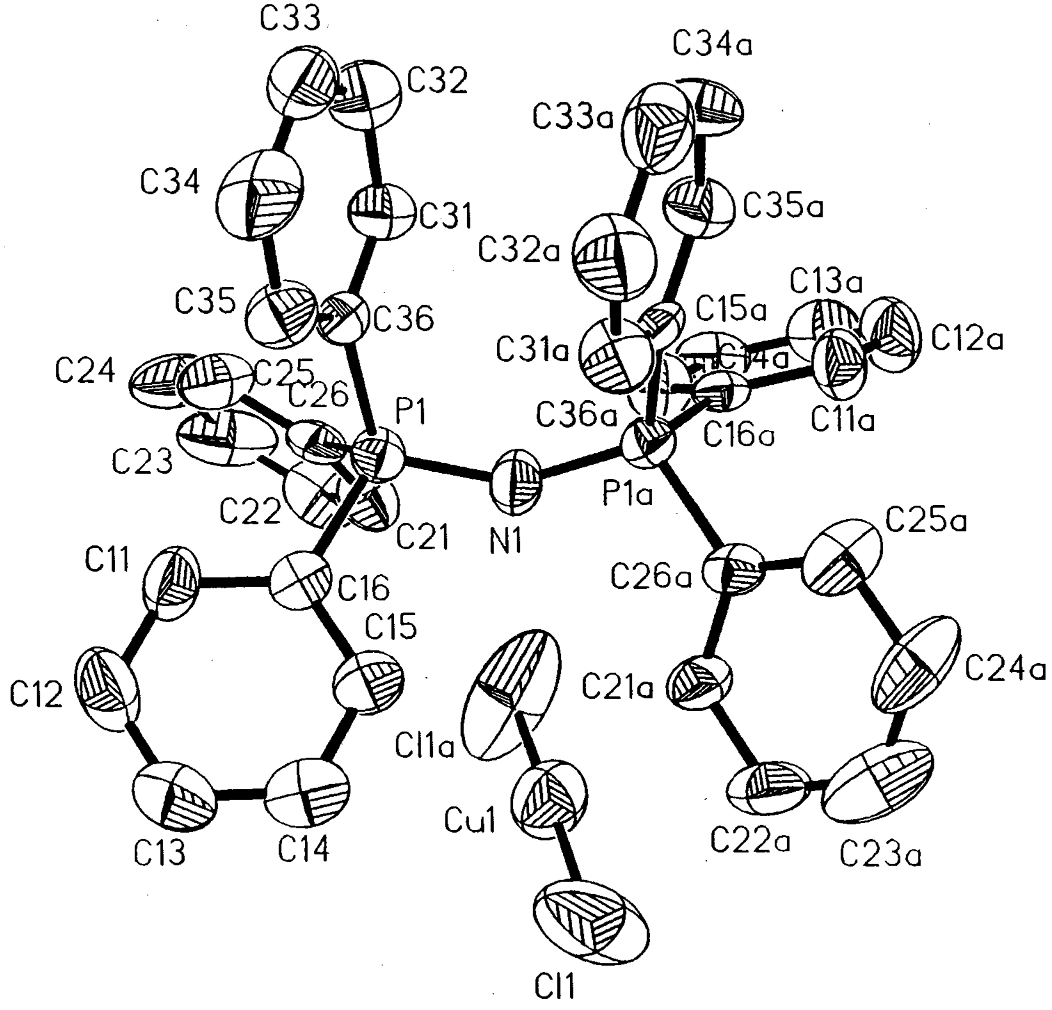

Figure 36. Projection View of $[(Ph_3P)_2N][CuCl_2]$.

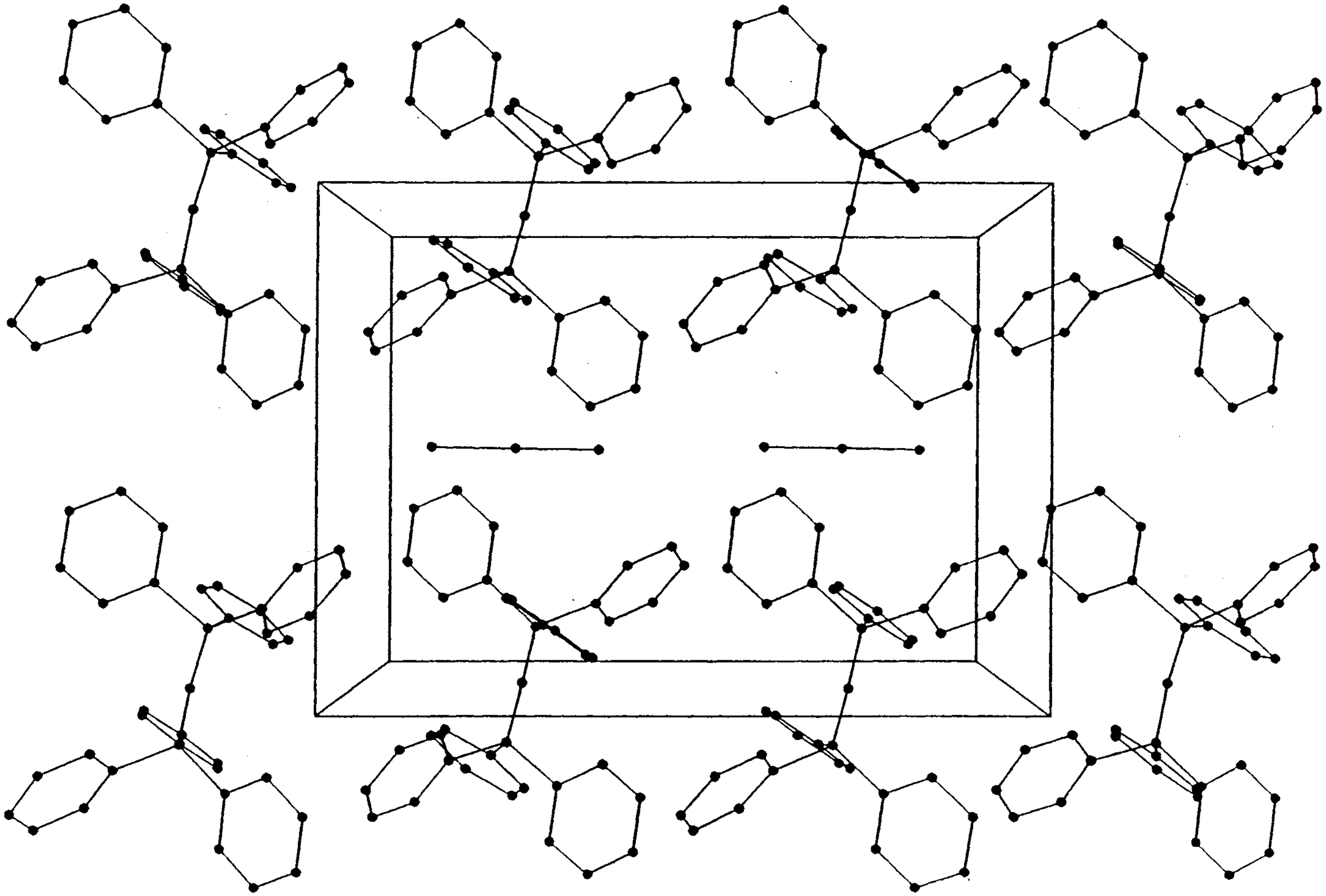

Figure 37. Packing Diagram for [$(Ph_3P)_2N$][$CuCl_2$].

TABLE 43

CRYSTAL DATA FOR $[(Ph_3P)_2N][CuCl_2]$

Formula	$CuCl_2NP_2C_{36}H_{30}$
MWT	673.0
a	11.911(1) Å
b	16.689(1)
c	16.351(2)
α	90.0°
β	90.0
γ	90.0
V	3250.3(16) $Å^3$
F (000)	1384
μMoK_α	9.61 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	1.375 g cm^{-3}
Z	4
Independent Refl.	3740
Obs. Refl. ($F > 4.0\sigma(F)$)	875
Variab.	156
R/R_w	5.6/5.9%
Space Group	Pbcn
Octants Meas.	+h, +k, +l

TABLE 44

POSITIONAL PARAMETERS FOR $[(Ph_3P)_2N][CuCl_2]$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cu1	0	0.1497 (1)	0.7500
Cl1	-0.0031 (4)	0.1453 (3)	0.6262 (2)
P1	0.1221 (2)	0.4764 (2)	0.7724 (2)
N1	0	0.4471 (6)	0.7500
C11	0.3345 (6)	0.4573 (4)	0.7051 (4)
C12	0.4097	0.4295	0.6462
C13	0.3698	0.3907	0.5764
C14	0.2546	0.3798	0.5656
C15	0.1794	0.4076	0.6245
C16	0.2193	0.4464	0.6942
C21	0.1231 (5)	0.3534 (4)	0.8831 (4)
C22	0.1615	0.3120	0.9517
C23	0.2446	0.3455	1.0012
C24	0.2893	0.4204	0.9820
C25	0.2509	0.4619	0.9134
C26	0.1678	0.4283	0.8639
C31	0.0764 (5)	0.6146 (5)	0.8549 (4)
C32	0.0779	0.6972	0.8677
C33	0.1376	0.7468	0.8146
C34	0.1959	0.7138	0.7487
C35	0.1944	0.6312	0.7359
C36	0.1347	0.5816	0.7890

TABLE 45

HYDROGEN POSITIONAL PARAMETERS FOR $[(Ph_3P)_2N][CuCl_2]$

ATOM	x	y	z
H11	0.3619	0.4839	0.7531
H12	0.4889	0.4370	0.6537
H13	0.4215	0.3716	0.5359
H14	0.2271	0.3532	0.5175
H15	0.1001	0.4001	0.6169
H21	0.0660	0.3303	0.8491
H22	0.1308	0.2604	0.9649
H23	0.2710	0.3170	1.0484
H24	0.3464	0.4435	1.0160
H25	0.2816	0.5134	0.9002
H31	0.0353	0.5804	0.8915
H32	0.0378	0.7200	0.9131
H33	0.1386	0.8037	0.8234
H34	0.2370	0.7480	0.7121
H35	0.2345	0.6085	0.6906

TABLE 46

ANISOTROPIC THERMAL PARAMETERS FOR $[(Ph_3P)_2N][CuCl_2]$

ATOM	U11	U22	U33	U12	U13	U23
Cu1	95 (2)	91 (2)	85 (2)	0	-14 (2)	0
Cl1	192 (4)	279 (6)	75 (3)	132 (5)	-23 (3)	-46 (3)
P1	39 (2)	35 (1)	46 (2)	2 (2)	-3 (2)	3 (2)
N1	38 (7)	46 (7)	75 (9)	0	-15 (7)	0
C11	45 (8)	78 (9)	54 (8)	-8 (7)	-12 (7)	-4 (7)
C12	44 (8)	102 (11)	69 (8)	3 (8)	13 (8)	2 (8)
C13	76 (10)	66 (9)	63 (9)	9 (8)	19 (8)	-3 (7)
C14	87 (10)	47 (8)	48 (7)	-8 (8)	7 (8)	4 (6)
C15	63 (8)	66 (8)	44 (7)	1 (8)	-3 (7)	-10 (7)
C16	50 (8)	34 (6)	31 (8)	-4 (6)	0 (6)	10 (5)
C21	54 (8)	44 (7)	65 (8)	11 (7)	3 (7)	18 (6)
C22	84 (10)	50 (7)	72 (9)	12 (8)	17 (7)	28 (8)
C23	157 (14)	69 (9)	50 (8)	41 (11)	-3 (9)	-1 (8)
C24	123 (12)	67 (9)	58 (9)	37 (10)	-44 (9)	-21 (7)
C25	87 (9)	49 (7)	56 (8)	12 (8)	-18 (7)	-9 (7)
C26	47 (8)	24 (7)	47 (7)	10 (5)	10 (6)	1 (6)
C31	58 (8)	46 (8)	69 (8)	3 (7)	3 (7)	-12 (7)
C32	71 (10)	56 (9)	104 (11)	-1 (8)	-1 (8)	-12 (9)
C33	63 (9)	59 (8)	100 (10)	4 (8)	-22 (9)	-14 (9)
C34	89 (10)	41 (8)	111 (11)	-21 (7)	-6 (10)	22 (8)
C35	62 (8)	47 (7)	58 (7)	-7 (6)	1 (7)	2 (6)
C36	38 (7)	27 (5)	40 (7)	5 (6)	-13 (5)	4 (5)

The anisotropic displacement exponent takes the form:
$\exp(-2\pi(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$
x 10^3 for Cu, Cl, P, N and C.

TABLE 47

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[(Ph_3P)_2N][CuCl_2]$

Cu1 - Cl1	2.025 (4)	Cl1 - Cu1 - Cl1'	175.8 (3)
Cu1 - Cl1'	2.025 (4)	N1 - P1 - C16	110.0 (3)
P1 - N1	1.577 (4)	N1 - P1 - C26	109.7 (3)
P1 - C16	1.796 (7)	C16 - P1 - C26	105.9 (3)
P1 - C26	1.783 (7)	N1 - P1 - C36	114.7 (4)
P1 - C36	1.782 (9)	C16 - P1 - C36	109.2 (3)
N1 - P1'	1.577 (4)	C26 - P1 - C36	106.8 (3)
C16 - C11	1.395	P1 - N1 - P1'	143.9 (7)
C11 - C12	1.395	P1 - C16 - C11	120.4 (2)
C12 - C13	1.395	P1 - C16 - C15	119.5 (2)
C13 - C14	1.395	P1 - C26 - C21	118.4 (2)
C14 - C15	1.395	P1 - C26 - C25	121.5 (2)
C15 - C16	1.395	P1 - C36 - C31	117.7 (2)
C26 - C21	1.395	P1 - C36 - C35	122.2 (2)
C21 - C22	1.395	C11 - C12 - C13	120.0
C22 - C23	1.395	C12 - C13 - C14	120.0
C23 - C24	1.395	C13 - C14 - C15	120.0
C24 - C25	1.395	C14 - C15 - C16	120.0
C25 - C26	1.395	C15 - C16 - C11	120.0
C36 - C31	1.395	C16 - C11 - C12	120.0
C31 - C32	1.395	C21 - C22 - C23	120.0
C32 - C33	1.395	C22 - C23 - C24	120.0
C33 - C34	1.395	C23 - C24 - C25	120.0
C34 - C35	1.395	C24 - C25 - C26	120.0
C35 - C36	1.395	C25 - C26 - C21	120.0
		C26 - C21 - C22	120.0
		C31 - C32 - C33	120.0
		C32 - C33 - C34	120.0
		C33 - C34 - C35	120.0
		C34 - C35 - C36	120.0

TABLE 47 (Continued)

C35 - C36 - C31	120.0
C36 - C31 - C32	120.0
C41 - C42 - C43	120.0
C42 - C43 - C44	120.0
C43 - C44 - C45	120.0
C44 - C45 - C46	120.0
C45 - C46 - C41	120.0
C46 - C41 - C42	120.0

Symmetry operation:

' = -x, y, 1.5-z.

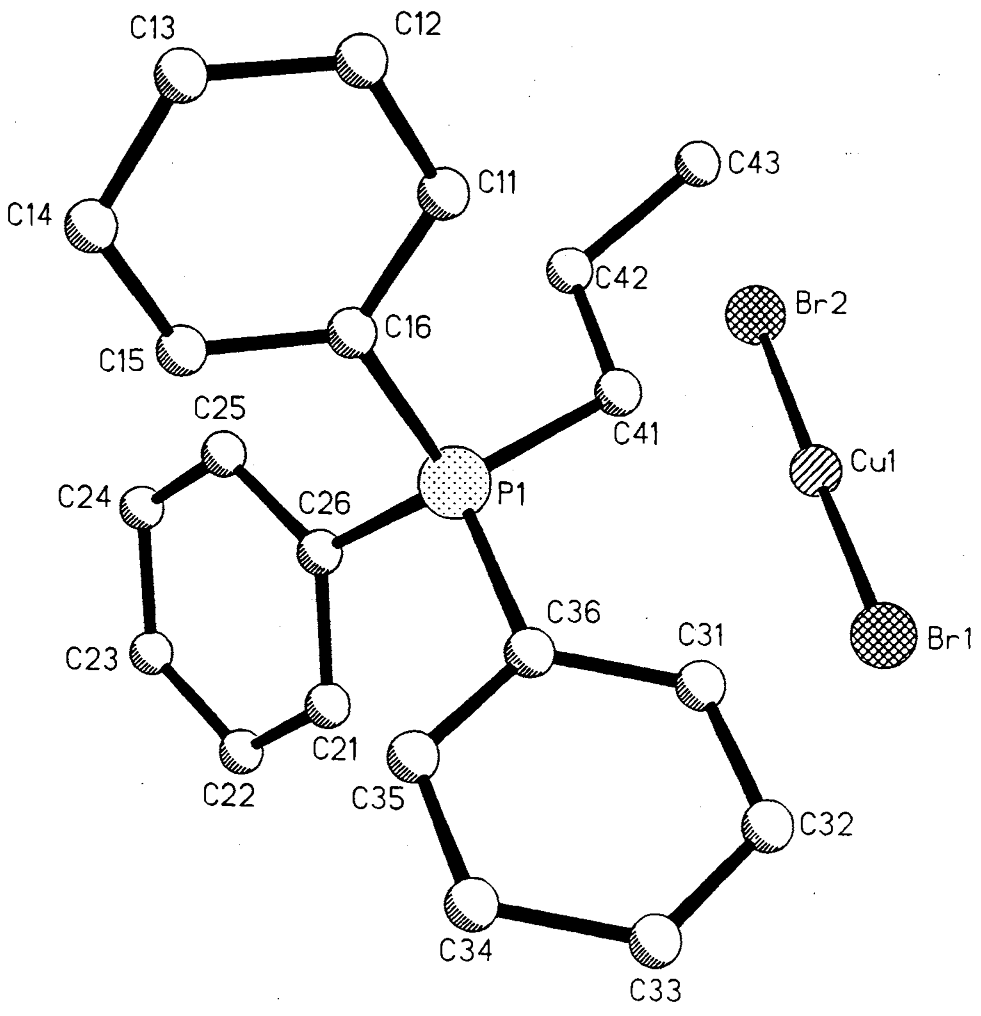

Figure 38. Projection View of [(*n*-Propyl)-Ph_3P][$CuBr_2$].

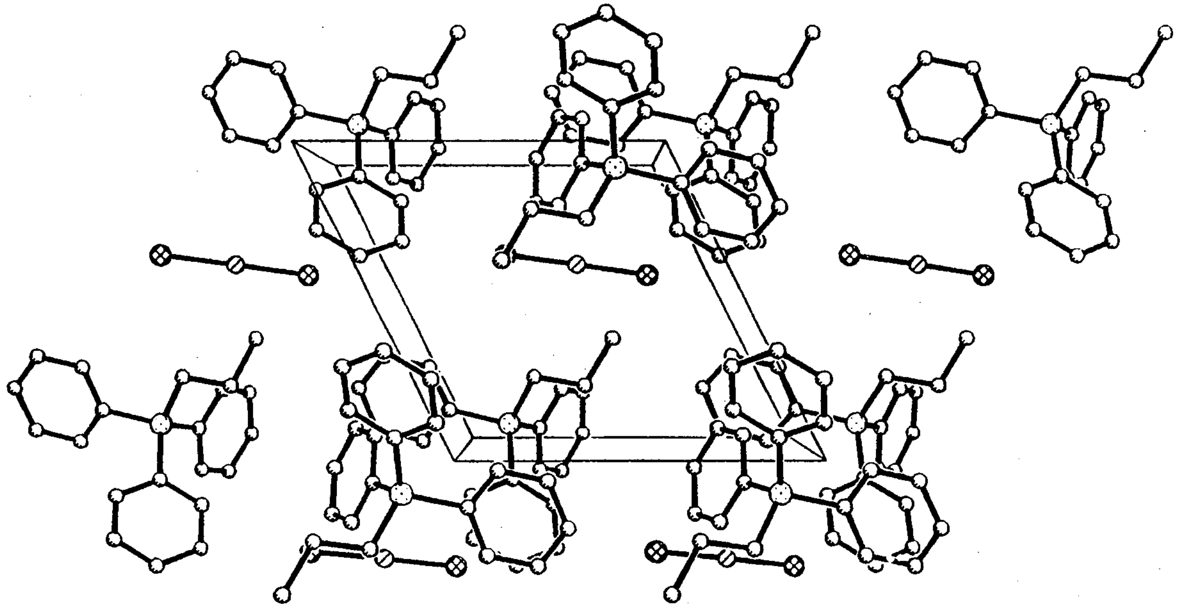

Figure 39. Packing Diagram for [(n-Propyl)-Ph_3P][$CuBr_2$].

TABLE 48

CRYSTAL DATA FOR [(*n*-Propyl)-Ph_3P][$CuBr_2$]

Formula	$CuBr_2PC_{21}H_{22}$
MWT	528.7
a	9.582(2) Å
b	12.741(3)
c	9.906(2)
α	90.0°
β	117.06(3)
γ	90.0
V	1076.9(4) $Å^3$
F (000)	524
μMoK_α	48.00 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	1.631 g cm^{-3}
Z	2
Independent. Refl.	2713
Obs. Refl. ($F > 2.6\sigma(F)$)	924
Variab.	253
R/R_w	7.0/6.8%
Space Group	$P2_1$
Octants Meas.	+h, +k, ±l

TABLE 49

POSITIONAL PARAMETERS FOR [(*n*-Propyl)-Ph_3P][$CuBr_2$]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Br1	0.4094 (4)	0.4231	0.7920 (4)
Br2	-0.3439 (4)	0.5455 (5)	0.4066 (5)
Cu1	-0.3746 (4)	0.4884 (6)	0.6017 (5)
P1	-0.0916 (1)	0.1020 (8)	0.8261 (8)
C11	-0.198 (2)	-0.066 (2)	0.630 (2)
C12	-0.183	-0.163	0.574
C13	-0.038	-0.215	0.637
C14	0.091	-0.169	0.757
C15	0.076	-0.071	0.813
C16	-0.069	-0.020	0.749
C21	0.135 (2)	0.232 (2)	1.026 (2)
C22	0.268	0.296	1.076
C23	0.352	0.302	0.993
C24	0.304	0.244	0.859
C25	0.171	0.180	0.810
C26	0.087	0.174	0.893
C31	-0.281 (2)	0.103 (2)	0.972 (2)
C32	-0.316	0.078	1.090
C33	-0.208	0.023	1.216
C34	-0.064	-0.006	1.224
C35	-0.028	0.020	1.107
C36	-0.136	0.074	0.980
C41	-0.251 (3)	0.176 (2)	0.682 (3)
C42	-0.224 (3)	0.207 (3)	0.551 (3)
C43	-0.379 (3)	0.231 (3)	0.406 (3)

TABLE 50

HYDROGEN POSITIONAL PARAMETERS FOR [(*n*-Propyl)-Ph_3P][$CuBr_2$]

ATOM	x	y	z
H11	-0.2972	-0.0304	0.5861
H12	-0.2717	-0.1949	0.4912
H13	-0.0281	0.2818	0.5983
H14	0.1901	-0.2042	0.8003
H15	0.1646	-0.0396	0.8951
H21	0.0773	0.2287	1.0836
H22	0.3015	0.3359	1.1677
H23	0.4437	0.3452	1.0269
H24	0.3616	0.2473	0.8019
H25	0.1374	0.1401	0.7178
H31	-0.3552	0.1409	0.8848
H32	-0.4155	0.0980	1.0837
H33	-0.2324	0.0059	1.2970
H34	0.0110	-0.0433	1.3114
H35	0.0712	-0.0004	1.1126
H41A	-0.2716	0.2379	0.7243
H41B	-0.3433	0.1324	0.6427
H42A	-0.1861	0.1464	0.5199
H42B	-0.1431	0.2595	0.5854
H43A	-0.3553	0.2500	0.3254
H43B	-0.4591	0.1782	0.3721
H43C	-0.4158	0.2921	0.4380

TABLE 51

ANISOTROPIC THERMAL PARAMETERS FOR $[(\textit{n}\text{-Propyl})\text{-Ph}_3\text{P}][\text{CuBr}_2]$

ATOM	U11	U22	U33	U12	U13	U23
Br1	61 (2)	101 (4)	69 (3)	-4 (3)	-35 (2)	-5 (3)
Br2	82 (3)	126 (5)	92 (4)	19 (3)	46 (3)	43 (3)
Cu1	52 (2)	82 (3)	78 (3)	1 (3)	29 (2)	11 (3)
P1	30 (5)	48 (6)	37 (5)	-2 (4)	14 (4)	2 (5)
C11	6 (2)	8 (3)	5 (2)	-2 (2)	3 (2)	-2 (2)
C12	10 (3)	7 (3)	3 (2)	1 (3)	2 (2)	-1 (2)
C13	10 (3)	3 (2)	7 (3)	6 (2)	4 (2)	3 (2)
C14	8 (2)	11 (4)	4 (2)	1 (3)	1 (2)	1 (3)
C15	7 (2)	3 (2)	8 (2)	4 (2)	4 (2)	3 (2)
C16	5 (2)	3 (2)	4 (2)	2 (2)	0 (2)	0 (2)
C21	3 (2)	4 (2)	6 (2)	0 (2)	3 (2)	-1 (2)
C22	8 (3)	4 (2)	2 (2)	-1 (2)	-1 (2)	-2 (2)
C23	3 (2)	9 (3)	7 (3)	0 (2)	3 (2)	-1 (3)
C24	8 (3)	4 (2)	9 (3)	4 (2)	6 (2)	3 (2)
C25	3 (2)	6 (2)	6 (2)	-1 (2)	4 (2)	0 (2)
C26	5 (2)	0 (2)	3 (2)	2 (2)	-1 (2)	0 (2)
C31	4 (2)	5 (2)	6 (2)	0 (2)	1 (2)	-1 (2)
C32	8 (2)	6 (3)	13 (3)	4 (2)	9 (3)	6 (3)
C33	10 (2)	5 (3)	8 (3)	-3 (2)	7 (2)	-2 (2)
C34	5 (2)	7 (3)	5 (2)	0 (2)	2 (2)	-1 (2)
C35	4 (2)	7 (3)	5 (2)	-1 (2)	1 (2)	4 (2)
C36	3 (2)	4 (2)	6 (2)	-2 (2)	0 (2)	-2 (2)
C41	9 (2)	1 (2)	6 (2)	-2 (2)	4 (2)	-1 (2)
C42	3 (2)	6 (3)	5 (2)	-1 (2)	1 (2)	2 (2)
C43	5 (2)	10 (3)	9 (3)	2 (2)	2 (2)	-3 (3)

The anisotropic displacement exponent takes the form:

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

$\times 10^3$ for Br, Cu, and P, $\times 10^2$ for C.

TABLE 52

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR [(*n*-Propyl)-Ph_3P][$CuBr_2$]

Cu1 - Br1	2.220 (7)	Br1 - Cu1 - Br2	177.1 (4)
Cu1 - Br2	2.207 (8)	C16 - P1 - C26	109 (1)
P1 - C16	1.79 (2)	C16 - P1 - C36	108 (1)
P1 - C26	1.78 (2)	C26 - P1 - C36	110 (1)
P1 - C36	1.80 (3)	C16 - P1 - C41	110 (1)
P1 - C41	1.81 (2)	C26 - P1 - C41	110 (1)
C41 - C42	1.49 (5)	C36 - P1 - C41	109 (1)
C42 - C43	1.55 (3)	P1 - C16 - C11	120 (1)
C11 - C12	1.395	P1 - C16 - C15	120 (1)
C12 - C13	1.395	P1 - C26 - C21	118 (1)
C13 - C14	1.395	P1 - C26 - C25	121 (1)
C14 - C15	1.395	P1 - C36 - C31	120 (1)
C15 - C16	1.395	P1 - C36 - C35	119 (1)
C16 - C11	1.395	P1 - C41 - C42	114 (2)
C21 - C22	1.395	C41 - C42 - C43	112 (2)
C22 - C23	1.395	C11 - C12 - C13	120.0
C23 - C24	1.395	C12 - C13 - C14	120.0
C24 - C25	1.395	C13 - C14 - C15	120.0
C25 - C26	1.395	C14 - C15 - C16	120.0
C26 - C21	1.395	C15 - C16 - C11	120.0
C31 - C32	1.395	C16 - C11 - C12	120.0
C32 - C33	1.395	C21 - C22 - C23	120.0
C33 - C34	1.395	C22 - C23 - C24	120.0
C34 - C35	1.395	C23 - C24 - C25	120.0
C35 - C36	1.395	C24 - C25 - C26	120.0
C36 - C31	1.395	C25 - C26 - C21	120.0
		C26 - C21 - C22	120.0
		C31 - C32 - C33	120.0
		C32 - C33 - C34	120.0
		C33 - C34 - C35	120.0

TABLE 52 (Continued)

	C34 - C35 - C36	120.0
	C35 - C36 - C31	120.0
	C36 - C31 - C32	120.0
	C41 - C42 - C43	120.0
	C42 - C43 - C44	120.0
	C43 - C44 - C45	120.0
	C44 - C45 - C46	120.0
	C45 - C46 - C41	120.0
	C46 - C41 - C42	120.0

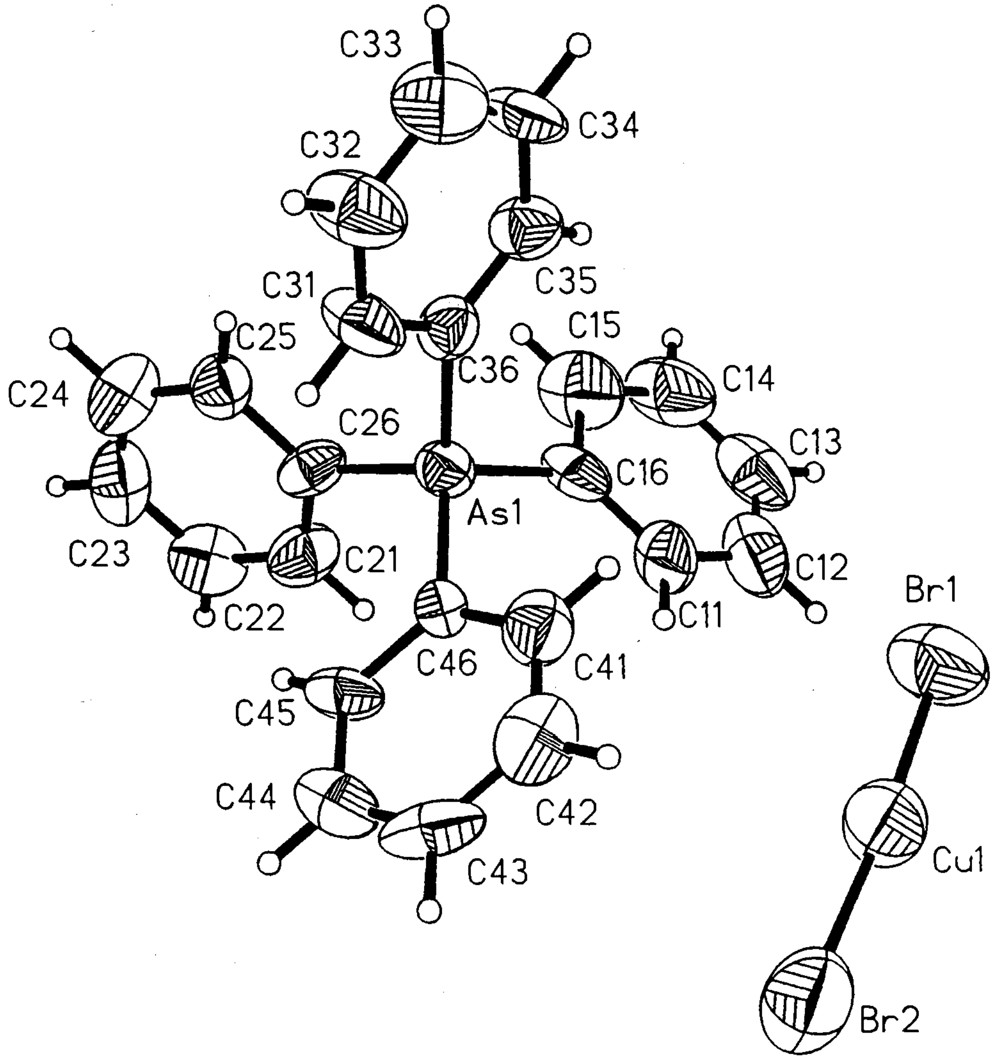

Figure 40. Projection View of $[Ph_4As][CuBr_2]$.

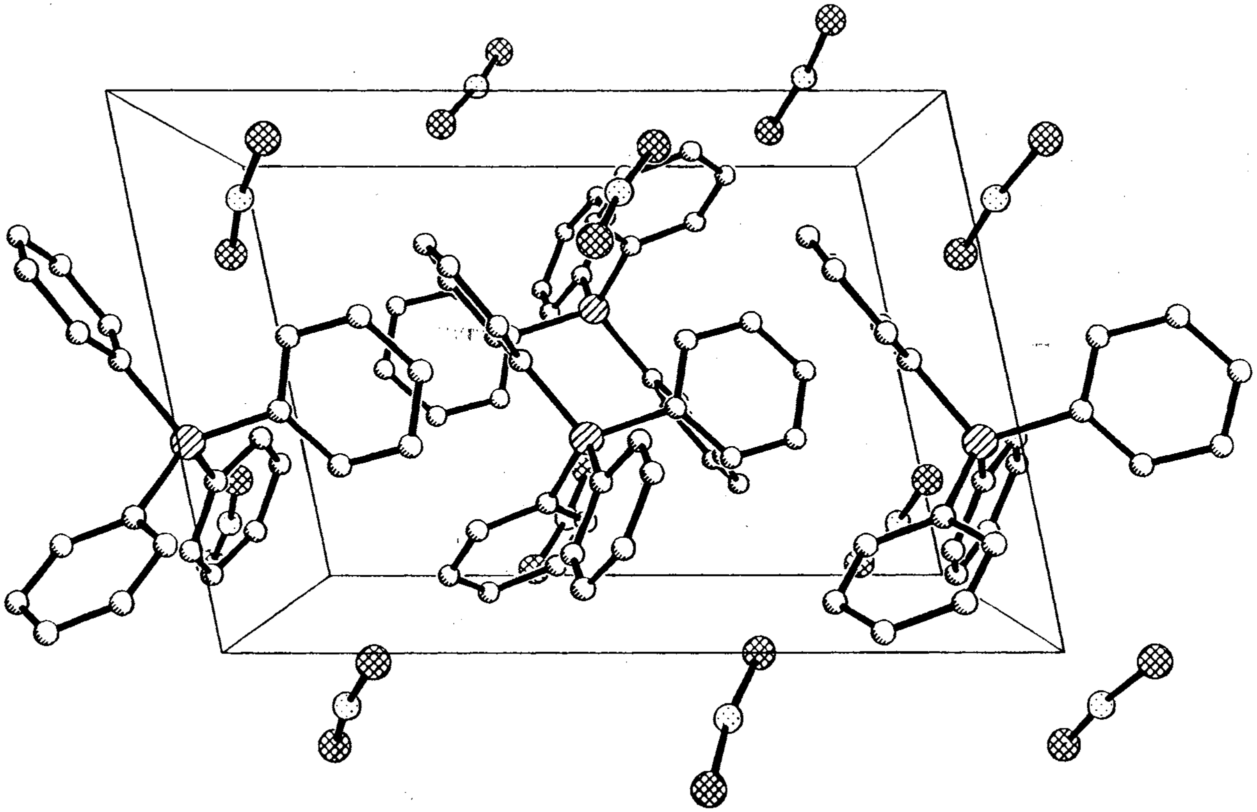

Figure 41. Packing Diagram for [Ph_4As][$CuBr_2$].

TABLE 53

CRYSTAL DATA FOR $[Ph_4As][CuBr_2]$

Formula	$CuBr_2AsC_{24}H_{20}$
MWT	606.70
a	9.438(2) Å
b	18.408(4)
c	13.700(3)
α	90.0°
β	102.06(3)
γ	90.0
V	2327.6(9) $Å^3$
F (000)	1184
μMoK_α	57.89 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	1.731 g cm^{-3}
Z	4
Independent Refl.	5344
Obs. Refl. ($F > 4.0\sigma(F)$)	1198
Variab.	206
R/R_W	3.4/2.4%
Space Group	$P2_1/c$
Octants Meas.	+h, +k, ±l

TABLE 54

POSITIONAL PARAMETERS FOR [Ph_4As][$CuBr_2$]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Br1	1.0549 (2)	0.2967 (1)	0.3513 (1)
Br2	1.2617 (2)	0.0886 (1)	0.4560 (1)
As1	0.6364 (1)	0.1683 (1)	0.0219 (1)
Cu1	1.1587 (2)	0.1947 (1)	0.4122 (1)
C11	0.8537 (11)	0.2785 (5)	0.0690 (5)
C12	0.9094	0.3481	0.0620
C13	0.8276	0.3999	0.0004
C14	0.6899	0.3822	-0.0541
C15	0.6342	0.3126	-0.0471
C16	0.7161	0.2608	0.0145
C21	0.6774 (6)	0.1314 (4)	-0.1689 (9)
C22	0.6394	0.1011	-0.2641
C23	0.5009	0.0725	-0.2977
C24	0.4004	0.0742	-0.2361
C25	0.4385	0.1045	-0.1409
C26	0.5769	0.1332	-0.1073
C31	0.4319 (11)	0.1057 (5)	0.1178 (7)
C32	0.3148	0.1044	0.1654
C33	0.2472	0.1691	0.1827
C34	0.2966	0.2351	0.1526
C35	0.4137	0.2365	0.1050
C36	0.4813	0.1718	0.0877
C41	0.8249 (10)	0.1172 (4)	0.1970 (8)
C42	0.9217	0.0684	0.2535
C43	0.9652	0.0066	0.2085
C44	0.9119	-0.0063	0.1072
C45	0.8151	0.0425	0.0507

TABLE 54 (Continued)

C46	0.7715	0.1043	0.0957

TABLE 55

HYDROGEN POSITIONAL PARAMETERS FOR $[Ph_4As][CuBr_2]$

ATOM	x	y	z
H11A	0.9101	0.2429	0.1113
H12A	1.0042	0.3603	0.0995
H13A	0.8659	0.4477	-0.0044
H14A	0.6336	0.4178	-0.0965
H15A	0.5395	0.3004	-0.0846
H21A	0.7727	0.1511	-0.1458
H22A	0.7085	0.0999	-0.3065
H23A	0.4747	0.0516	-0.3632
H24A	0.3051	0.0545	-0.2593
H25A	0.3693	0.1057	-0.0986
H31A	0.4785	0.0612	0.1059
H32A	0.2808	0.0590	0.1861
H33A	0.1666	0.1682	0.2155
H34A	0.2500	0.2797	0.1645
H35A	0.4477	0.2819	0.0843
H41A	0.7949	0.1597	0.2279
H42A	0.9584	0.0773	0.3232
H43A	1.0319	-0.0270	0.2474
H44A	0.9419	-0.0488	0.0763
H45A	0.7784	0.0336	-0.0190

TABLE 56

ANISOTROPIC THERMAL PARAMETERS FOR $[Ph_4As][CuBr_2]$

ATOM	U11	U22	U33	U12	U13	U23
Br1	98 (1)	78 (1)	131 (1)	22 (1)	32 (1)	6 (1)
Br2	112 (1)	75 (1)	113 (1)	-5 (1)	-23 (1)	13 (1)
As1	45 (1)	41 (1)	54 (1)	3 (1)	13 (1)	1 (1)
Cu1	85 (1)	67 (1)	87 (1)	1 (1)	6 (1)	4 (1)
C11	7 (1)	4 (1)	9 (1)	-2 (1)	2 (1)	0 (1)
C12	10 (1)	7 (1)	9 (1)	-2 (1)	4 (1)	-3 (1)
C13	10 (1)	5 (1)	12 (1)	-1 (1)	8 (1)	-1 (1)
C14	9 (1)	6 (1)	14 (1)	2 (1)	4 (1)	2 (1)
C15	10 (1)	6 (1)	12 (1)	0 (1)	4 (1)	2 (1)
C16	6 (1)	5 (1)	6 (1)	1 (1)	3 (2)	0 (1)
C21	5 (1)	9 (1)	5 (1)	0 (1)	0 (1)	0 (1)
C22	8 (1)	8 (1)	5 (1)	1 (1)	3 (1)	1 (1)
C23	11 (1)	5 (1)	6 (1)	0 (1)	-4 (1)	1 (1)
C24	7 (1)	9 (1)	8 (1)	-2 (1)	1 (1)	0 (1)
C25	6 (1)	5 (1)	5 (1)	0 (1)	0 (1)	0 (1)
C26	4 (1)	5 (1)	6 (1)	0 (1)	1 (1)	2 (1)
C31	8 (1)	4 (1)	12 (1)	0 (1)	6 (1)	0 (1)
C32	9 (1)	6 (1)	11 (1)	2 (1)	5 (1)	2 (1)
C33	8 (1)	10 (1)	8 (1)	0 (1)	4 (1)	1 (1)
C34	6 (1)	7 (1)	10 (1)	4 (1)	2 (1)	-1 (1)
C35	5 (1)	5 (1)	7 (1)	0 (1)	2 (1)	1 (1)
C36	4 (1)	4 (1)	6 (1)	0 (1)	1 (1)	1 (1)
C41	6 (1)	6 (1)	6 (1)	-1 (1)	1 (1)	0 (1)
C42	8 (1)	10 (1)	6 (1)	-2 (1)	2 (1)	0 (1)
C43	4 (1)	9 (1)	10 (1)	2 (1)	1 (1)	4 (1)
C44	7 (1)	6 (1)	9 (1)	2 (1)	3 (1)	0 (1)
C45	5 (1)	5 (1)	7 (1)	2 (1)	2 (1)	2 (1)

TABLE 56 (Continued)

C46	4 (1)	4 (1)	4 (1)	0 (1)	1 (1)	0 (1)

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

TABLE 57

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR [Ph_4As][$CuBr_2$]

Br1 - Cu1	2.199 (2)	Br1 - Cu1 - Br2	173.6 (1)
Br2 - Cu1	2.209 (2)	C16 - As1 - C26	108.0 (3)
As1 - C16	1.87 (1)	C16 - As1 - C36	111.0 (4)
As1 - C26	1.86 (1)	C26 - As1 - C36	111.0 (3)
As1 - C36	1.87 (1)	C16 - As1 - C46	111.5 (4)
As1 - C46	1.87 (1)	C26 - As1 - C46	109.3 (4)
C11 - C12	1.395	C36 - As1 - C46	105.9 (4)
C12 - C13	1.395	C12 - C11 - C16	120.0
C13 - C14	1.395	C11 - C12 - C13	120.0
C14 - C15	1.395	C12 - C13 - C14	120.0
C15 - C16	1.395	C13 - C14 - C15	120.0
C16 - C11	1.395	C14 - C15 - C16	120.0
C21 - C22	1.395	As1 - C16 - C11	121.5 (3)
C22 - C23	1.395	As1 - C16 - C15	118.5 (3)
C23 - C24	1.395	C11 - C16 - C15	120.0
C24 - C25	1.395	C22 - C21 - C26	120.0
C25 - C26	1.395	C21 - C22 - C23	120.0
C26 - C21	1.395	C22 - C23 - C24	120.0
C31 - C32	1.395	C23 - C24 - C25	120.0
C32 - C33	1.395	C24 - C25 - C26	120.0
C33 - C34	1.395	As1 - C26 - C21	118.4 (2)
C34 - C35	1.395	As1 - C26 - C25	121.4 (2)
C35 - C36	1.395	C21 - C26 - C25	120.0
C36 - C31	1.395	C32 - C31 - C36	120.0
C41 - C42	1.395	C31 - C32 - C33	120.0
C42 - C43	1.395	C32 - C33 - C34	120.0
C43 - C44	1.395	C33 - C34 - C35	120.0
C44 - C45	1.395	C34 - C35 - C36	120.0

TABLE 57 (Continued)

C45 - C46	1.395	As1 - C36 - C31	117.2 (3)
C46 - C41	1.395	As1 - C36 - C35	122.8 (3)
		C31 - C36 - C35	120.0
		C42 - C41 - C46	120.0
		C41 - C42 - C43	120.0
		C42 - C43 - C44	120.0
		C43 - C44 - C45	120.0
		C44 - C45 - C46	120.0
		As1 - C46 - C41	119.6 (3)
		As1 - C46 - C45	120.4 (3)
		C41 - C46 - C45	120.0

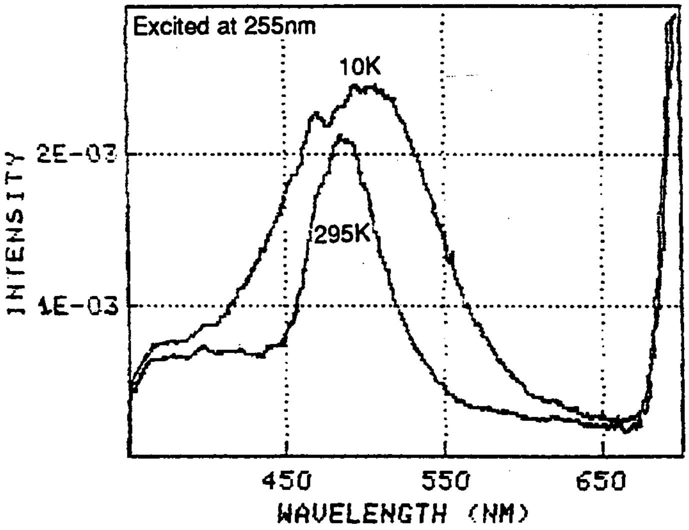

Figure 42. Emission Spectra of [Rb-(15-Crown-5)$_2$][CuBr$_2$].

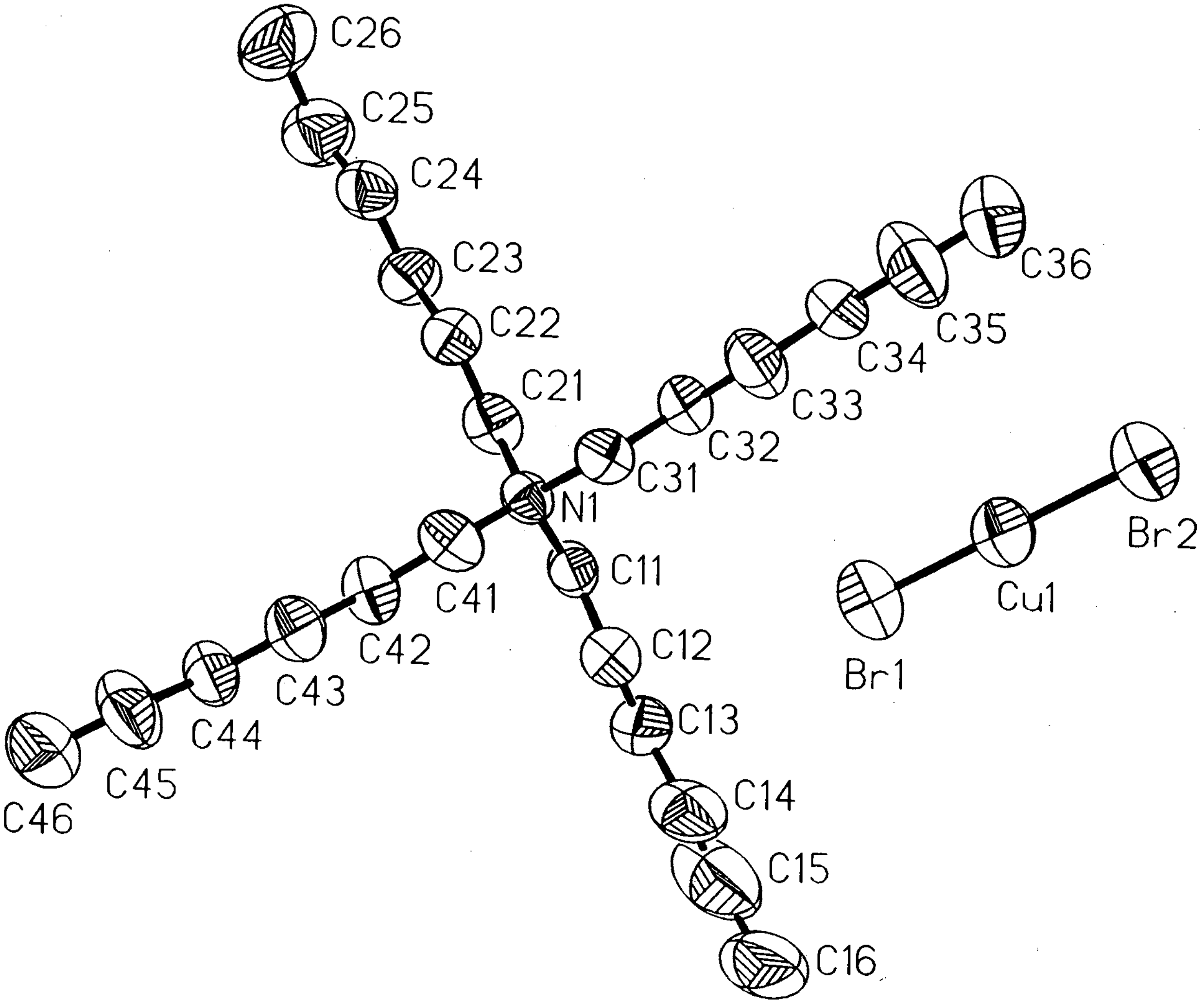

Figure 43. Projection View of [(*n*-Hexyl)$_4$N][CuBr$_2$].

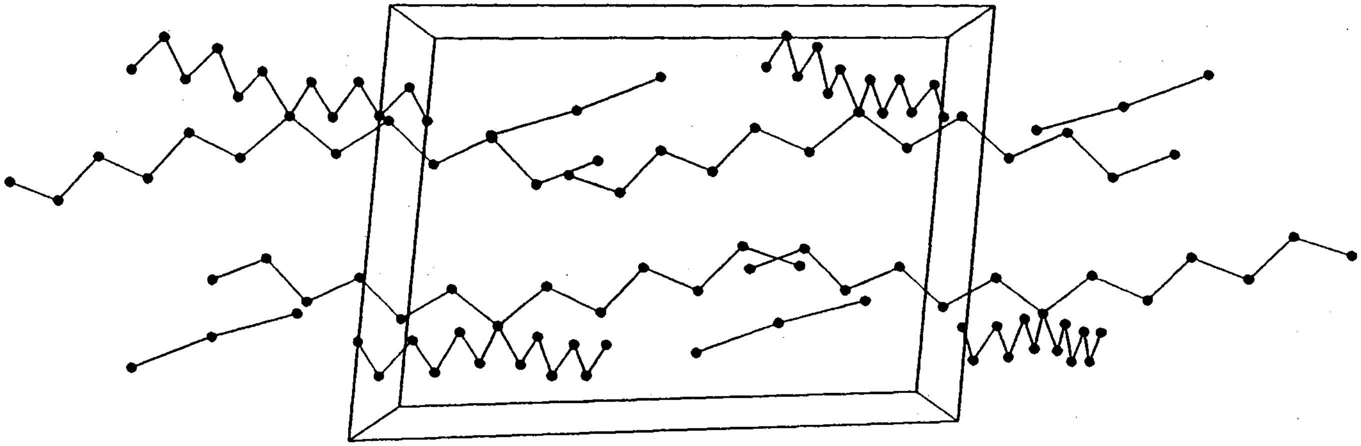

Figure 44. Packing Diagram for [(*n*-Hexyl)$_4$N][CuBr$_2$].

TABLE 58

CRYSTAL DATA FOR $[(n\text{-Hexyl})_4N][CuBr_2]$

Formula	$CuBr_2NC_{24}H_{52}$
MWT	578.0
a	9.350(2) Å
b	12.292(2)
c	13.494(3)
α	76.44(3)°
β	83.73(3)
γ	87.46(3)
V	1498.4(5) $Å^3$
F (000)	604
μMoK_α	34.05 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	1.281 g cm^{-3}
Z	2
Independent Refl.	5240
Obs. Refl. $(F > 4.0\sigma(F))$	1313
Variab.	254
R/R_w	4.2/4.4%
Space Group	P1bar
Octants Meas.	+h, ±k, ±l

TABLE 59

POSITIONAL PARAMETERS FOR $[(n\text{-Hexyl})_4N][CuBr_2]$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cu1	0.2226 (1)	0.5498 (1)	1.6989 (1)
Br1	0.1451 (2)	0.6430 (1)	1.5546 (1)
Br2	0.2795 (2)	0.4543 (1)	1.8502 (1)
N1	0.232 (1)	0.555 (9)	1.194 (1)
C11	0.126 (1)	0.635 (1)	1.237 (1)
C12	0.193 (1)	0.737 (1)	1.260 (1)
C13	0.084 (2)	0.819 (1)	1.289 (1)
C14	0.161 (2)	0.913 (1)	1.321 (1)
C15	0.071 (2)	0.996 (2)	1.349 (1)
C16	0.149 (2)	1.088 (1)	1.380 (2)
C21	0.143 (1)	0.465 (1)	1.173 (1)
C22	0.227 (1)	0.370 (1)	1.139 (1)
C23	0.133 (1)	0.292 (1)	1.107 (1)
C24	0.218 (1)	0.200 (1)	1.072 (1)
C25	0.138 (2)	0.124 (1)	1.028 (1)
C26	0.225 (2)	0.031 (1)	0.996 (1)
C31	0.332 (1)	0.503 (1)	1.276 (1)
C32	0.266 (1)	0.431 (1)	1.376 (1)
C33	0.378 (1)	0.384 (1)	1.445 (1)
C34	0.319 (1)	0.308 (1)	1.545 (1)
C35	0.429 (2)	0.260 (1)	1.615 (1)
C36	0.379 (2)	0.192 (1)	1.715 (1)
C41	0.328 (1)	0.615 (1)	1.103 (1)
C42	0.251 (1)	0.680 (1)	1.012 (1)
C43	0.360 (1)	0.732 (1)	0.926 (1)
C44	0.298 (1)	0.793 (1)	0.829 (1)
C45	0.413 (1)	0.838 (1)	0.745 (1)
C46	0.358 (1)	0.894 (1)	0.645 (1)

TABLE 60

HYDROGEN POSITIONAL PARAMETERS FOR $[(n\text{-Hexyl})_4N][CuBr_2]$

ATOM	x	y	z
H11A	0.0674	0.5966	1.2968
H11B	0.0646	0.6657	1.1846
H12A	0.2596	0.7704	1.2024
H12B	0.2466	0.7075	1.3173
H13A	0.0124	0.7833	1.3422
H13B	0.0367	0.8524	1.2297
H14A	0.2339	0.9467	1.2689
H14B	0.2076	0.8785	1.3814
H15A	-0.0014	0.9626	1.4024
H15B	0.0233	1.0299	1.2893
H16A	0.0811	1.1437	1.3950
H16B	0.1952	1.0535	1.4399
H16C	0.2201	1.1214	1.3258
H21A	0.0870	0.4982	1.1176
H21B	0.0779	0.4324	1.2313
H22A	0.2751	0.3282	1.1956
H22B	0.2977	0.4004	1.0832
H23A	0.0852	0.3348	1.0505
H23B	0.0622	0.2632	1.1626
H24A	0.2562	0.1522	1.1305
H24B	0.2969	0.2294	1.0229
H25A	0.1005	0.1704	0.9687
H25B	0.0592	0.0933	1.0766
H26A	0.1697	-0.0139	0.9660
H26B	0.3040	0.0629	0.9477
H26C	0.2624	-0.0146	1.0562
H31A	0.3817	0.5616	1.2930
H31B	0.4020	0.4574	1.2461

TABLE 60 (Continued)

H32A	0.2203	0.3684	1.3622
H32B	0.1945	0.4743	1.4077
H33A	0.4203	0.4467	1.4604
H33B	0.4512	0.3444	1.4110
H34A	0.2730	0.2474	1.5292
H34B	0.2484	0.3488	1.5802
H35A	0.4763	0.3223	1.6285
H35B	0.4987	0.2200	1.5793
H36A	0.4586	0.1663	1.7540
H36B	0.3107	0.2317	1.7520
H36C	0.3333	0.1282	1.7023
H41A	0.3881	0.5594	1.0791
H41B	0.3884	0.6657	1.1226
H42A	0.1890	0.7367	1.0341
H42B	0.1932	0.6309	0.9883
H43A	0.4261	0.6756	0.9100
H43B	0.4120	0.7852	0.9497
H44A	0.2367	0.8535	0.8431
H44B	0.2408	0.7414	0.8073
H45A	0.4750	0.7770	0.7332
H45B	0.4680	0.8900	0.7668
H46A	0.4346	0.9221	0.5931
H46B	0.3035	0.8415	0.6233
H46C	0.2965	0.9553	0.6572

TABLE 61

ANISOTROPIC THERMAL PARAMETERS FOR $[(n\text{-Hexyl})_4N][CuBr_2]$

ATOM	U11	U22	U33	U12	U13	U23
Cu1	78 (1)	101 (1)	82 (1)	-5 (1)	0 (1)	-14 (1)
Br1	121 (1)	136 (2)	88 (1)	-2 (1)	-15 (1)	-1 (1)
Br2	90 (2)	127 (1)	87 (1)	6 (1)	-11 (1)	-4 (1)
N1	51 (6)	57 (7)	57 (6)	8 (7)	-7 (6)	-6 (6)
C11	8 (1)	7 (1)	5 (1)	1 (1)	0 (1)	0 (1)
C12	11 (1)	7 (1)	8 (1)	0 (1)	-1 (1)	-1 (1)
C13	15 (2)	8 (1)	9 (1)	1 (1)	-3 (1)	-2 (1)
C14	15 (2)	7 (1)	12 (1)	4 (1)	3 (1)	-1 (1)
C15	20 (2)	14 (2)	15 (2)	2 (2)	4 (2)	2 (1)
C16	30 (2)	10 (2)	13 (2)	-4 (2)	7 (2)	-1 (1)
C21	5 (1)	8 (1)	8 (1)	-2 (1)	0 (1)	0 (1)
C22	5 (1)	7 (1)	8 (1)	1 (1)	-1 (1)	-2 (1)
C23	9 (1)	7 (1)	9 (1)	-2 (1)	-2 (1)	-2 (1)
C24	11 (1)	7 (1)	8 (1)	-2 (1)	-1 (1)	-1 (1)
C25	13 (1)	10 (1)	12 (1)	-1 (1)	-2 (1)	-3 (1)
C26	17 (2)	11 (1)	14 (1)	-3 (1)	-1 (1)	-6 (1)
C31	5 (1)	6 (1)	7 (1)	0 (1)	-2 (1)	-1 (1)
C32	9 (1)	7 (1)	6 (1)	0 (1)	-1 (1)	-1 (1)
C33	11 (1)	9 (1)	7 (1)	-1 (1)	-2 (1)	1 (1)
C34	14 (1)	7 (1)	8 (1)	1 (1)	-3 (1)	-1 (1)
C35	16 (2)	14 (2)	8 (1)	1 (1)	-2 (1)	2 (1)
C36	22 (2)	13 (1)	10 (1)	0 (1)	-6 (1)	-2 (1)
C41	4 (1)	7 (1)	8 (1)	-3 (1)	1 (1)	0 (1)
C42	5 (1)	10 (1)	7 (1)	0 (1)	0 (1)	-1 (1)
C43	6 (1)	8 (1)	7 (1)	-1 (1)	0 (1)	-1 (1)
C44	8 (1)	8 (1)	6 (1)	1 (1)	0 (1)	0 (1)
C45	12 (1)	11 (1)	7 (1)	2 (1)	-1 (1)	2 (1)

TABLE 61 (Continued)

C46	14 (1)	11 (1)	11 (1)	-2 (1)	1 (1)	0 (1)

The anisotropic displacement exponent takes the form:
$\exp(-2\pi (U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$
x 10^3 for Cu and Br, and x 10^2 for N and C.

TABLE 62

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[(n\text{-Hexyl})_4N][CuBr_2]$

Cu1 - Br1	2.195 (2)	Br1 - Cu1 - Br2	174.7 (1)
Cu1 - Br2	2.210 (2)	C11 - N1 - C21	106.6 (9)
N1 - C11	1.53 (2)	C11 - N1 - C31	107.9 (8)
N1 - C21	1.51 (2)	C21 - N1 - C31	109.4 (8)
N1 - C31	1.54 (1)	C11 - N1 - C41	112.2 (8)
N1 - C41	1.50 (1)	C21 - N1 - C41	114.5 (9)
C11 - C12	1.53 (2)	C31 - N1 - C41	106.0 (8)
C12 - C13	1.49 (2)	N1 - C11 - C12	115.6 (9)
C13 - C14	1.56 (2)	C11 - C12 - C13	113 (1)
C14 - C15	1.39 (2)	C12 - C13 - C14	110 (1)
C15 - C16	1.53 (3)	C13 - C14 - C15	115 (1)
C21 - C22	1.51 (2)	C14 - C15 - C16	114 (2)
C22 - C23	1.49 (2)	N1 - C21 - C22	115.8 (9)
C23 - C24	1.49 (2)	C21 - C22 - C23	112.6 (9)
C24 - C25	1.48 (2)	C22 - C23 - C24	112 (1)
C25 - C26	1.49 (2)	C23 - C24 - C25	117 (1)
C31 - C32	1.52 (1)	C24 - C25 - C26	116 (1)
C32 - C33	1.49 (2)	N1 - C31 - C32	118.2 (9)
C33 - C34	1.51 (2)	C31 - C32 - C33	111 (1)
C34 - C35	1.48 (2)	C32 - C33 - C34	114 (1)
C35 - C36	1.45 (2)	C33 - C34 - C35	115 (1)
C41 - C42	1.52 (2)	C34 - C35 - C36	118 (1)
C42 - C43	1.50 (1)	N1 - C41 - C42	115.5 (8)
C43 - C44	1.51 (1)	C41 - C42 - C43	109.4 (9)
C44 - C45	1.50 (2)	C42 - C43 - C44	114.9 (9)
C45 - C46	1.49 (2)	C43 - C44 - C45	112.3 (9)
		C44 - C45 - C46	115 (1)

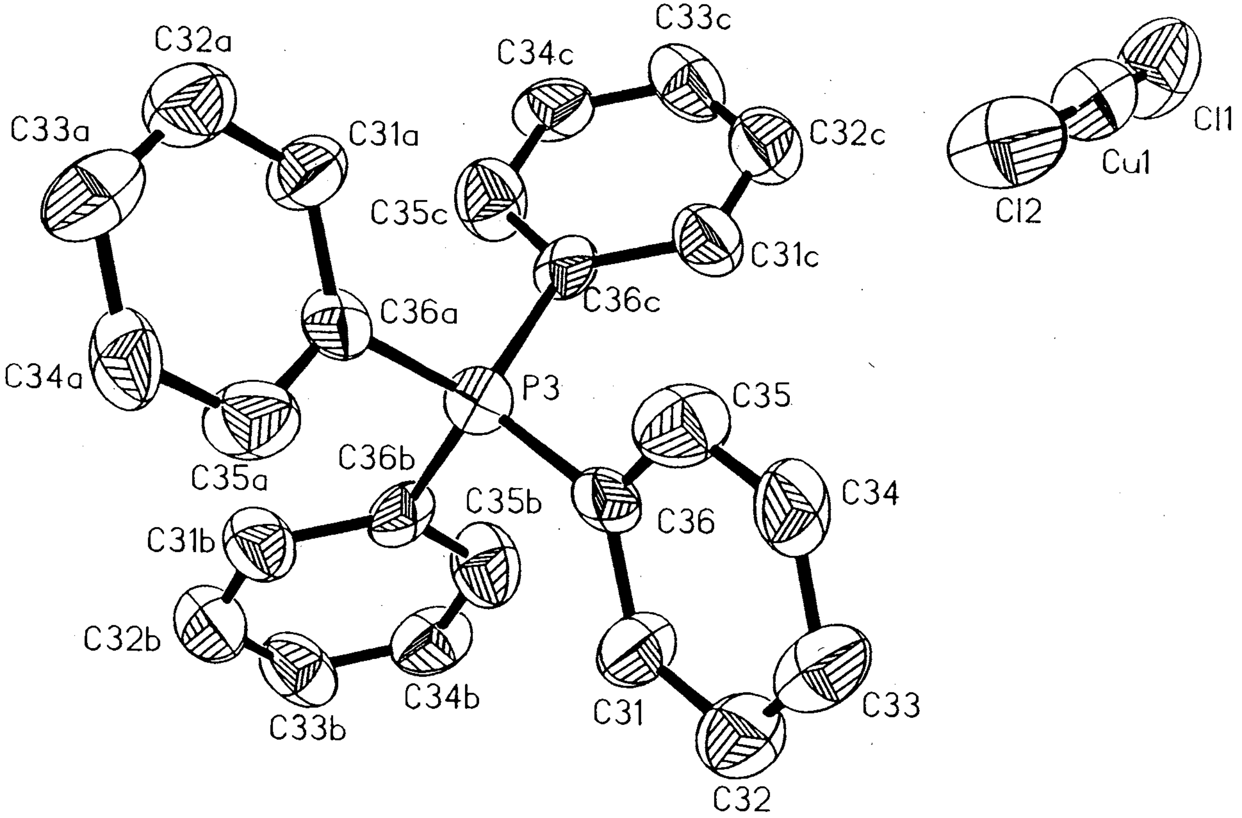

Figure 45. Projection View of $[Ph_4P][CuCl_2]$.

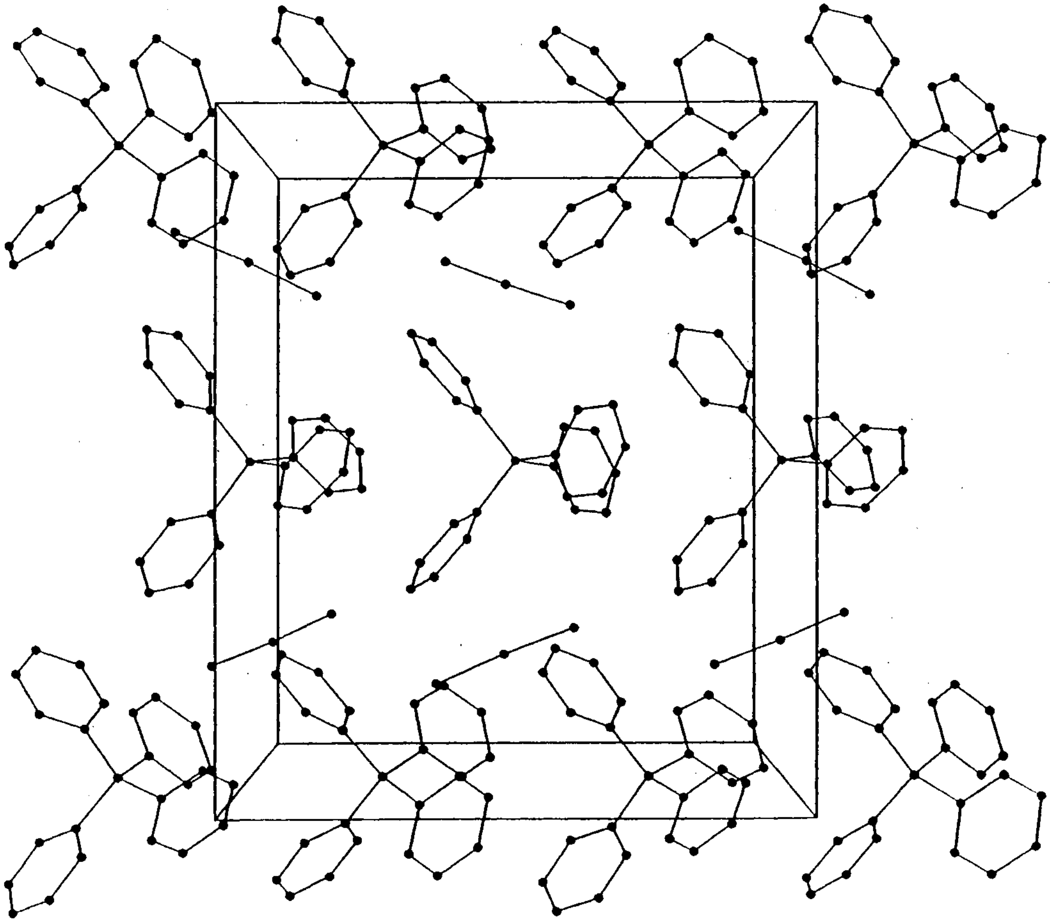

Figure 46. Packing Diagram for $[Ph_4P][CuCl_2]$.

TABLE 63

CRYSTAL DATA FOR $[Ph_4P][CuCl_2]$

Formula	$CuCl_2PC_{24}H_{20}$
MWT	473.8
a	17.341(2) Å
b	17.341(2)
c	14.568(3)
α	90.0°
β	90.0
γ	90.0
V	4381.0(12) $Å^3$
F (000)	1936
μMoK_α	13.21 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	1.437 g cm^{-3}
Z	8
Independent Refl.	3255
Obs. Refl. ($F > 4.0\sigma(F)$)	1059
Variab.	204
R/R_W	4.5/3.9%
Space Group	I4bar
Octants Meas.	+h, +k, +l

TABLE 64

POSITIONAL PARAMETERS FOR [Ph_4P][$CuCl_2$]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cu1	0.2929 (1)	0.1994 (1)	0.0297 (1)
Cl1	0.2560 (2)	0.1570 (3)	-0.1053 (3)
Cl2	0.3340 (2)	0.2478 (2)	0.1409 (3)
P1	0.5000	0	-0.7500
P2	0.5000	0.5000	0.5000
P3	0.5000	0.5000	0
P4	0	0.5000	0.2500
C11	0.3867 (6)	0.1039 (6)	-0.6958 (5)
C12	0.3252	0.1278	-0.6409
C13	0.3008	0.0820	-0.5678
C14	0.3378	0.0122	-0.5495
C15	0.3993	-0.0117	-0.6044
C16	0.4237	0.0342	-0.6775
C21	0.5797 (5)	0.4024 (6)	0.3859 (7)
C22	0.5858	0.3414	0.3239
C23	0.5212	0.2968	0.3031
C24	0.4505	0.3131	0.3444
C25	0.4444	0.3741	0.4065
C26	0.5090	0.4187	0.4272
C31	0.3655 (6)	0.5679 (5)	0.0669 (5)
C32	0.3025	0.5726	0.1263
C33	0.2914	0.5160	0.1930
C34	0.3432	0.4548	0.2004
C35	0.4061	0.4501	0.1410
C36	0.4173	0.5067	0.0743
C41	0.1119 (5)	0.3934 (5)	0.2036 (5)
C42	0.1411	0.3323	0.1519
C43	0.1004	0.3053	0.0758

TABLE 64 (Continued)

C44	0.0304	0.3393	0.0516
C45	0.0011	0.4004	0.1033
C46	0.0419	0.4274	0.1794

TABLE 65

HYDROGEN POSITIONAL PARAMETERS FOR $[Ph_4P][CuCl_2]$

ATOM	x	y	z
H11	0.4035	0.1355	-0.7461
H12	0.2998	0.1759	-0.6535
H13	0.2585	0.0985	-0.5300
H14	0.3210	-0.0193	-0.4992
H15	0.4247	-0.0597	-0.5919
H21	0.6242	0.4331	0.4002
H22	0.6345	0.3302	0.2955
H23	0.5254	0.2548	0.2605
H24	0.4060	0.2824	0.3302
H25	0.3957	0.3853	0.4349
H31	0.3732	0.6069	0.0210
H32	0.2669	0.6147	0.1212
H33	0.2481	0.5192	0.2339
H34	0.3355	0.4158	0.2464
H35	0.4417	0.4079	0.1461
H41	0.1399	0.4120	0.2560
H42	0.1893	0.3090	0.1686
H43	0.1205	0.2633	0.0402
H44	0.0023	0.3207	-0.0008
H45	-0.0470	0.4238	0.0866

TABLE 66

ANISOTROPIC THERMAL PARAMETERS FOR $[Ph_4P][CuCl_2]$

ATOM	U11	U22	U33	U12	U13	U23
Cu1	57 (1)	69 (1)	74 (1)	8 (1)	3 (1)	-2 (1)
Cl1	63 (3)	112 (4)	80 (3)	-5 (2)	-2 (3)	-24 (3)
Cl2	86 (3)	87 (3)	84 (3)	23 (2)	-14 (3)	-17 (3)
P1	44 (4)	44 (4)	37 (5)	0	0	0
P2	36 (2)	36 (2)	44 (6)	0	0	0
P3	42 (3)	42 (3)	46 (6)	0	0	0
P4	35 (3)	35 (3)	38 (5)	0	0	0
C11	6 (1)	5 (1)	5 (1)	-1 (1)	-1 (1)	-3 (1)
C12	5 (1)	8 (1)	6 (1)	1 (1)	-1 (1)	-2 (1)
C13	3 (1)	10 (1)	8 (1)	1 (1)	1 (1)	-4 (1)
C14	4 (1)	9 (1)	6 (1)	-1 (1)	2 (1)	-1 (1)
C15	5 (1)	8 (1)	5 (1)	-1 (1)	0 (1)	-1 (1)
C16	3 (1)	3 (1)	4 (1)	0 (1)	-2 (1)	-1 (1)
C21	7 (1)	5 (1)	4 (1)	0 (1)	0 (1)	-2 (1)
C22	6 (1)	8 (1)	6 (1)	2 (1)	1 (1)	0 (1)
C23	12 (2)	5 (1)	4 (1)	2 (1)	0 (1)	-2 (1)
C24	8 (1)	4 (1)	7 (1)	-1 (1)	0 (1)	-2 (1)
C25	4 (1)	5 (1)	6 (1)	0 (1)	0 (1)	-1 (1)
C26	2 (1)	4 (1)	4 (1)	0 (1)	0 (1)	-1 (1)
C31	4 (1)	6 (1)	6 (1)	1 (1)	0 (1)	0 (1)
C32	6 (1)	6 (1)	8 (1)	1 (1)	-1 (1)	0 (1)
C33	5 (1)	8 (1)	6 (1)	1 (1)	-1 (1)	-2 (1)
C34	6 (1)	6 (1)	6 (1)	-2 (1)	3 (1)	0 (1)
C35	7 (1)	6 (1)	6 (1)	1 (1)	0 (1)	2 (1)
C36	5 (1)	3 (1)	5 (1)	0 (1)	1 (1)	-2 (1)
C41	4 (1)	3 (1)	6 (1)	2 (1)	1 (1)	2 (1)
C42	5 (1)	6 (1)	7 (1)	2 (1)	0 (1)	1 (1)
C43	6 (1)	4 (1)	7 (1)	0 (1)	2 (1)	-1 (1)

TABLE 66 (Continued)

C44	6 (1)	7 (1)	6 (1)	-2 (1)	1 (1)	-1 (1)
C45	5 (1)	7 (1)	5 (1)	2 (1)	-2 (1)	0 (1)
C46	5 (1)	4 (1)	3 (1)	0 (1)	0 (1)	0 (1)

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

TABLE 67

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[Ph_4P][CuCl_2]$

Cu1 - Cl1	2.079 (4)	Cl1 - Cu1 - Cl2	175.8 (2)
Cu1 - Cl2	2.068 (4)	C16 - P1 - C16'	107.9 (6)
P1 - C16	1.79 (1)	C16 - P1 - C16"	110.3 (3)
P1 - C16'	1.79 (1)	C16' - P1 - C16"	110.3 (3)
P1 - C16"	1.79 (1)	C16 - P1 - C16'''	110.3 (3)
P1 - C16'''	1.79 (1)	C16' - P1 - C16'''	110.3 (3)
P2 - C26	1.77 (1)	C16" - P1 - C16'''	107.9 (6)
P2 - C26^{iv}	1.77 (1)	C26 - P2 - C26^{iv}	106.4 (6)
P2 - C26^{v}	1.77 (1)	C26 - P2 - C26^{v}	111.0 (3)
P2 - C26^{vi}	1.77 (1)	C26 - P2 - C26^{vi}	111.0 (3)
P3 - C36	1.80 (1)	C26^{iv} - P2 - C26^{vi}	111.0 (3)
P3 - C36^{vii}	1.80 (1)	C26^{v} - P2 - C26^{vi}	106.4 (6)
P3 - C3^{viii}	1.80 (1)	C36 - P3 - C36^{vii}	106.1 (6)
P3 - C36^{ix}	1.80 (1)	C36 - P3 - C36^{viii}	111.2 (3)
P4 - C46	1.78 (1)	C36^{vii} - P3 - C36^{viii}	111.2 (3)
P4 - C46^{x}	1.78 (1)	C36 - P3 - C36^{ix}	111.2 (3)
P4 - C4^{xi}	1.78 (1)	C36^{vii} - P3 - C36^{ix}	111.2 (3)
P4 - C46^{xii}	1.78 (1)	C36^{viii} - P3 - C36^{ix}	106.1 (6)
C11 - C12	1.395	C46 - P4 - C46^{x}	109.4 (5)
C12 - C13	1.395	C46 - P4 - C46^{xi}	109.5 (3)
C13 - C14	1.395	C46^{x} - P4 - C46^{xi}	109.5 (3)
C14 - C15	1.395	C46 - P4 - C46^{xii}	109.5 (3)
C15 - C16	1.395	C46^{x} - P4 - C46^{xii}	109.5 (3)
C16 - C11	1.395	C46^{xi} - P4 - C46^{xii}	109.4 (5)
C21 - C22	1.395	P1 - C16 - C11	120.9 (3)
C22 - C23	1.395	P1 - C16 - C15	119.0 (3)
C23 - C24	1.395	P2 - C26 - C21	119.8 (3)
C24 - C25	1.395	P2 - C26 - C25	120.0 (3)
C25 - C26	1.395	P3 - C36 - C31	121.0 (3)
C26 - C21	1.395	P3 - C36 - C35	119.0 (3)

TABLE 67 (Continued)

C31 - C32	1.395	P4 - C46 - C41	120.5 (3)
C32 - C33	1.395	P4 - C46 - C45	119.3 (3)
C33 - C34	1.395	C11 - C12 - C13	120.0
C34 - C35	1.395	C12 - C11 - C16	120.0
C35 - C36	1.395	C12 - C13 - C14	120.0
C36 - C31	1.395	C13 - C14 - C15	120.0
C41 - C42	1.395	C14 - C15 - C16	120.0
C42 - C43	1.395	C11 - C16 - C15	120.0
C43 - C44	1.395	C21 - C22 - C23	120.0
C44 - C45	1.395	C22 - C21 - C26	120.0
C45 - C46	1.395	C22 - C23 - C24	120.0
C46 - C41	1.395	C23 - C24 - C25	120.0
		C24 - C25 - C26	120.0
		C21 - C26 - C25	120.0
		C31 - C32 - C33	120.0
		C32 - C31 - C36	120.0
		C32 - C33 - C34	120.0
		C33 - C34 - C35	120.0
		C34 - C35 - C36	120.0
		C31 - C36 - C35	120.0
		C41 - C42 - C43	120.0
		C42 - C41 - C46	120.0
		C42 - C43 - C44	120.0
		C43 - C44 - C45	120.0
		C44 - C45 - C46	120.0

TABLE 67 (Continued)

	C41 - C46 - C45	120.0

Symmetry operations:

' = 1.0-x, -y, z.
" = 0.5+y, 0.5-x, z-1.5.
"' = 0.5-y, x-0.5, z-1.5.
iv = 1-x, 1.0-y, z.
v = y, 1.0-x, 1.0-z.
vi = 1.0-y, x, 1.0-z.
vii = 1.0-x, 1.0-y, z.
viii = y, 1.0-x, -z.
ix = 1.0-y, x, -z.
x = -x, 1.0-y, z.
xi = y-0.5, 0.5-x, 0.5-z.
xii = 0.5-y, 0.5-x, 0.5-z.

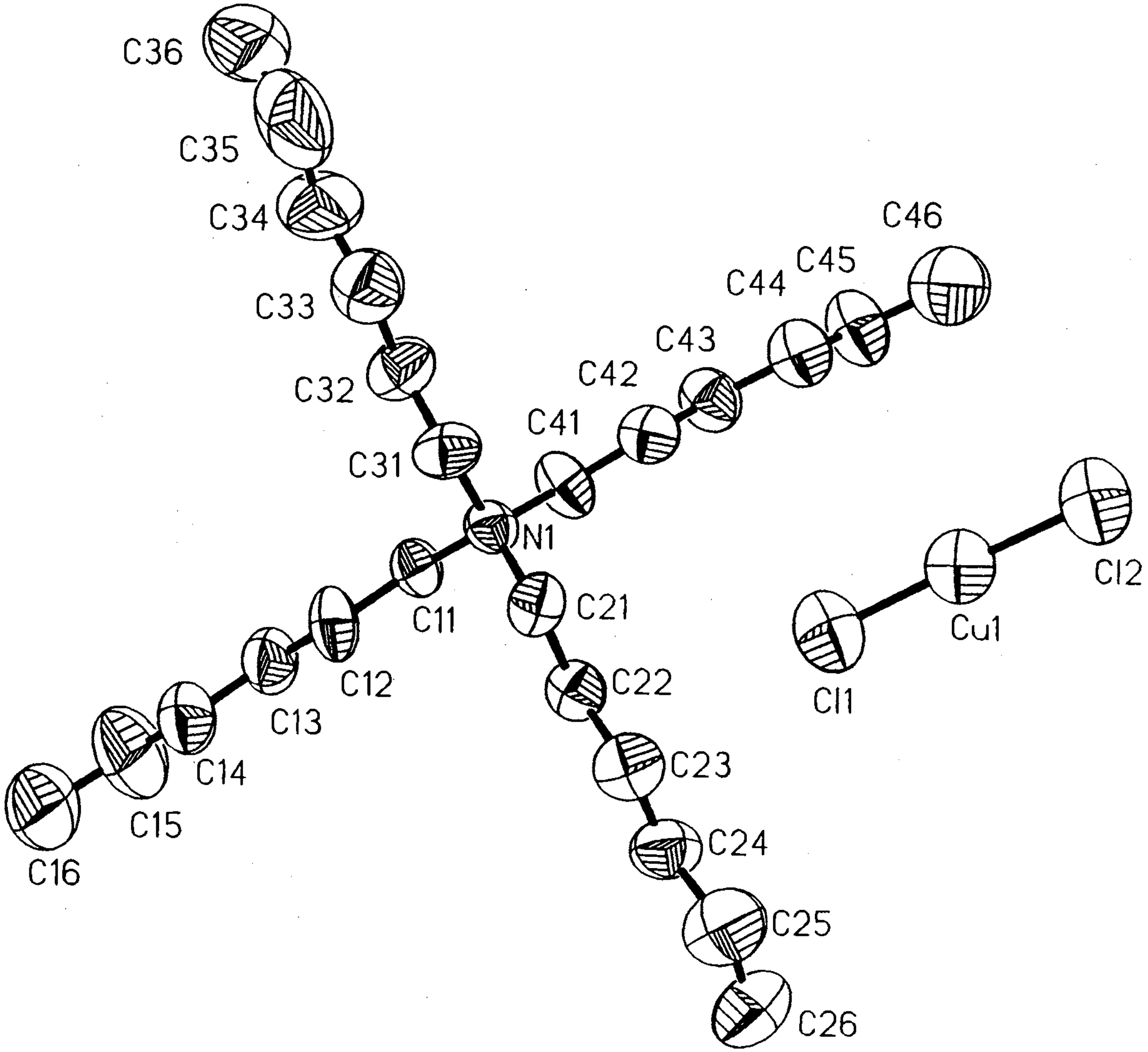

Figure 47. Projection View of $[(n\text{-Hexyl})_4N][CuCl_2]$.

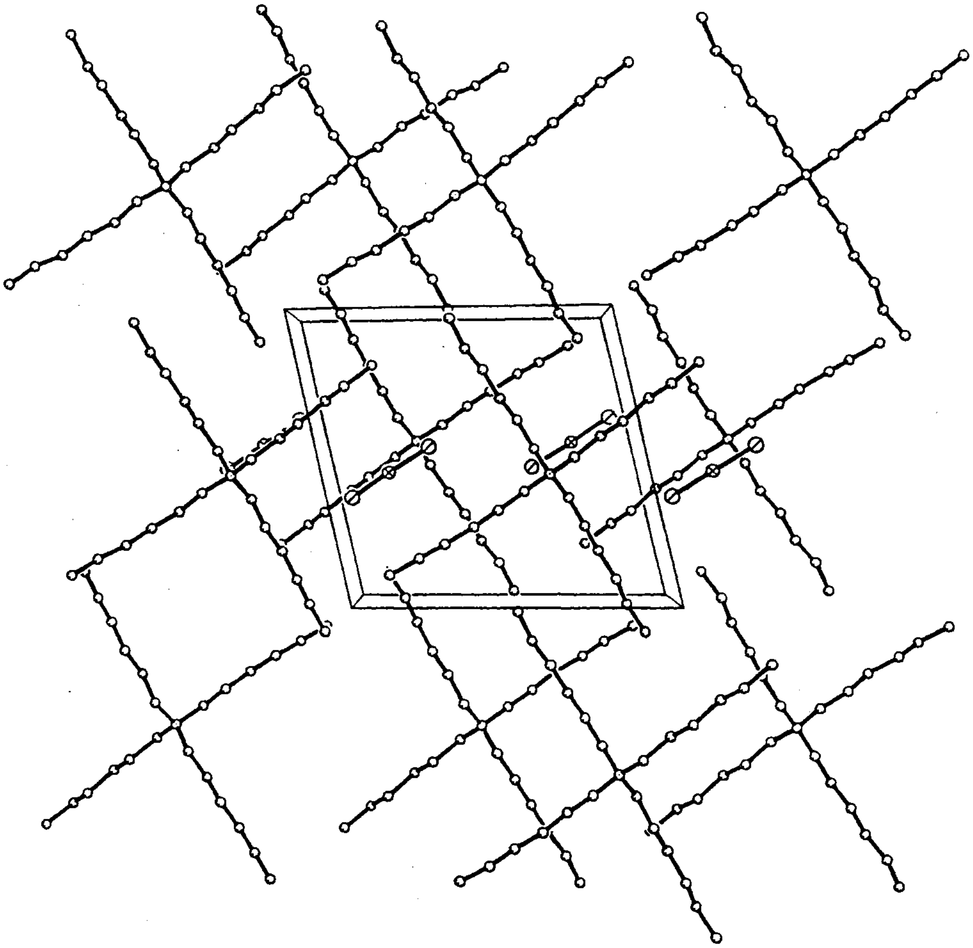

Figure 48. Packing Diagram for [(*n*-Hexyl)$_4$N][CuCl$_2$].

TABLE 68

CRYSTAL DATA FOR [(*n*-Hexyl)$_4$N][CuCl$_2$]

Formula	$CuCl_2NC_{24}H_{52}$
MWT	489.1
a	9.331(2) Å
b	12.283(2)
c	13.143(3)
α	77.02(3)°
β	83.57(3)
γ	86.04(3)
V	1457.2(5) Å^3
F (000)	532
μMoK_α	9.42 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	1.115 g cm^{-3}
Z	2
Independent. Refl.	6663
Obs. Refl. ($F > 2.8\sigma(F)$)	1265
Variab.	253
R/R$_w$	6.1/4.7%
Space Group	P1bar
Octants Meas.	+h, ±k, ±l

TABLE 69

POSITIONAL PARAMETERS FOR $[(n\text{-Hexyl})_4N][CuCl_2]$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cu1	0.2740 (2)	0.4489 (2)	0.7982 (1)
Cl1	0.2100 (4)	0.5366 (3)	0.6543 (2)
Cl2	0.3524 (4)	0.3623 (3)	0.9366 (3)
N1	0.272 (1)	0.442 (1)	1.301 (1)
C11	0.379 (1)	0.359 (1)	1.260 (1)
C12	0.311 (1)	0.263 (1)	1.231 (1)
C13	0.422 (2)	0.176 (1)	1.203 (1)
C14	0.339 (2)	0.081 (1)	1.171 (1)
C15	0.427 (2)	-0.007 (2)	1.154 (1)
C16	0.346 (2)	-0.097 (1)	1.117 (1)
C21	0.172 (1)	0.497 (1)	1.218 (1)
C22	0.242 (1)	0.569 (1)	1.118 (1)
C23	0.130 (1)	0.616 (1)	1.046 (1)
C24	0.181 (1)	0.694 (1)	0.946 (1)
C25	0.072 (2)	0.740 (1)	0.875 (1)
C26	0.121 (2)	0.812 (1)	0.773 (1)
C31	0.359 (1)	0.527 (1)	1.331 (1)
C32	0.276 (1)	0.624 (1)	1.366 (1)
C33	0.368 (1)	0.700 (1)	1.402 (1)
C34	0.280 (1)	0.796 (1)	1.435 (1)
C35	0.359 (2)	0.872 (1)	1.476 (1)
C36	0.274 (1)	0.973 (1)	1.501 (1)
C41	0.175 (1)	0.383 (1)	1.396 (1)
C42	0.252 (1)	0.318 (1)	1.488 (1)
C43	0.141 (1)	0.264 (1)	1.575 (1)
C44	0.201 (1)	0.204 (1)	1.676 (1)
C45	0.086 (1)	0.160 (1)	1.762 (1)
C46	0.143 (1)	0.103 (1)	1.864 (1)

TABLE 70

HYDROGEN POSITIONAL PARAMETERS FOR [(*n*-Hexyl)$_4$N][CuCl$_2$]

ATOM	x	y	z
H11A	0.4430	0.3279	1.3230
H11B	0.4361	0.3981	1.1996
H12A	0.2555	0.2925	1.1725
H12B	0.2474	0.2274	1.2890
H13A	0.4757	0.1438	1.2613
H13B	0.4868	0.2110	1.1448
H14A	0.2945	0.1125	1.1077
H14B	0.2652	0.0546	1.2258
H15A	0.4696	-0.0402	1.2174
H15B	0.5033	0.0199	1.1004
H16A	0.4111	-0.1577	1.1059
H16B	0.2702	-0.1239	1.1707
H16C	0.3042	-0.0634	1.0528
H21A	0.1003	0.5432	1.2493
H21B	0.1237	0.4390	1.1997
H22A	0.3092	0.5225	1.0831
H22B	0.2951	0.6249	1.1358
H23A	0.0658	0.6220	1.0827
H23B	0.0749	0.5580	1.0337
H24A	0.2466	0.6484	0.9095
H24B	0.2345	0.7527	0.9580
H25A	0.0055	0.7856	0.9107
H25B	0.0178	0.6812	0.8621
H26A	0.0411	0.8412	0.7334
H26B	0.1722	0.8727	0.7842
H26C	0.1847	0.7670	0.7349
H31A	0.4205	0.5599	1.2695
H31B	0.4204	0.4901	1.3836

TABLE 70 (Continued)

H32A	0.2092	0.5918	1.4242
H32B	0.2212	0.6663	1.3113
H33A	0.4385	0.7297	1.3454
H33B	0.4190	0.6591	1.4599
H34A	0.2069	0.7657	1.4890
H34B	0.2341	0.8390	1.3763
H35A	0.4399	0.8942	1.4254
H35B	0.3958	0.8309	1.5396
H36A	0.3352	1.0183	1.5263
H36B	0.2385	1.0151	1.4369
H36C	0.1939	0.9512	1.5523
H41A	0.1180	0.3326	1.3728
H41B	0.1110	0.4378	1.4208
H42A	0.3113	0.3671	1.5115
H42B	0.3128	0.2599	1.4658
H43A	0.0850	0.2144	1.5505
H43B	0.0766	0.3239	1.5918
H44A	0.2599	0.2530	1.6993
H44B	0.2616	0.1422	1.6605
H45A	0.0329	0.1065	1.7406
H45B	0.0210	0.2211	1.7727
H46A	0.0650	0.0770	1.9165
H46B	0.2069	0.0405	1.8547
H46C	0.1950	0.1563	1.8871

TABLE 71

ANISOTROPIC THERMAL PARAMETERS FOR $[(n\text{-Hexyl})_4\text{N}][\text{CuCl}_2]$

ATOM	U11	U22	U33	U12	U13	U23
Cu1	69 (1)	113 (1)	82 (2)	-6 (1)	3 (1)	-20 (1)
Cl1	108 (3)	136 (3)	85 (3)	9 (3)	-5 (3)	2 (2)
Cl2	124 (4)	158 (4)	96 (3)	3 (3)	-22 (3)	-15 (3)
N1	49 (6)	69 (7)	50 (7)	-2 (7)	-3 (6)	-12 (6)
C11	7 (1)	8 (1)	6 (1)	1 (1)	0 (1)	-1 (1)
C12	9 (1)	9 (1)	8 (1)	0 (1)	0 (1)	-2 (1)
C13	13 (2)	11 (1)	9 (1)	0 (1)	-2 (1)	0 (1)
C14	13 (2)	11 (2)	12 (1)	4 (1)	2 (1)	-2 (1)
C15	13 (2)	20 (2)	11 (1)	0 (2)	5 (1)	2 (1)
C16	22 (2)	14 (2)	12 (1)	-4 (1)	2 (1)	-4 (1)
C21	5 (1)	7 (1)	6 (1)	0 (1)	-1 (1)	-1 (1)
C22	7 (1)	9 (1)	6 (1)	0 (1)	-2 (1)	-1 (1)
C23	10 (1)	9 (1)	7 (1)	-2 (1)	-3 (1)	0 (1)
C24	11 (1)	9 (1)	7 (1)	0 (1)	-2 (1)	0 (1)
C25	14 (2)	13 (1)	8 (1)	-1 (1)	-4 (1)	2 (1)
C26	20 (2)	16 (2)	11 (1)	-1 (1)	-7 (1)	-2 (1)
C31	6 (1)	8 (1)	6 (1)	-2 (1)	-1 (1)	-1 (1)
C32	6 (1)	8 (1)	6 (1)	1 (1)	-1 (1)	-1 (1)
C33	7 (1)	7 (1)	8 (1)	-2 (1)	-2 (1)	-3 (1)
C34	8 (1)	8 (1)	9 (1)	-1 (1)	-1 (1)	-3 (1)
C35	14 (2)	11 (1)	11 (1)	-1 (1)	-1 (1)	-3 (1)
C36	18 (2)	10 (1)	13 (1)	-3 (1)	2 (1)	-3 (1)
C41	6 (1)	8 (1)	6 (1)	-1 (1)	1 (1)	-1 (1)
C42	5 (1)	8 (1)	5 (1)	-1 (1)	0 (1)	-1 (1)
C43	7 (1)	7 (1)	8 (1)	0 (1)	0 (1)	-1 (1)
C44	7 (1)	8 (1)	6 (1)	0 (1)	0 (1)	0 (1)
C45	8 (1)	10 (1)	10 (1)	1 (1)	-1 (1)	0 (1)

TABLE 71 (Continued)

C46	14 (1)	15 (1)	9 (1)	0 (1)	1 (1)	2 (1)

The anisotropic displacement exponent takes the form:
$\exp(-2\pi(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^{*}b^{*}+2U_{13}hla^{*}c^{*}+2U_{23}klb^{*}c^{*}))$
$\times 10^{43}$ for Cu, Cl and N, $\times 10^2$ for C.

TABLE 72

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[(n\text{-Hexyl})_4N][CuCl_2]$

Cu1 - Cl1	2.084 (3)	Cl1 - Cu1 - Cl2	176.0 (2)
Cu1 - Cl2	2.073 (4)	C11 - N1 - C21	110.9 (9)
N1 - C11	1.51 (2)	C11 - N1 - C31	106.9 (9)
N1 - C21	1.53 (2)	C21 - N1 - C31	111.1 (9)
N1 - C31	1.51 (2)	C21 - N1 - C41	106.1 (9)
N1 - C41	1.52 (1)	C31 - N1 - C41	110.7 (9)
C11 - C12	1.52 (2)	N1 - C11 - C12	115 (1)
C12 - C13	1.51 (2)	C11 - C12 - C13	113 (1)
C13 - C14	1.60 (2)	C12 - C13 - C14	109 (1)
C14 - C15	1.36 (2)	C13 - C14 - C15	114 (1)
C15 - C16	1.57 (2)	C14 - C15 - C16	113 (1)
C21 - C22	1.52 (1)	N1 - C21 - C22	116 (1)
C22 - C23	1.49 (1)	C21 - C22 - C23	110 (1)
C23 - C24	1.49 (2)	C22 - C23 - C24	116 (1)
C24 - C25	1.46 (2)	C23 - C24 - C25	116 (1)
C25 - C26	1.47 (2)	C24 - C25 - C26	117 (1)
C31 - C32	1.51 (2)	N1 - C31 - C32	117 (1)
C32 - C33	1.50 (2)	C31 - C32 - C33	114 (1)
C33 - C34	1.51 (2)	C32 - C33 - C34	112 (1)
C34 - C35	1.44 (2)	C33 - C34 - C35	116 (1)
C35 - C36	1.51 (2)	C34 - C35 - C36	116 (1)
C41 - C42	1.52 (2)	N1 - C41 - C42	116 (1)
C42 - C43	1.52 (2)	C41 - C42 - C43	109 (1)
C43 - C44	1.52 (2)	C42 - C43 - C44	115 (1)
C44 - C45	1.50 (2)	C43 - C44 - C45	113 (1)
C45 - C46	1.50 (2)	C44 - C45 - C46	114 (1)

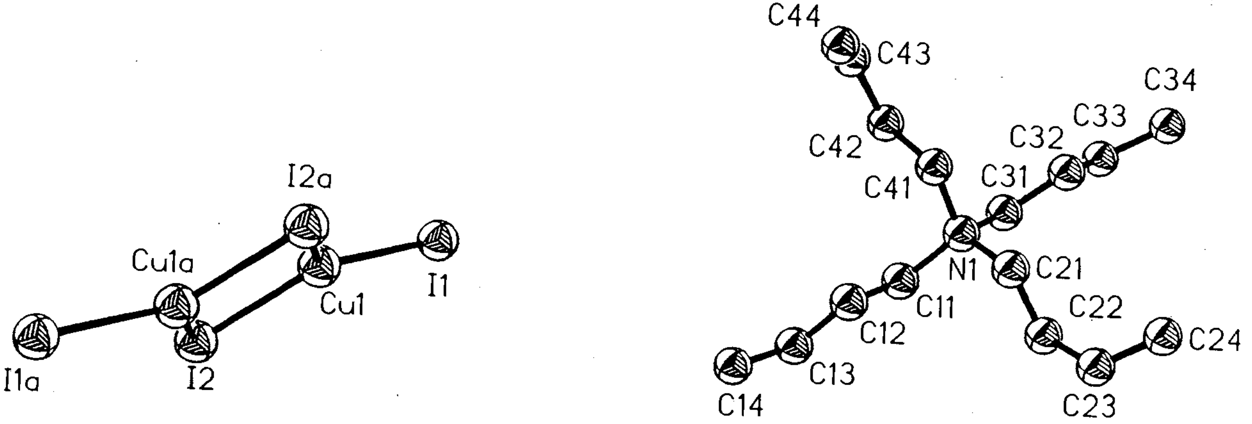

Figure 49. Projection View of $[(Bu_4N)_2][Cu_2I_4]$.

TABLE 73

CRYSTAL DATA FOR $[(Bu_4N)_2][Cu_2I_4]$

Formula	$Cu_2I_4N_2C_{32}H_{72}$
MWT	1119.64
a	12.033(6) Å
b	21.111(9)
c	9.164(3)
α	90.0°
β	95.48(3)
γ	90.0
V	2317.2(16)$Å^3$
F (000)	1096
μMoK_α	35.78 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.604 g cm^{-3}
Z	2
Obs. Refl.	6672
Contribut. Refl.	1020
Variab.	181
R/R_w	4.2/5.3%
Space Group	$P2_1/n$
Octants Meas.	±h, +k, +l

TABLE 74

POSITIONAL PARAMETERS FOR $[(Bu_4N)_2][Cu_2I_4]$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	0.0258 (2)	0.1822 (1)	0.5068 (2)
I2	-0.0859 (2)	0.0081 (1)	0.2802 (2)
Cu1	0.0096 (3)	0.0643 (1)	0.5094 (4)
N1	0.324 (2)	0.675 (1)	0.503 (2)
C11	0.281 (2)	0.646 (1)	0.355 (2)
C12	0.278 (2)	0.577 (1)	0.345 (3)
C13	0.234 (2)	0.557 (2)	0.200 (4)
C14	0.209 (4)	0.495 (3)	0.168 (5)
C21	0.446 (2)	0.657 (1)	0.546 (3)
C22	0.523 (3)	0.680 (1)	0.440 (3)
C23	0.640 (4)	0.660 (2)	0.498 (4)
C24	0.696 (4)	0.691 (2)	0.611 (5)
C31	0.312 (2)	0.749 (1)	0.498 (3)
C32	0.356 (2)	0.783 (1)	0.626 (3)
C33	0.342 (3)	0.851 (2)	0.608 (4)
C34	0.395 (3)	0.892 (2)	0.722 (5)
C41	0.260 (2)	0.648 (1)	0.626 (3)
C42	0.137 (3)	0.660 (1)	0.612 (3)
C43	0.070 (5)	0.628 (2)	0.728 (6)
C44	0.096 (6)	0.580 (5)	0.807 (11)

TABLE 75

HYDROGEN POSITIONAL PARAMETERS FOR $[(Bu_4N)_2][Cu_2I_4]$

ATOM	x	y	z
H111	0.2048	0.6618	0.3262
H112	0.3276	0.6630	0.2773
H121	0.3595	0.5604	0.3703
H122	0.2388	0.5592	0.4256
H131	0.1585	0.5791	0.1740
H132	0.2799	0.5756	0.1210
H141	0.2953	0.4685	0.1987
H142	0.1739	0.4719	0.2517
H143	0.1901	0.4776	0.0821
H211	0.4747	0.6739	0.6430
H212	0.4568	0.6103	0.5521
H221	0.4999	0.6639	0.3403
H222	0.5199	0.7270	0.4329
H231	0.6422	0.6133	0.5145
H232	0.6924	0.6641	0.4118
H241	0.6994	0.7355	0.5947
H242	0.6493	0.6847	0.6974
H243	0.7710	0.6767	0.6510
H311	0.3475	0.7625	0.4101
H312	0.2308	0.7565	0.4756
H321	0.3172	0.7695	0.7105
H322	0.4352	0.7731	0.6479
H331	0.3767	0.8633	0.5184
H332	0.2626	0.8605	0.5912
H341	0.3587	0.8802	0.8217
H342	0.4728	0.8831	0.7489
H343	0.3840	0.9374	0.7198
H411	0.2763	0.6023	0.6353

TABLE 75 (Continued)

H412	0.2910	0.6676	0.7202
H421	0.1275	0.7045	0.5767
H422	0.1097	0.6346	0.5162
H431	0.1268	0.6569	0.8291
H432	0.0081	0.6587	0.7382
H441	0.0338	0.5685	0.6613
H442	0.1525	0.5666	0.7522
H443	0.0429	0.5729	0.8350

TABLE 76

ANISOTROPIC THERMAL PARAMETERS FOR $[(Bu_4N)_2][Cu_2I_4]$

ATOM	U11	U22	U33	U12	U13	U23
I1	124 (1)	54 (1)	68 (1)	7 (1)	-9 (1)	-2 (1)
I2	145 (2)	58 (1)	84 (1)	-10 (1)	-30 (1)	-1 (1)
Cu1	93 (2)	60 (2)	82 (2)	-1 (2)	-2 (2)	-2 (2)
N1	8 (1)	7 (1)	6 (1)	1 (1)	0 (1)	1 (1)
C11	7 (2)	10 (2)	6 (1)	-1 (2)	1 (1)	0 (2)
C12	10 (2)	13 (3)	8 (2)	-3 (2)	3 (2)	-2 (2)
C13	9 (3)	16 (3)	15 (3)	-6 (2)	1 (2)	-2 (3)
C14	32 (6)	28 (6)	23 (5)	-22 (5)	10 (4)	-13 (4)
C21	9 (2)	5 (1)	8 (2)	0 (1)	1 (2)	1 (1)
C22	10 (2)	9 (2)	7 (2)	0 (2)	-2 (2)	-1 (2)
C23	20 (5)	21 (5)	14 (4)	-8 (4)	2 (3)	-5 (3)
C24	17 (4)	26 (6)	21 (5)	1 (4)	0 (4)	-1 (4)
C31	10 (2)	7 (2)	9 (2)	3 (2)	0 (2)	3 (2)
C32	13 (3)	7 (2)	10 (2)	1 (2)	0 (2)	2 (2)
C33	11 (3)	11 (3)	16 (3)	-2 (2)	-2 (2)	2 (2)
C34	9 (2)	10 (3)	34 (6)	1 (2)	2 (3)	4 (3)
C41	8 (2)	8 (2)	7 (2)	2 (1)	-1 (1)	0 (1)
C42	14 (3)	11 (2)	8 (2)	0 (2)	0 (2)	4 (2)
C43	25 (5)	20 (5)	22 (5)	8 (4)	6 (4)	7 (4)
C44	16 (6)	70 (19)	71 (17)	14 (9)	19 (8)	32 (14)

The anisotropic displacement exponent takes the form:
$\exp(-2\pi(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$
x 10^3 for I and Cu, and x 10^2 for N and C.

TABLE 77

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[(Bu_4N)_2][Cu_2I_4]$

Cu1 - I1	2.494 (3)	I1 - Cu1 - I2	118.6 (1)
Cu1 - I2	2.584 (4)	I1 - Cu1 - I2'	125.4 (1)
Cu1 - I2'	2.559 (4)	Cu1 - I2 - Cu1'	64.0 (1)
Cu1 ··· Cu1'	2.724 (4)	I2 - Cu1 - I2'	116.0 (1)
I2 - Cu1'	2.558 (4)	I2 - Cu1' - I2'	116.0 (1)
I1' - Cu1'	2.494 (3)	I2' - Cu1' - I1'	118.6 (1)
I2' - Cu1'	2.584 (4)	I2 - Cu1' - I1'	125.4 (1)
N1 - C11	1.53 (3)	C11 - N1 - C21	111 (2)
N1 - C21	1.54 (3)	C11 - N1 - C31	110 (2)
N1 - C31	1.56 (3)	C11 - N1 - C41	111 (2)
N1 - C41	1.53 (3)	C21 - N1 - C31	110 (2)
C11 - C12	1.47 (4)	C21 - N1 - C41	105 (2)
C12 - C13	1.45 (4)	C31 - N1 - C41	110 (2)
C13 - C14	1.36 (6)	N1 - C11 - C12	117 (2)
C21 - C22	1.47 (4)	C11 - C12 - C13	110 (2)
C22 - C23	1.52 (5)	C12 - C13 - C14	122 (3)
C23 - C24	1.34 (6)	N1 - C21 - C22	113 (2)
C31 - C32	1.44 (4)	C21 - C22 - C23	108 (2)
C32 - C33	1.44 (4)	C22 - C23 - C24	121 (4)
C33 - C34	1.46 (5)	N1 - C31 - C32	117 (2)
C41 - C42	1.49 (4)	C31 - C32 - C33	112 (2)
C42 - C43	1.55 (6)	C32 - C33 - C34	118 (3)
C43 - C44	1.26 (11)	N1 - C41 - C42	116 (2)
		C41 - C42 - C43	116 (3)
		C42 - C43 - C44	129 (6)

Symmetry operation:

' = -x, -y, 1.0-z.

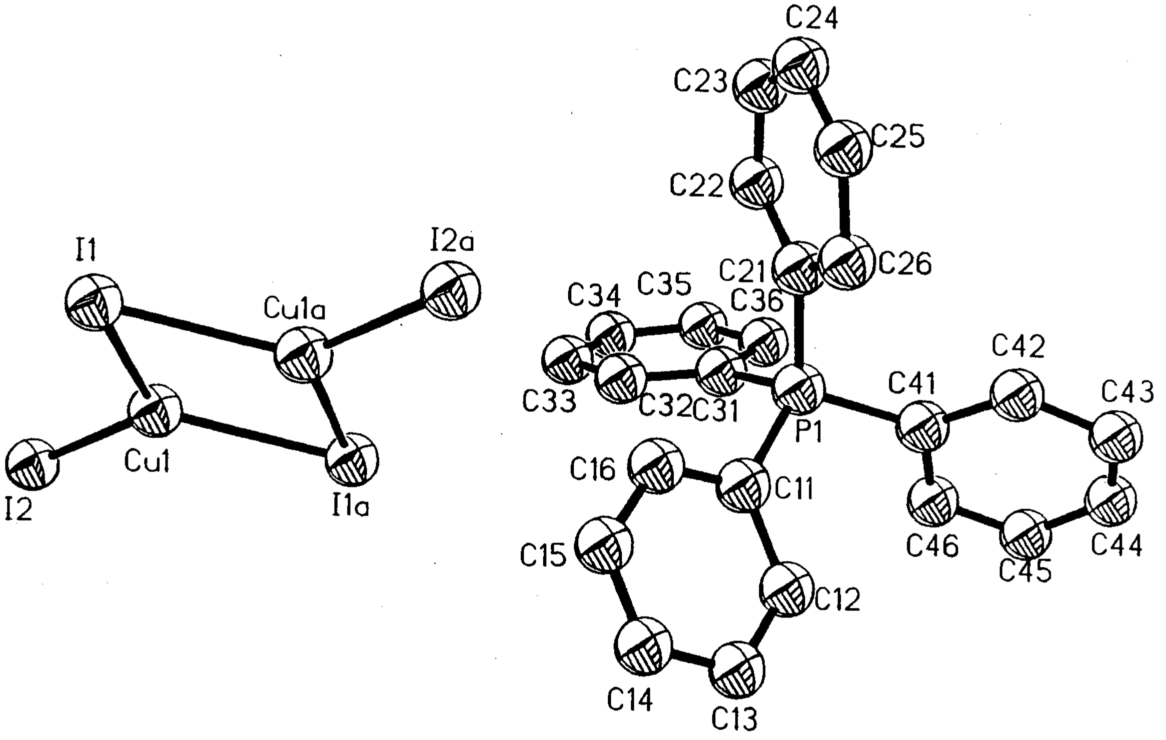

Figure 50. Projection View of $[(Ph_4P)_2][Cu_2I_4]$.

TABLE 78

CRYSTAL DATA FOR $[(Ph_4P)_2][Cu_2I_4]$

Formula	$Cu_2I_4P_2C_{48}H_{40}$
MWT	1313.50
a	20.773(7) Å
b	7.838(2)
c	14.668(5)
α	90.0°
β	102.42(3)
γ	90.0
V	2332.4(13) Å^3
F (000)	1256
μMoK_α	36.33 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.870 g cm^{-3}
Z	2
Obs. Refl.	6515
Contribut. Refl.	1599
Variab.	254
R/R_w	5.1/10.5%
Space Group	$P2_1/n$
Octants Meas.	±h, +k, +l

TABLE 79

POSITIONAL PARAMETERS FOR $[(Ph_4P)_2][Cu_2I_4]$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	0.9307 (1)	0.1607 (3)	0.9127 (1)
I2	0.9254 (1)	0.1495 (4)	1.2147 (2)
Cu1	0.9763 (2)	0.0612 (6)	1.0827 (3)
P1	0.3242 (4)	0.5790 (11)	0.0343 (5)
C11	0.248 (1)	0.465 (4)	0.007 (2)
C12	0.247 (2)	0.289 (4)	0.032 (2)
C13	0.187 (2)	0.210 (5)	0.013 (3)
C14	0.130 (2)	0.300 (5)	-0.029 (2)
C15	0.132 (1)	0.460 (4)	-0.053 (2)
C16	0.191 (1)	0.543 (4)	-0.035 (2)
C21	0.326 (1)	0.719 (4)	-0.063 (2)
C22	0.340 (2)	0.893 (4)	-0.047 (2)
C23	0.342 (2)	0.993 (4)	-0.124 (2)
C24	0.331 (2)	0.940 (5)	-0.210 (3)
C25	0.318 (2)	0.778 (6)	-0.225 (2)
C26	0.314 (2)	0.649 (5)	-0.153 (2)
C31	0.327 (2)	0.714 (4)	0.136 (2)
C32	0.271 (2)	0.789 (4)	0.149 (2)
C33	0.274 (2)	0.900 (4)	0.222 (2)
C34	0.332 (2)	0.938 (4)	0.282 (2)
C35	0.388 (2)	0.870 (5)	0.269 (2)
C36	0.389 (2)	0.755 (4)	0.196 (2)
C41	0.391 (1)	0.432 (4)	0.057 (2)
C42	0.425 (1)	0.381 (4)	-0.013 (2)
C43	0.475 (2)	0.246 (5)	0.006 (3)
C44	0.490 (2)	0.178 (4)	0.093 (2)
C45	0.457 (2)	0.213 (5)	0.159 (2)
C46	0.408 (2)	0.338 (5)	0.145 (2)

TABLE 80

HYDROGEN POSITIONAL PARAMETERS FOR $[(Ph_4P)_2][Cu_2I_4]$

ATOM	x	y	z
H12	0.2890	0.2247	0.0548
H13	0.1830	0.0897	0.0352
H14	0.0886	0.2375	-0.0431
H15	0.0906	0.5144	-0.0853
H22	0.3487	0.9396	0.0152
H23	0.3513	1.1178	-0.1116
H24	0.3344	1.0169	-0.2623
H25	0.3085	0.7268	-0.2906
H32	0.2258	0.7570	0.1084
H33	0.2325	0.9568	0.2315
H34	0.3327	1.0271	0.3316
H35	0.4295	0.8870	0.3148
H42	0.4144	0.4421	-0.0749
H43	0.4986	0.2097	-0.0430
H44	0.5279	0.0980	0.1064
H45	0.4666	0.1536	0.2185

TABLE 81

ANISOTROPIC THERMAL PARAMETERS FOR [$(Ph_4P)_2$][Cu_2I_4]

ATOM	U11	U22	U33	U12	U13	U23
I1	52 (1)	64 (2)	39 (1)	20 (2)	9 (1)	11 (1)
I2	67 (2)	71 (2)	45 (1)	16 (2)	19 (1)	7 (2)
Cu1	54 (3)	55 (3)	46 (2)	-3 (2)	11 (2)	-2 (2)
P1	33 (4)	27 (5)	22 (3)	2 (4)	4 (3)	0 (4)
C11	3 (2)	5 (2)	2 (1)	0 (2)	1 (1)	0 (1)
C12	4 (2)	3 (2)	6 (2)	0 (2)	2 (2)	0 (2)
C13	8 (3)	2 (2)	9 (3)	-3 (2)	3 (3)	-2 (2)
C14	3 (2)	7 (3)	7 (2)	-3 (2)	0 (2)	-1 (2)
C15	4 (2)	3 (2)	6 (2)	0 (2)	0 (2)	0 (2)
C16	2 (2)	4 (2)	4 (2)	-1 (2)	0 (1)	0 (2)
C21	3 (2)	4 (2)	1 (1)	0 (1)	0 (1)	-1 (1)
C22	5 (2)	3 (2)	4 (2)	-1 (2)	0 (1)	-1 (1)
C23	7 (2)	1 (2)	4 (2)	-1 (2)	0 (2)	0 (1)
C24	8 (3)	4 (2)	7 (2)	-1 (2)	2 (2)	2 (2)
C25	8 (3)	12 (4)	1 (1)	3 (3)	1 (2)	2 (2)
C26	5 (2)	6 (2)	4 (2)	0 (2)	1 (2)	-1 (2)
C31	6 (2)	2 (2)	3 (2)	-1 (2)	2 (1)	0 (1)
C32	4 (2)	2 (2)	4 (2)	0 (2)	1 (2)	-1 (2)
C33	6 (2)	4 (2)	6 (2)	2 (2)	3 (2)	-1 (2)
C34	8 (3)	3 (2)	4 (2)	-2 (2)	1 (2)	-2 (2)
C35	6 (2)	6 (3)	3 (2)	2 (2)	-1 (2)	-2 (2)
C36	4 (2)	4 (2)	4 (2)	1 (2)	-1 (1)	2 (2)
C41	3 (2)	4 (2)	3 (1)	-1 (2)	1 (1)	-1 (1)
C42	4 (2)	5 (2)	3 (1)	-2 (2)	0 (1)	1 (2)
C43	5 (2)	4 (2)	8 (3)	-1 (2)	2 (2)	-3 (2)
C44	7 (2)	4 (2)	7 (2)	2 (2)	0 (2)	-1 (2)
C45	7 (3)	6 (3)	6 (2)	4 (2)	1 (2)	0 (2)

TABLE 81 (Continued)

C46	7 (2)	8 (3)	3 (2)	-2 (2)	1 (2)	-1 (2)

The anisotropic displacement exponent takes the form:

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

$\times 10^3$ for I, Cu and P, and $\times 10^2$ for C.

TABLE 82

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[(Ph_4P)_2][Cu_2I_4]$

Cu1 - I1	2.589 (5)	I1 - Cu1 - I2	122.4 (2)
Cu1 - I2	2.496 (5)	I2 - Cu1 - I1'	127.1 (1)
Cu1 - I1'	2.590 (4)	I1 - Cu1 - I1'	110.1 (1)
I1 - Cu1'	2.587 (5)	I1 - Cu1' - I1'	110.1 (2)
I1' - Cu1'	2.589 (4)	I1' - Cu1' - I2'	122.4 (2)
I2' - Cu1'	2.496 (5)	I1 - Cu1' - I2'	127.2 (2)
Cu1 ··· Cu1'	2.966 (6)	P1 - C41 - C42	122 (2)
P1 - C11	1.79 (3)	C11 - P1 - C21	107 (1)
P1 - C21	1.81 (3)	C11 - P1 - C31	110 (1)
P1 - C31	1.82 (3)	C11 - P1 - C41	110 (1)
P1 - C41	1.78 (3)	C21 - P1 - C31	107 (1)
C11 - C12	1.43 (5)	C21 - P1 - C41	113 (1)
C12 - C13	1.36 (5)	C31 - P1 - C41	110 (1)
C13 - C14	1.41 (5)	P1 - C11 - C12	119 (2)
C14 - C15	1.30 (5)	C11 - C12 - C13	116 (3)
C15 - C16	1.36 (4)	C12 - C13 - C14	121 (3)
C16 - C11	1.36 (4)	C13 - C14 - C15	121 (3)
C21 - C22	1.40 (4)	C14 - C15 - C16	119 (3)
C22 - C23	1.39 (4)	C15 - C16 - C11	122 (3)
C23 - C24	1.30 (5)	C16 - C11 - P1	122 (2)
C24 - C25	1.31 (6)	C16 - C11 - C12	120 (3)
C25 - C26	1.47 (5)	P1 - C21 - C22	120 (2)
C26 - C21	1.41 (4)	C21 - C22 - C23	117 (3)
C31 - C32	1.36 (5)	C22 - C23 - C24	126 (3)
C32 - C33	1.37 (5)	C23 - C24 - C25	117 (3)
C33 - C34	1.37 (4)	C24 - C25 - C26	126 (3)
C34 - C35	1.33 (5)	C25 - C26 - C21	112 (3)
C35 - C36	1.40 (5)	C26 - C21 - P1	118 (2)
C36 - C31	1.44 (4)	C26 - C21 - C22	122 (3)

TABLE 82 (Continued)

C41 - C42	1.42 (4)	P1 - C21 - C22	120 (2)
C42 - C43	1.47 (5)	C31 - C32 - C33	119 (3)
C43 - C44	1.35 (5)	C32 - C33 - C34	122 (3)
C44 - C45	1.34 (6)	C33 - C34 - C35	120 (3)
C45 - C46	1.40 (5)	C34 - C35 - C36	121 (3)
C46 - C41	1.46 (4)	C35 - C36 - C31	117 (3)
		C36 - C31 - P1	120 (2)
		C36 - C31 - C32	120 (3)
		P1 - C31 - C32	120 (2)
		C41 - C42 - C43	120 (3)
		C42 - C43 - C44	118 (3)
		C43 - C44 - C45	124 (3)
		C44 - C45 - C46	121 (3)
		C45 - C46 - C41	120 (3)
		C46 - C41 - P1	121 (2)
		C46 - C41 - C42	116 (3)

Symmetry operation:

' = 2.0-x, -y, 2.0-z.

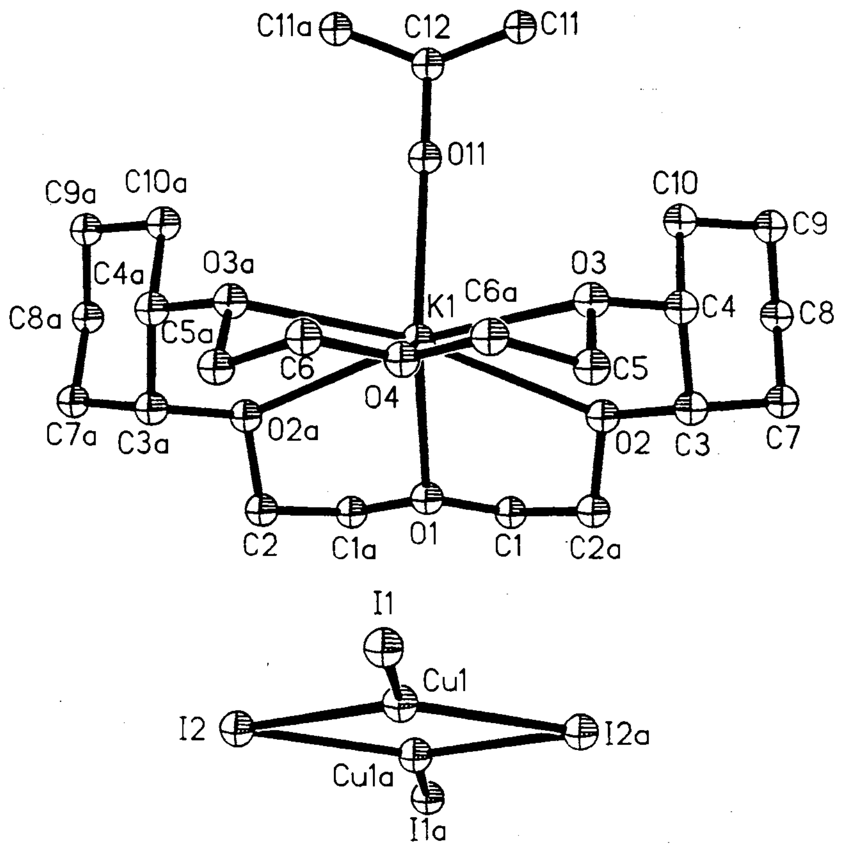

Figure 51. Projection View of [K-(DC18-Crown-6)-acetone]$_2$[Cu$_2$I$_4$].

TABLE 83

CRYSTAL DATA FOR [K-(Dicyclohexano-18-Crown-6)-acetone]$_2$[Cu_2I_4]

Formula	$Cu_2I_4K_2C_{46}O_{14}H_{84}$
MWT	1574.07
a	14.155(7) Å
b	17.938(9)
c	11.920(4)
α	90.0°
β	90.73(3)
γ	90.0
V	3026.4(22) Å^3
F (000)	1560
μMoK_α	29.14 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.727 g cm^{-3}
Z	2
Obs. Refl.	4499
Contribut. Refl.	1058
Variab.	165
R/R_w	6.0/7.6 %
Space Group	C2/m
Octants Meas.	±h, +k, +l

TABLE 84

POSITIONAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)-acetone]$_2$[Cu_2I_4]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	0.1320 (2)	0.5000	0.2215 (2)
I2	0.0000	0.3764 (1)	0.5000
Cu1	0.0459 (3)	0.5000	0.4032 (3)
K1	0.3336 (5)	0.5000	0.7102 (5)
O1	0.164 (2)	0.5000	0.819 (2)
O2	0.252 (1)	0.638 (1)	0.775 (1)
O3	0.382 (1)	0.631 (1)	0.600 (1)
O4	0.341 (1)	0.5000	0.483 (1)
O11	0.499 (4)	0.5000	0.853 (3)
C1	0.140 (2)	0.564 (1)	0.878 (2)
C2	0.154 (1)	0.370 (1)	0.804 (2)
C3	0.268 (1)	0.704 (1)	0.708 (2)
C4	0.369 (1)	0.696 (1)	0.662 (2)
C5	0.333 (2)	0.632 (1)	0.493 (2)
C6	0.367 (2)	0.436 (1)	0.424 (2)
C7	0.266 (2)	0.774 (1)	0.778 (2)
C8	0.340 (2)	0.773 (1)	0.874 (2)
C9	0.432 (2)	0.766 (1)	0.829 (2)
C10	0.443 (1)	0.696 (1)	0.753 (2)
C11	0.622 (2)	0.573 (1)	0.926 (2)
C12	0.587 (4)	0.5000	0.926 (7)

TABLE 85

HYDROGEN POSITIONAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)-acetone]$_2$[Cu$_2$I$_4$]

ATOM	x	y	z
H11	0.0753	0.5614	0.9040
H12	0.1817	0.5691	0.9451
H21	0.1158	0.6241	0.7345
H22	0.1325	0.6762	0.8401
H51	0.2672	0.6462	0.4989
H52	0.3638	0.6662	0.4404
H61	0.3266	0.4062	0.3744
H62	0.4259	0.4074	0.4371
H71	0.4322	0.6513	0.8009
H72	0.5059	0.6932	0.7229
H81	0.2811	0.8167	0.7322
H82	0.2048	0.7799	0.8110
H91	0.3339	0.8193	0.9181
H92	0.3260	0.7314	0.9243
H101	0.4476	0.8100	0.7833
H102	0.4801	0.7637	0.8901

TABLE 86

ANISOTROPIC THERMAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)-acetone]$_2$[Cu_2I_4]

ATOM	U11	U22	U33	U12	U13	U23
I1	59 (2)	63 (2)	56 (1)	0	13 (1)	0
I2	113 (2)	51 (2)	51 (1)	0	14 (1)	0
Cu1	76 (3)	62 (3)	52 (2)	0	8 (2)	0
K1	52 (4)	37 (4)	42 (4)	0	14 (3)	0
O1	9 (2)	4 (1)	7 (2)	0	4 (1)	0
O2	4 (1)	3 (1)	7 (1)	0 (1)	0 (1)	0 (1)
O3	5 (1)	3 (1)	4 (1)	0 (1)	-1 (1)	1 (1)
O4	6 (1)	4 (1)	4 (1)	0	1 (1)	0
O11	28 (5)	7 (2)	13 (3)	0	2 (3)	0
C1	6 (2)	6 (2)	7 (2)	0 (1)	1 (1)	-1 (1)
C2	1 (1)	4 (1)	7 (1)	0 (1)	-1 (1)	0 (1)
C3	4 (1)	3 (1)	7 (1)	-1 (1)	0 (1)	1 (1)
C4	6 (1)	2 (1)	5 (1)	-1 (1)	0 (1)	-2 (1)
C5	10 (2)	5 (1)	4 (1)	2 (1)	0 (1)	1 (1)
C6	9 (2)	3 (1)	4 (1)	0 (1)	0 (1)	0 (1)
C7	8 (2)	2 (1)	8 (2)	1 (1)	-1 (1)	1 (1)
C8	11 (2)	3 (1)	6 (2)	0 (1)	1 (2)	-2 (1)
C9	6 (2)	6 (2)	7 (2)	0 (1)	-1 (1)	-1 (1)
C10	1 (1)	6 (1)	7 (1)	2 (1)	0 (1)	0 (1)
C11	5 (1)	5 (1)	7 (1)	-2 (1)	1 (1)	1 (1)
C12	9 (4)	19 (7)	38 (10)	0	14 (5)	0

The anisotropic displacement exponent takes the form:

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

x 10^3 for Cu, I and K, and x 10^2 for O and C.

TABLE 87

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR [K-(Dicyclohexano-18-Crown-6)-acetone]$_2$[Cu$_2$I$_4$]

Cu1 - I1	2.498 (5)	I1 - Cu1 - I2	121.0 (1)
Cu1 - I2	2.585 (3)	I1 - Cu1 - I2'	121.0 (1)
Cu1 - I2'	2.585 (3)	I2 - Cu1 - I2'	118.0 (2)
Cu1' - I1'	2.498 (5)	I2 - Cu1' - I2'	118.0 (2)
Cu1' - I2'	2.585 (3)	Cu1 - I2 - Cu1'	62.0 (1)
Cu1 ··· Cu1'	2.662 (6)	I1' - Cu1' - I2'	121.0 (1)
K1 - O1	2.74 (2)	Cu1 - I2' - Cu1'	62.0 (1)
K1 - O2	2.85 (1)	I2 - Cu1' - I1'	121.0 (1)
K1 - O3	2.78 (1)	O4 - K1 - O11	123.5 (10)
K1 - O4	2.71 (2)	O1 - K1 - O2	60.7 (3)
K1- O11	2.88 (5)	O1 - K1 - O3	116.4 (3)
O1 - C1	1.39 (3)	O1 - K1 - O4	121.0 (6)
C1 - C2	1.50 (3)	O1 - K1 - O11	115.4 (10)
C2 - O2	1.43 (2)	O2 - K1 - O3	59.7 (4)
O2 - C3	1.44 (2)	O2 - K1 - O4	106.9 (4)
C3 - C4	1.53 (3)	O2 - K1 - O11	99.7 (5)
C3 - C7	1.51 (3)	O3 - K1 - O4	61.0 (3)
C7 - C8	1.54 (3)	C1 - O1 - C1"	111 (2)
C8 - C9	1.43 (4)	K1 - O1 - C1	117 (1)
C9 - C10	1.55 (3)	O1 - C1 - C2	108 (2)
C4 - C10	1.50 (3)	C1 - C2 - O2	111 (2)
C4 - O3	1.40 (2)	C2 - O2 - C3	112 (1)
O3 - C5	1.43 (2)	C2 - O2 - K1	112 (1)
C5 - C6"	1.55 (3)	C3 - O2 - K1	119 (1)
C6 - O4	1.39 (2)	O2 - C3 - C4	106 (1)
O4 - C6"	1.39 (2)	O2 - C3 - C7	111 (2)
O1 - C1	1.39 (3)	C3 - C4 - C10	113 (2)
C11 - C12	1.40 (3)	C4 - C3 - C7	108 (2)
C12 - O11	1.51 (8)	C3 - C7 - C8	112 (2)

TABLE 87 (Continued)

	C7 - C8 - C9	110 (2)
	C8 - C9 - C10	113 (2)
	C9 - C10 - C4	110 (2)
	C10 - C4 - O3	107 (2)
	C3 - C4 - O3	113 (2)
	C4 - O3 - K1	115 (1)
	C4 - O3 - C5	114 (1)
	C5 - O3 - K1	108 (1)
	O3 - C5 - C6"	108 (2)
	C5" - C6 - O4	107 (2)
	C6 - O4 - K1	121 (1)
	C6" - O4 - K1	121 (1)
	C1" - O1 - K1	117 (1)

Symmetry operations:

' = -x, 1.0-y, 1.0-z.
" = x, 1.0-y, z.

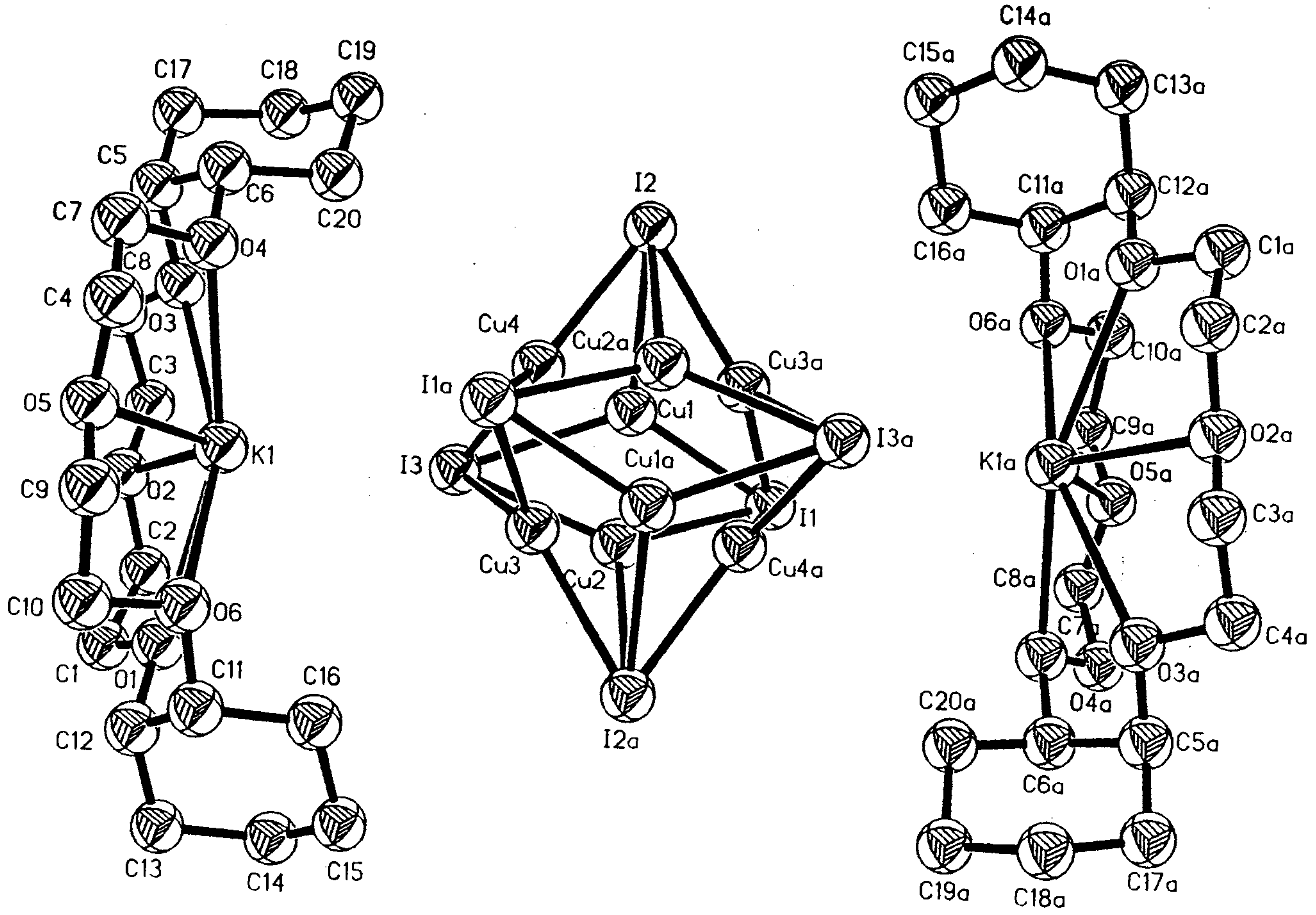

Figure 52. Projection View of $[K\text{-}(DC18\text{-}Crown\text{-}6)]_2[Cu_4I_6]$.

TABLE 88

CRYSTAL DATA FOR $[K\text{-(Dicyclohexano-18-Crown-6)}]_2[Cu_4I_6]$

Formula	$Cu_4I_6K_2C_{40}O_{12}H_{72}$
MWT	1838.81
a	20.175(10) Å
b	11.771(3)
c	12.766(3)
α	90.0°
β	104.95(3)
γ	90.0
V	2929.2(17) $Å^3$
F (000)	1760
μMoK_α	47.58 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.084 g cm^{-3}
Z	2
Obs. Refl.	8452
Contribut. Refl.	1612
Variab.	308
R/R_w	5.7/7.2%
Space Group	$P2_1/n$
Octants Meas.	±h, +k, +l

TABLE 89

POSITIONAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)]$_2$[Cu$_4$I$_6$]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	-0.0864 (1)	0.4798 (2)	0.7570 (2)
I2	-0.1282 (1)	0.5959 (2)	1.0714 (2)
I3	-0.0436 (1)	0.2588 (2)	1.0492 (2)
Cu1	-0.0802 (4)	0.4486 (7)	0.9545 (6)
Cu2	0.0002 (4)	0.3906 (7)	0.9228 (6)
Cu3	0.0580 (4)	0.3993 (7)	1.0638 (6)
Cu4	-0.0273 (4)	0.4654 (6)	1.1179 (5)
K1	0.0442 (3)	0.1764 (5)	0.3136 (5)
O1	0.110 (1)	-0.012 (1)	0.238 (1)
O2	-0.020 (1)	-0.042 (2)	0.286 (1)
O3	-0.090 (1)	0.137 (2)	0.360 (2)
O4	-0.004 (1)	0.317 (2)	0.453 (1)
O5	0.132 (1)	0.231 (2)	0.517 (1)
O6	0.183 (1)	0.172 (2)	0.342 (2)
C1	0.079 (1)	-0.118 (3)	0.237 (2)
C2	0.004 (2)	-0.104 (2)	0.202 (2)
C3	-0.090 (2)	-0.033 (3)	0.267 (2)
C4	-0.109 (2)	0.021 (3)	0.356 (3)
C5	-0.107 (1)	0.198 (2)	0.447 (2)
C6	-0.077 (1)	0.316 (2)	0.443 (2)
C7	0.035 (2)	0.310 (2)	0.560 (2)
C8	0.109 (1)	0.324 (3)	0.566 (2)
C9	0.200 (2)	0.243 (3)	0.514 (2)
C10	0.222 (2)	0.150 (4)	0.446 (3)
C11	0.208 (1)	0.109 (2)	0.269 (2)
C12	0.185 (1)	-0.013 (2)	0.260 (2)
C13	0.204 (1)	-0.075 (2)	0.172 (2)
C14	0.180 (1)	-0.020 (3)	0.060 (3)

TABLE 89 (Continued)

C15	0.202 (1)	0.101 (3)	0.064 (2)
C16	0.185 (1)	0.166 (2)	0.159 (2)
C17	-0.180 (2)	0.207 (2)	0.435 (2)
C18	-0.216 (2)	0.267 (3)	0.332 (3)
C19	-0.187 (2)	0.385 (3)	0.322 (3)
C20	-0.109 (2)	0.375 (2)	0.339 (2)

TABLE 90

HYDROGEN POSITIONAL PARAMETERS FOR $[K\text{-}(Dicyclohexano\text{-}18\text{-}Crown\text{-}6)]_2[Cu_4I_6]$

ATOM	x	y	z
H11	0.0895	-0.1733	0.1830
H12	0.0901	-0.1590	0.3066
H21	-0.0085	-0.0626	0.1373
H22	-0.0197	-0.1783	0.1936
H31	-0.1111	0.0079	0.1977
H32	-0.1129	-0.1112	0.2547
H41	-0.1612	0.0174	0.3436
H42	-0.0892	-0.0167	0.4213
H71	0.0191	0.3597	0.6140
H72	0.0300	0.2292	0.5932
H81	0.1138	0.3995	0.5313
H82	0.1381	0.3358	0.6441
H91	0.2068	0.3185	0.4780
H92	0.2306	0.2490	0.5876
H101	0.2723	0.1524	0.4595
H102	0.2113	0.0777	0.4790
H131	0.2553	-0.0864	0.1863
H132	0.1867	-0.1581	0.1664
H141	0.1926	-0.0640	0.0032
H142	0.1281	-0.0208	0.0408
H151	0.2536	0.0965	0.0765
H152	0.1846	0.1343	-0.0069
H161	0.2027	0.2426	0.1596
H162	0.1333	0.1729	0.1381
H171	-0.2029	0.1310	0.4353
H172	-0.1927	0.2509	0.4936
H181	-0.2056	0.2179	0.2714
H182	-0.2646	0.2672	0.3197

TABLE 90 (Continued)

H191	-0.2089	0.4208	0.2527
H912	-0.1962	0.4340	0.3798
H201	-0.0993	0.3321	0.2774
H202	-0.0881	0.4517	0.3361

TABLE 91

ANISOTROPIC THERMAL PARAMETERS FOR $[\text{K-(Dicyclohexano-18-Crown-6)}]_2[\text{Cu}_4\text{I}_6]$

ATOM	U11	U22	U33	U12	U13	U23
I1	55 (1)	91 (2)	48 (1)	-3 (1)	5 (1)	-4 (1)
I2	57 (1)	69 (2)	78 (1)	15 (1)	28 (1)	6 (1)
I3	83 (1)	54 (1)	51 (1)	-12 (1)	15 (1)	-1 (1)
Cu1	49 (5)	62 (6)	68 (5)	-2 (4)	16 (4)	2 (4)
Cu2	63 (5)	58 (5)	53 (5)	9 (4)	14 (4)	-1 (4)
Cu3	64 (5)	61 (5)	56 (5)	11 (4)	19 (4)	13 (4)
Cu4	56 (5)	59 (5)	42 (4)	8 (4)	14 (4)	1 (4)
K1	45 (4)	48 (4)	47 (4)	0 (3)	10 (3)	-10 (4)
O1	5 (1)	2 (1)	6 (1)	0 (1)	2 (1)	-2 (1)
O2	4 (1)	5 (1)	6 (1)	-2 (1)	1 (1)	-2 (1)
O3	3 (1)	4 (1)	9 (2)	1 (1)	3 (1)	2 (1)
O4	6 (1)	8 (2)	2 (1)	-2 (1)	0 (1)	-1 (1)
O5	6 (1)	7 (2)	4 (1)	-2 (1)	2 (1)	0 (1)
O6	6 (1)	6 (1)	6 (1)	3 (1)	4 (1)	0 (1)
C1	5 (2)	7 (2)	4 (2)	2 (2)	1 (1)	-1 (2)
C2	10 (3)	2 (2)	6 (2)	-3 (2)	2 (2)	-1 (2)
C3	5 (2)	7 (2)	5 (2)	-6 (2)	0 (1)	0 (2)
C4	7 (2)	8 (3)	10 (3)	2 (2)	6 (2)	4 (2)
C5	2 (1)	6 (2)	8 (2)	1 (1)	3 (1)	-1 (2)
C6	2 (1)	5 (2)	7 (2)	- 2 (1)	0 (1)	-3 (2)
C7	7 (2)	4 (2)	9 (2)	3 (2)	4 (2)	-2 (2)
C8	3 (2)	8 (2)	9 (2)	-4 (2)	4 (2)	-2 (2)
C9	5 (2)	11 (3)	5 (2)	-3 (2)	1 (1)	0 (2)
C10	5 (2)	12 (4)	8 (3)	0 (2)	2 (2)	2 (3)
C11	4 (2)	5 (2)	4 (2)	1 (2)	0 (1)	0 (2)
C12	7 (2)	6 (2)	3 (1)	3 (2)	3 (1)	1 (2)
C13	6 (2)	4 (2)	7 (2)	1 (2)	3 (2)	2 (2)
C14	5 (2)	5 (2)	10 (2)	1 (2)	5 (2)	-3 (2)

TABLE 91 (Contiuned)

C15	8 (2)	6 (2)	4 (2)	0 (2)	4 (2)	4 (2)
C16	3 (1)	5 (2)	8 (2)	0 (2)	2 (1)	-3 (2)
C17	9 (2)	4 (2)	3 (2)	0 (2)	0 (2)	0 (1)
C18	6 (2)	8 (3)	9 (2)	3 (2)	2 (2)	1 (2)
C19	9 (3)	7 (3)	8 (2)	6 (2)	0 (2)	0 (2)
C20	10 (2)	2 (2)	6 (2)	3 (2)	4 (2)	3 (2)

The anisotropic displacement exponent takes the form:
$\exp(-2\pi (U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$
$\times 10^3$ for Cu, I and K, and $\times 10^2$ for O and C.

TABLE 92

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[\text{K-(Dicyclohexano-18-Crown-6)}]_2[\text{Cu}_4\text{I}_6]$

Cu1 - I1	2.519 (9)	I1 - Cu1 - I2	122.8 (3)
Cu1 - I2	2.630 (9)	I1 - Cu1 - I3	122.3 (3)
Cu1 - I3	2.557 (8)	I2 - Cu1 - I3	114.3 (3)
Cu1 ··· Cu2	1.896 (11)	Cu2 - Cu1 - Cu3	94.2 (5)
Cu1 ··· Cu3	1.874 (11)	Cu2 - Cu1 - Cu4	90.2 (4)
Cu1 ··· Cu4	2.092 (10)	Cu3 - Cu1 - Cu4	87.6 (4)
Cu1 ··· Cu2'	2.707 (10)	I1 - Cu2 - I3	119.5 (3)
Cu1 ··· Cu3'	2.834 (10)	Cu3 - Cu2 - Cu4	58.9 (3)
Cu1 ··· Cu4'	2.757 (12)	Cu1 - Cu2 - Cu3	42.6 (3)
Cu2 - I1	2.592 (7)	Cu1 - Cu2 - Cu4	47.7 (3)
Cu2 - I3	2.554 (8)	I1 - Cu3 - I2	123.6 (3)
Cu2 ··· Cu3	2.761 (12)	Cu1 - Cu3 - Cu2	43.2 (3)
Cu2 ··· Cu4	2.828 (11)	Cu1 - Cu3 - Cu4	49.5 (3)
Cu2 ··· Cu3'	1.878 (9)	Cu2 - Cu3 - Cu4	61.8 (3)
Cu2 ··· Cu4'	1.893 (11)	Cu3 - Cu2 - Cu4'	51.1 (4)
Cu3 - I1	2.628 (8)	Cu4 - Cu2 - Cu3'	49.6 (3)
Cu3 - I2	2.500 (9)	Cu1 - Cu2 - Cu3'	97.4 (5)
Cu3 ··· Cu4	2.749 (10)	Cu1 - Cu2 - Cu4'	93.4 (5)
Cu3 ··· Cu2'	1.878 (9)	Cu1 - Cu3 - Cu4'	86.0 (4)
Cu3 ··· Cu4'	2.156 (11)	Cu1 - Cu3 - Cu2'	92.4 (5)
Cu4 - I2	2.496 (8)	Cu2 - Cu3 - Cu4'	43.1 (3)
Cu4 - I3	2.578 (8)	I2 - Cu4 - I3	118.4 (2)
Cu4 ··· Cu2'	1.893 (11)	Cu1 - Cu4 - Cu3	42.9 (3)
Cu4 ··· Cu3'	2.156 (12)	Cu2 - Cu4 - Cu3	59.3 (3)
I1 - Cu4'	2.515 (7)	Cu1 - Cu4 - Cu2	42.1 (3)
I2 - Cu2'	2.568 (8)	Cu3 - Cu4 - Cu2'	43.0 (3)
I3 - Cu3'	2.601 (8)	Cu1 - Cu4 - Cu3'	83.7 (4)
K1 - O1	2.88 (2)	Cu1 - Cu4 - Cu2'	85.4 (4)

TABLE 92 (Continued)

K1 - O2	2.86 (2)	Cu2 - Cu4 - Cu3'	41.6 (2)
K1 - O3	2.96 (2)	Cu3 - Cu1 - Cu4'	51.3 (4)
K1 - O4	2.79 (2)	Cu3 - Cu1 - Cu2'	43.9 (3)
K1 - O5	2.81 (2)	Cu4 - Cu1 - Cu3'	49.1 (3)
K1 - O6	2.72 (2)	Cu4 - Cu1 - Cu2'	44.2 (3)
O1 - C1	1.40 (4)	Cu2 - Cu1 - Cu4'	43.3 (3)
O1 - C12	1.46 (3)	O1 - K1 - O2	59.8 (5)
C1 - C2	1.46 (4)	O1 - K1 - O3	118.3 (6)
C2 - O2	1.48 (4)	O1 - K1 - O5	104.7 (5)
O2 - C3	1.37 (4)	O1 - K1 - O6	58.7 (5)
C3 - C4	1.44 (5)	O2 - K1 - O3	58.5 (6)
C4 - O3	1.41 (4)	O2 - K1 - O4	113.3 (6)
O3 - C5	1.43 (4)	O2 - K1 - O6	114.3 (6)
C5 - C6	1.52 (4)	O3 - K1 - O4	58.4 (6)
C5 - C17	1.44 (4)	O3 - K1 - O5	104.0 (6)
C19 - C20	1.53 (5)	O4 - K1 - O5	60.8 (5)
C6 - O4	1.44 (3)	O4 - K1 - O6	116.3 (6)
C6 - C20	1.49 (4)	K1 - O1 - C1	116 (2)
O4 - C7	1.38 (3)	O1 - C1 - C2	110 (2)
C7 - C8	1.48 (4)	C2 - O2 - C3	115 (2)
C8 - O5	1.39 (4)	C2 - O2 - K1	108 (2)
O5 - C9	1.40 (4)	C3 - O2 - K1	111 (2)
C9 - C10	1.53 (5)	O2 - C3 - C4	112 (2)
C10 - O6	1.38 (4)	C3 - C4 - O3	109 (3)
C11 - O6	1.39 (4)	C1 - C2 - O2	109 (2)
C11 - C12	1.51 (4)	C6 - C5 - C17	109 (2)
C11 - C16	1.51 (4)	C4 - O3 - C5	114 (2)
C12 - O1	1.46 (3)	O3 - C5 - C6	105 (2)

TABLE 92 (Continued)

C12 - C13	1.47 (4)	C4 - O3 - K1	113 (2)
C13 - C14	1.53 (4)	C5 - O3 - K1	119 (1)
C14 - C15	1.49 (4)	C5 - C6 - O4	114 (2)
C15 - C16	1.54 (4)	C6 - O4 - C7	113 (2)
C17 - C18	1.50 (4)	C6 - O4 - K1	117 (1)
C18 - C19	1.53 (5)	C7 - O4 - K1	113 (2)
		O4 - C7 - C8	110 (3)
		C7 - C8 - O5	110 (2)
		C8 - O5 - C9	112 (2)
		C8 - O5 - K1	113 (1)
		C9 - O5 - K1	113 (2)
		O5 - C9 - C10	112 (3)
		C9 - C10 - O6	104 (3)
		C10 - O6 - C11	109 (2)
		C11 - O6 - K1	118 (1)
		O6 - C11 - C12	113 (2)
		O6 - C11 - C16	108 (2)
		C11 - C12 - C13	113 (2)
		C11 - C12 - O1	107 (2)
		C12 - O1 - K1	119 (1)
		C12 - O1 - C1	116 (2)
		C12 - C13 - C14	114 (2)
		O1 - C12 - C13	109 (2)
		C13 - C14 - C15	111 (2)
		C14 - C15 - C16	111 (3)
		C15 - C16 - C11	116 (2)
		O3 - C5 - C17	113 (2)

TABLE 92 (Continued)

	C5 - C17 - C18	112 (3)
	C17 - C18 - C19	113 (2)
	C18 - C19 - C20	108 (3)
	C19 - C20 - C6	111 (3)
	C20 - C6 - O4	106 (2)
	C20 - C6 - C5	111 (2)

Symmetry operation:

' = -x, 1.0-y, 2.0-z

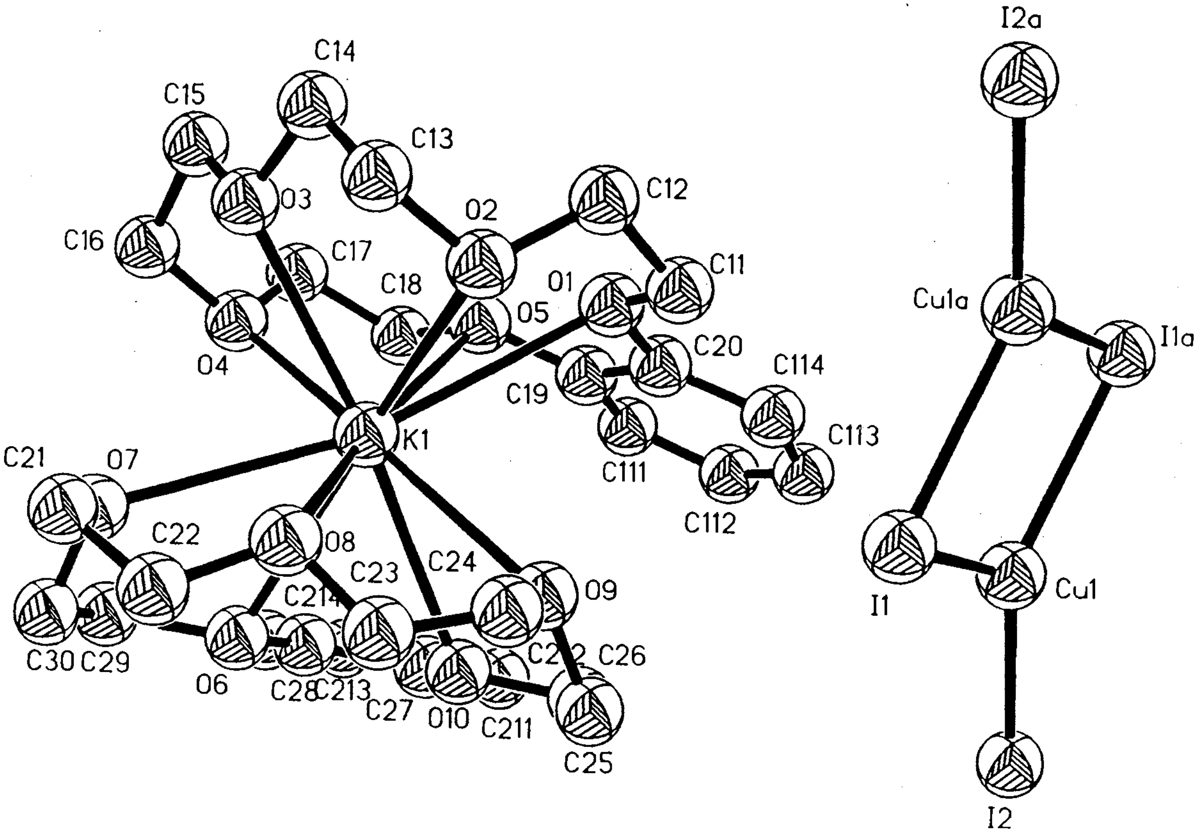

Figure 53. Projection View of $[K\text{-}(Benzo\text{-}15\text{-}Crown\text{-}5)_2]_2[Cu_2I_4]$.

TABLE 93

CRYSTAL DATA FOR $[K\text{-(Benzo-15-Crown-5)}_2]_2[Cu_2I_4]$

Formula	$Cu_2I_4K_2C_{56}O_{20}H_{80}$
MWT	1786.14
a	12.479(3) Å
b	12.614(4)
c	12.304(3)
α	94.63(2)°
β	111.20(2)
γ	104.26(2)
V	1718.8(7) $Å^3$
F (000)	884
μMoK_α	25.82 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.725 g cm^{-3}
Z	1
Obs. Refl.	9947
Contribut. Refl.	2448
Variab.	380
R/R_w	5.4/6.6%
Space Group	P1bar
Octants Meas.	±h, ±k, +l

TABLE 94

POSITIONAL PARAMETERS FOR $[K\text{-}(Benzo\text{-}15\text{-}Crown\text{-}5)_2]_2[Cu_2I_4]$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	0.1788 (1)	0.0263 (1)	0.6047 (1)
I2	0.0296 (1)	0.3203 (1)	0.6034 (1)
Cu1	0.0144 (2)	0.1252 (2)	0.5420 (2)
K1	0.3679 (2)	0.2108 (2)	0.2198 (2)
O1	0.1099 (8)	0.0930 (8)	0.1605 (7)
O2	0.2836 (9)	-0.0133 (7)	0.2420 (8)
O3	0.3781 (8)	0.0426 (7)	0.0654 (7)
O4	0.3482 (8)	0.2470 (7)	-0.0143 (7)
O5	0.1399 (8)	0.2212 (7)	0.0227 (7)
O6	0.5122 (9)	0.4474 (8)	0.2572 (8)
O7	0.6168 (9)	0.2811 (8)	0.2412 (10)
O8	0.5489 (9)	0.1758 (9)	0.4106 (8)
O9	0.3551 (9)	0.2226 (9)	0.4462 (8)
O10	0.3680 (8)	0.4110 (9)	0.3553 (9)
C11	0.107 (1)	0.016 (1)	0.240 (1)
C12	0.162 (2)	-0.068 (1)	0.214 (1)
C13	0.342 (2)	-0.076 (1)	0.195 (2)
C14	0.320 (2)	-0.069 (1)	0.069 (1)
C15	0.354 (1)	0.057 (1)	-0.054 (1)
C16	0.406 (1)	0.180 (1)	-0.051 (1)
C17	0.241 (1)	0.247 (1)	-0.101 (1)
C18	0.170 (1)	0.293 (1)	-0.050 (1)
C19	0.072 (1)	0.247 (1)	0.080 (1)
C20	0.055 (1)	0.175 (1)	0.156 (1)
C21	0.677 (1)	0.216 (1)	0.316 (2)
C22	0.667 (2)	0.214 (2)	0.429 (1)
C23	0.541 (2)	0.188 (2)	0.522 (1)
C24	0.434 (2)	0.172 (2)	0.517 (2)

TABLE 94 (Continued)

C25	0.349 (2)	0.320 (2)	0.505 (1)
C26	0.299 (1)	0.389 (1)	0.422 (2)
C27	0.346 (1)	0.485 (1)	0.273 (1)
C28	0.430 (1)	0.497 (1)	0.221 (1)
C29	0.602 (1)	0.456 (1)	0.207 (1)
C30	0.681 (2)	0.393 (2)	0.267 (2)
C111	0.020 (1)	0.327 (1)	0.071 (1)
C112	-0.041 (2)	0.342 (2)	0.137 (2)
C113	-0.053 (2)	0.275 (3)	0.216 (2)
C114	-0.008 (1)	0.189 (2)	0.224 (2)
C211	0.257 (1)	0.534 (1)	0.247 (2)
C212	0.247 (2)	0.608 (2)	0.161 (2)
C213	0.330 (2)	0.611 (2)	0.114 (2)
C214	0.422 (2)	0.567 (1)	0.140 (2)

TABLE 95

HYDROGEN POSITIONAL PARAMETERS FOR $[K\text{-}(Benzo\text{-}15\text{-}Crown\text{-}5)_2]_2[Cu_2I_4]$

ATOM	x	y	z
H111	0.1485	0.0520	0.3225
H112	0.0215	-0.0224	0.2274
H121	0.1535	-0.1262	0.2627
H122	0.1194	-0.1034	0.1305
H131	0.4336	-0.0484	0.2399
H132	0.3217	-0.1560	0.2034
H141	0.3461	-0.1247	0.0308
H142	0.2309	-0.0894	0.0241
H151	0.3830	0.0094	-0.0941
H152	0.2650	0.0383	-0.0991
H161	0.4949	0.2013	0.0017
H162	0.4061	0.1897	-0.1317
H171	0.2546	0.2881	-0.1631
H172	0.1922	0.1692	-0.1450
H181	0.2178	0.3694	-0.0030
H182	0.0963	0.3025	-0.1111
H211	0.6453	0.1372	0.2738
H212	0.7638	0.2397	0.3279
H221	0.7173	0.1738	0.4777
H222	0.7036	0.2951	0.4744
H231	0.5861	0.1447	0.5728
H232	0.5840	0.2688	0.5638
H241	0.3941	0.0859	0.4822
H242	0.4344	0.1757	0.5981
H251	0.2958	0.3006	0.5517
H252	0.4267	0.3676	0.5652
H261	0.2138	0.3470	0.3714
H262	0.2965	0.4579	0.4644

TABLE 95 (Continued)

H291	0.5666	0.4215	0.1209
H292	0.6486	0.5333	0.2128
H301	0.7548	0.4054	0.2485
H302	0.7156	0.4229	0.3559
H1111	0.0321	0.3825	0.0144
H1121	-0.0830	0.4039	0.1258
H1131	-0.0930	0.2878	0.2719
H1141	-0.0199	0.1323	0.2788
H2111	0.1965	0.5177	0.2872
H2121	0.1846	0.6486	0.1484
H2131	0.3198	0.6625	0.0484
H2141	0.4811	0.5831	0.1009

TABLE 96

ANISOTROPIC THERMAL PARAMETERS FOR [K-(Benzo-15-Crown-5)$_2$]$_2$[Cu$_2$I$_4$]

ATOM	U11	U22	U33	U12	U13	U23
I1	805 (7)	801 (7)	617 (6)	111 (5)	146 (5)	111 (5)
I2	995 (8)	804 (8)	985 (8)	138 (6)	-80 (7)	166 (6)
Cu1	100 (2)	86 (1)	67 (1)	11 (1)	26 (1)	25 (1)
K1	51 (2)	48 (2)	41 (1)	5 (1)	14 (1)	8 (1)
O1	60 (6)	125 (8)	48 (5)	-2 (6)	18 (4)	30 (5)
O2	103 (8)	61 (6)	64 (6)	2 (6)	26 (5)	18 (5)
O3	94 (7)	65 (6)	46 (5)	28 (5)	15 (5)	-1 (4)
O4	57 (6)	70 (6)	52 (5)	22 (5)	12 (4)	10 (4)
O5	82 (6)	59 (5)	52 (5)	10 (5)	35 (4)	22 (4)
O6	104 (8)	74 (6)	75 (6)	22 (6)	48 (6)	21 (5)
O7	94 (8)	64 (6)	123 (8)	12 (6)	46 (7)	2 (6)
O8	89 (8)	147 (10)	84 (7)	74 (7)	24 (6)	38 (7)
O9	106 (8)	131 (9)	54 (6)	32 (7)	36 (6)	20 (6)
O10	83 (7)	84 (7)	99 (7)	30 (6)	50 (6)	17 (6)
C11	7 (1)	13 (1)	6 (1)	-3 (1)	3 (1)	3 (1)
C12	16 (2)	7 (1)	7 (1)	-3 (1)	4 (1)	2 (1)
C13	12 (1)	6 (1)	11 (1)	1 (1)	2 (1)	3 (1)
C14	14 (1)	5 (1)	6 (1)	3 (1)	2 (1)	-2 (1)
C15	7 (1)	7 (1)	6 (1)	4 (1)	2 (1)	-1 (1)
C16	5 (1)	8 (1)	6 (1)	2 (1)	1 (1)	2 (1)
C17	7 (1)	8 (1)	4 (1)	1 (1)	2 (1)	3 (1)
C18	8 (1)	6 (1)	6 (1)	2 (1)	1 (1)	0 (1)
C19	5 (1)	9 (1)	5 (1)	-1 (1)	3 (1)	-1 (1)
C20	4 (1)	11 (1)	6 (1)	2 (1)	1 (1)	0 (1)
C21	5 (1)	9 (1)	19 (2)	2 (1)	4 (1)	3 (1)
C22	10 (1)	14 (2)	9 (1)	8 (1)	0 (1)	0 (1)
C23	18 (2)	16 (2)	6 (1)	7 (2)	1 (1)	3 (1)
C24	11 (2)	36 (4)	11 (2)	3 (2)	3 (1)	16 (2)

TABLE 96 (Contiuned)

C25	11 (1)	15 (2)	4 (1)	0 (1)	4 (1)	0 (1)
C26	7 (1)	11 (1)	12 (1)	2 (1)	5 (1)	-4 (1)
C27	8 (1)	3 (1)	9 (1)	2 (1)	1 (1)	-2 (1)
C28	10 (1)	7 (1)	5 (1)	2 (1)	1 (1)	2 (1)
C29	10 (1)	4 (1)	12 (1)	0 (1)	8 (1)	0 (1)
C30	11 (1)	11 (1)	14 (2)	3 (1)	9 (1)	1 (1)
C111	8 (1)	8 (1)	10 (1)	3 (1)	4 (1)	-1 (1)
C112	8 (1)	15 (2)	14 (2)	7 (1)	4 (1)	-2 (2)
C113	8 (2)	31 (4)	12 (2)	6 (2)	7 (2)	-2 (2)
C114	5 (1)	17 (2)	10 (1)	0 (1)	4 (1)	2 (1)
C211	8 (1)	7 (1)	14 (2)	4 (1)	1 (1)	-3 (1)
C212	11 (2)	6 (1)	18 (2)	6 (1)	-4 (2)	0 (1)
C213	12 (2)	8 (1)	14 (2)	4 (1)	-3 (2)	0 (1)
C214	11 (1)	8 (1)	10 (1)	-1 (1)	1 (1)	1 (1)

The anisotropic displacement exponent takes the form:
$\exp(-2\pi (U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$
$\times 10^4$ for I, $\times 10^3$ for Cu, K and O, and $\times 10^2$ for C.

TABLE 97

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[\text{K-(Benzo-15-Crown-5)}_2]_2[\text{Cu}_2\text{I}_4]$

Cu1 - I1	2.575 (3)	I1 - Cu1 - I2	128.9 (1)
Cu1 - I2	2.585 (3)	I2 - Cu1 - I1'	125.6 (1)
Cu1 - I1'	2.596 (2)	I1 - Cu1 - I1'	105.4 (1)
Cu1' - I1'	2.575 (3)	I1 - Cu1' - I1'	105.4 (1)
Cu1' - I2'	2.456 (2)	Cu1 - I1 - Cu1'	74.5 (1)
Cu1 ··· Cu1'	3.131 (3)	I1' - Cu1' - I2'	128.9 (1)
K1 - O1	2.98 (1)	I1 - Cu1' - I2'	125.6 (1)
K1 - O2	2.83 (1)	O1 - K1 - O2	56.4 (3)
K1 - O3	2.79 (1)	O2 - K1 - O3	61.6 (3)
K1 - O4	2.88 (1)	O3 - K1 - O4	61.3 (3)
K1 - O5	3.04 (1)	O4 - K1 - O5	55.1 (3)
K1 - O6	2.98 (1)	O5 - K1 - O1	49.0 (2)
K1 - O7	2.92 (1)	O1 - K1 - O3	90.2 (3)
K1 - O8	2.76 (1)	O1 - K1 - O4	98.3 (2)
K1 - O9	2.84 (1)	O2 - K1 - O4	116.2 (2)
K1 - O10	2.91 (1)	O2 - K1 - O5	97.9 (2)
O1 - C11	1.44 (2)	O3 - K1 - O5	88.4 (2)
C11 - C12	1.47 (3)	K1 - O1 - C11	107 (1)
C12 - O2	1.40 (2)	O1 - C11 - C12	108 (1)
O2 - C13	1.42 (2)	C11 - C12 -O2	108 (1)
C13 - C14	1.48 (2)	C12 - O2 - K1	123 (1)
C14 - O3	1.43 (2)	C12 - O2 - C13	114 (1)
O3 - C15	1.42 (2)	K1 - O2 - C13	107 (1)
C15 - C16	1.51 (2)	O2 - C13 - C14	112 (1)
C16 - O4	1.38 (2)	C13 - C14 - O3	108 (1)
O4 - C17	1.38 (1)	C14 - O3 - C15	111 (1)
C17 - C18	1.47 (2)	K1 - O3 - C15	117 (1)
C18 - O5	1.40 (2)	O3 - C15 - C16	108 (1)
O5 - C19	1.37 (2)	C15 - C16 - O4	114 (1)
C19 - C20	1.39 (2)	C16 - O4 - C17	114 (1)

TABLE 97 (Continued)

C20 - O1	1.37 (2)	C16 - O4 - K1	106 (1)
C20 - C114	1.37 (3)	O4 - C17 - C18	111 (1)
C114 - C113	1.33 (5)	C17 - C18 - O5	107 (1)
C113 - C112	1.37 (4)	C18 - O5 - C19	118 (1)
C112 - C111	1.32 (4)	C18 - O5 - K1	110 (1)
C111 - C19	1.31 (2)	O5 - C19 - C20	113 (1)
O7 - C21	1.42 (2)	O5 - C19 - C111	130 (1)
C21 - C22	1.45 (3)	C19 - C20 - O1	115 (1)
C22 - O8	1.36 (2)	C20 - O1 - K1	106 (1)
O8 - C23	1.41 (2)	C20 - C19 - C111	118 (2)
C23 - C24	1.28 (3)	C19 - C111 - C112	122 (2)
C24 - O9	1.38 (3)	C111 - C112 - C113	121 (3)
O9 - C25	1.41 (2)	C112 - C113 - C114	120 (3)
C25 - C26	1.46 (3)	C113 - C114 - C20	118 (2)
C26 - O10	1.39 (2)	C114 - C20 - C19	121 (2)
O10 - C27	1.43 (2)	C114 - C20 - O1	124 (2)
C27 - C28	1.41 (2)	C20 - O1 - C11	121 (1)
C28 - O6	1.29 (2)	K1 - O7 - C21	106 (1)
O6 - C29	1.45 (2)	O7 - C21 - C22	117 (2)
C29 - C30	1.45 (3)	C21 - C22 -O8	109 (1)
C30 - O7	1.39 (2)	C22 - O8 - K1	123 (1)
C28 - C214	1.37 (2)	C22 - O8 - C23	107 (1)
C214 - C213	1.34 (4)	K1 - O8 - C23	118 (1)
C213 - C212	1.35 (4)	O8 - C23 - C24	114 (1)
C212 - C211	1.46 (3)	C23 - C24 - O9	122 (1)
C211 - C27	1.35 (2)	C24 - O9 - C25	115 (1)
		K1 - O9 - C25	121 (1)
		O9 - C25 - C26	112 (1)
		C25 - C26 - O10	107 (2)
		C26 - O10 - C27	120 (1)
		C26 - O10 - K1	113 (1)

TABLE 97 (Continued)

	O10 - C27 - C28	109 (1)
	C27 - C28 - O6	118 (1)
	C28 - O6 - C29	121 (1)
	C28 - O6 - K1	102 (1)
	O6 - C29 - C30	107 (2)
	C29 - C30 - O7	110 (1)
	C30 - O7 - K1	121 (1)
	C28 - C27 - C211	125 (2)
	C27 - C211 - C212	119 (2)
	C211 - C212 - C213	111 (2)
	C212 - C213 - C214	132 (2)
	C213 - C214 - C28	117 (2)
	C214 - C28 - C27	116 (2)
	C214 - C28 - O6	126 (2)
	C211 - C27 - O10	127 (2)
	C30 - O7 - C21	114 (1)

Symmetry operation:

' = -x, -y, 1.0-z.

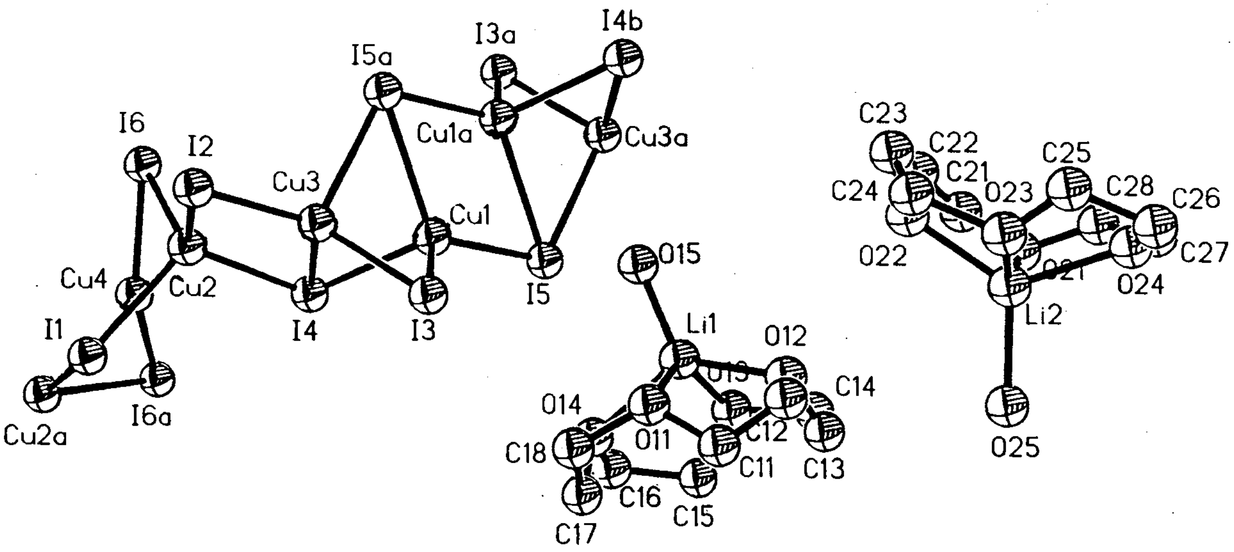

Figure 54. Projection View of $[Li\text{-}(12\text{-}Crown\text{-}4)\text{-}H_2O]_2[Cu_4I_6]$.

TABLE 98

CRYSTAL DATA FOR $[Li-(12-Crown-4)-H_2O]_2[Cu_4I_6]$

Formula	$Cu_4I_6Li_2C_{16}O_{10}H_{36}$
MWT	1417.94
a	27.061(4) Å
b	13.568(4)
c	19.081(4)
α	90.0°
β	94.97(1)
γ	90.0
V	6979.8(27) Å^3
F (000)	5216
μMoK_α	77.08 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.698 g cm^{-3}
Z	8
Obs. Refl.	9619
Contribut. Refl.	2089
Variab.	336
R/R_W	5.3/7.1%
Space Group	A2/a
Octants Meas.	±h, +k, +l

TABLE 99

POSITIONAL PARAMETERS FOR $[Li\text{-}(12\text{-}Crown\text{-}4)\text{-}H_2O]_2[Cu_4I_6]$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	0.7500	0.2674 (2)	1.0000
I2	0.6322 (1)	0.2774 (2)	1.1305 (1)
I3	0.5049 (1)	0.2646 (2)	0.9603 (1)
I4	0.6237 (1)	0.0670 (2)	0.9463 (1)
I5	0.4690 (1)	-0.0317 (2)	0.8842 (1)
I6	0.7253 (1)	-0.0035 (2)	1.1131 (1)
Cu1	0.5239 (2)	0.0730 (4)	0.9673 (3)
Cu2	0.6783 (2)	0.1589 (4)	1.0518 (2)
Cu3	0.5776 (2)	0.1841 (4)	1.0410 (3)
Cu4	0.7500	0.0682 (6)	1.0000
O11	0.364 (1)	0.405 (2)	0.836 (1)
O12	0.288 (1)	0.292 (2)	0.792 (1)
O13	0.346 (1)	0.158 (2)	0.732 (1)
O14	0.425 (1)	0.280 (2)	0.781 (1)
O15	0.376 (1)	0.173 (2)	0.906 (1)
O21	0.128 (1)	0.241 (2)	0.834 (2)
O22	0.180 (1)	0.355 (3)	0.928 (2)
O23	0.118 (2)	0.485 (3)	0.924 (3)
O24	0.055 (3)	0.367 (6)	0.847 (5)
O25	0.145 (1)	0.444 (2)	0.758 (1)
C11	0.323 (2)	0.445 (2)	0.793 (2)
C12	0.280 (2)	0.393 (3)	0.803 (2)
C13	0.277 (2)	0.268 (3)	0.721 (3)
C14	0.291 (1)	0.168 (3)	0.711 (2)
C15	0.378 (3)	0.191 (3)	0.683 (2)
C16	0.431 (1)	0.210 (4)	0.722 (2)
C17	0.428 (1)	0.379 (4)	0.760 (2)
C18	0.415 (1)	0.434 (3)	0.824 (2)

TABLE 99 (Continued)

C21	0.160 (3)	0.201 (5)	0.875 (5)
C22	0.177 (2)	0.232 (5)	0.932 (2)
C23	0.178 (2)	0.368 (5)	0.992 (2)
C24	0.164 (2)	0.476 (4)	0.979 (2)
C25	0.076 (3)	0.474 (5)	0.944 (5)
C26	0.035 (3)	0.447 (6)	0.883 (5)
C27	0.042 (2)	0.299 (5)	0.830 (4)
C28	0.079 (2)	0.202 (4)	0.827 (3)
Li1	0.358 (2)	0.249 (4)	0.824 (3)
Li2	0.130 (3)	0.381 (5)	0.846 (3)

TABLE 100

ANISOTROPIC THERMAL PARAMETERS FOR [Li-(12-Crown-4)-H_2O]$_2$[Cu_4I_6]

ATOM	U11	U22	U33	U12	U13	U23
I1	46 (2)	42 (2)	58 (2)	0	15 (2)	0
I2	51 (2)	62 (2)	60 (2)	-4 (1)	11 (1)	-25 (1)
I3	56 (2)	53 (2)	69 (2)	13 (1)	2 (1)	3 (1)
I4	41 (2)	66 (3)	53 (2)	2 (1)	3 (1)	-18 (1)
I5	52 (2)	60 (2)	52 (2)	-8 (1)	-1 (1)	-1 (1)
I6	55 (2)	58 (2)	46 (2)	2 (1)	14 (1)	10 (1)
Cu1	81 (4)	73 (4)	139 (5)	-14 (3)	-23 (4)	-26 (4)
Cu2	60 (3)	69 (4)	76 (4)	3 (2)	21 (2)	-11 (3)
Cu3	84 (4)	96 (4)	111 (4)	11 (3)	-32 (3)	-40 (4)
Cu4	227 (11)	70 (6)	94 (6)	0	110 (7)	0
O11	8 (2)	8 (2)	6 (2)	2 (1)	0 (1)	-1 (1)
O12	6 (2)	12 (2)	6 (2)	-1 (2)	- 2 (1)	0 (2)
O13	13 (2)	5 (2)	6 (2)	-1 (2)	2 (2)	0 (1)
O14	7 (2)	10 (2)	9 (2)	0 (2)	2 (1)	1 (2)
O15	5 (1)	8 (2)	5 (1)	1 (1)	1 (1)	1 (1)
O21	18 (3)	8 (2)	14 (3)	-2 (2)	6 (2)	2 (2)
O22	10 (3)	28 (5)	9 (3)	-5 (3)	-3 (2)	8 (3)
O23	31 (7)	8 (3)	24 (5)	5 (4)	21 (6)	6 (3)
O24	16 (6)	35 (10)	33 (12)	-8 (6)	12 (6)	-2 (9)
O25	6 (1)	8 (2)	6 (1)	0 (1)	3 (1)	0 (1)
C11	11 (4)	1 (2)	12 (3)	-1 (2)	-3 (3)	-3 (2)
C12	10 (3)	2 (2)	14 (4)	0 (2)	2 (3)	-1 (2)
C13	8 (3)	7 (3)	18 (5)	1 (3)	-3 (3)	-2 (3)
C14	8 (3)	8 (3)	12 (4)	-2 (3)	-6 (3)	3 (3)
C15	37 (9)	6 (3)	9 (4)	-6 (4)	13 (5)	-1 (3)
C16	4 (2)	21 (6)	13 (4)	1 (3)	2 (2)	-3 (4)
C17	6 (3)	13 (4)	8 (3)	-1 (3)	0 (2)	4 (3)
C18	7 (3)	10 (4)	10 (4)	-4 (3)	0 (3)	2 (3)

TABLE 100 (Continued)

C21	23 (10)	9 (5)	41 (12)	3 (6)	-4 (9)	10 (7)
C22	18 (6)	27 (9)	8 (4)	5 (6)	0 (4)	5 (5)
C23	18 (6)	26 (8)	4 (3)	5 (5)	3 (3)	2 (4)
C24	14 (5)	11 (4)	12 (4)	2 (4)	4 (3)	-1 (3)
C25	12 (6)	12 (5)	31 (12)	5 (5)	4 (7)	0 (6)
C26	10 (6)	15 (7)	22 (8)	6 (5)	5 (5)	7 (6)
C27	8 (4)	21 (6)	29 (7)	4 (4)	-14 (4)	-11 (6)
C28	15 (5)	14 (4)	20 (6)	-10 (4)	6 (4)	-10 (4)
Li1	2 (3)	6 (4)	3 (3)	-1 (3)	1 (2)	0 (3)
Li2	9 (5)	7 (5)	4 (4)	0 (4)	1 (4)	5 (4)

The anisotropic displacement exponent takes the form:
$\exp(-2\pi (U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$
$\times 10^3$ for I and Cu, and $\times 10^2$ for O, C and Li.

TABLE 101

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[Li\text{-}(12\text{-}Crown\text{-}4)\text{-}H_2O]_2[Cu_4I_6]$

Cu1 - I3	2.651 (6)	Cu2 - I1 - Cu4	56.8 (1)
Cu1 - I4	2.764 (6)	I1 - Cu4 - I6	112.8 (2)
Cu1 - I5	2.516 (6)	Cu4 - I6 - Cu2	58.1 (2)
Cu2 - I1	2.692 (5)	I6 - Cu2 - I1	105.8 (2)
Cu2 - I2	2.592 (6)	I6 - Cu2 - I4	98.7 (2)
Cu2 - I4	2.697 (5)	I6 - Cu2 - I2	118.5 (2)
Cu2 - I6	2.753 (5)	I1 - Cu2 - I2	105.8 (2)
Cu3 - I2	2.502 (6)	I1 - Cu2 - I4	110.2 (1)
Cu3 - I3	2.627 (6)	Cu2 - I2 - Cu3	65.0 (2)
Cu3 - I4	2.782 (6)	Cu2 - I4 - Cu1	110.9 (2)
Cu4 - I1	2.703 (9)	Cu2 - I4 - Cu3	59.9 (2)
Cu4 - I6	2.511 (4)	I2 - Cu3 - I3	123.8 (2)
Cu1 ··· Cu3	2.450 (8)	I2 - Cu3 - I4	117.3 (2)
Cu2 ··· Cu3	2.737 (7)	I4 - Cu3 - I3	102.2 (2)
Cu2 ··· Cu4	2.566 (6)	Cu3 - I4 - Cu1	52.4 (2)
I5 - Cu1'	2.879 (7)	Cu3 - I3 - Cu1	55.3 (2)
I5 - Cu3'	2.866 (6)	I4 - Cu1 - I3	102.1 (2)
Cu1 - I5'	2.878 (7)	I3 - Cu1 - I5	114.9 (2)
Cu1' - I5'	2.515 (6)	I4 - Cu1 - I5	115.0 (2)
Cu1' - I3'	2.651 (6)	Cu1 - I5 - Cu3'	110.7 (2)
Cu3' - I3'	2.627 (6)	Cu1 - I5 - Cu1'	60.3 (2)
Cu4 - I6"	2.511 (4)	I5' - Cu1 - I5	119.7 (2)
I1- Cu2"	2.691 (5)	Cu1' - I5' - Cu1	60.3 (2)
I6" - Cu2"	2.753 (5)	I5 - Cu1' - I5'	119.7 (2)
Cu1 ··· Cu1'	2.727 (8)	I1 - Cu4 - I6"	112.8 (2)
Cu1' ··· Cu3'	2.450 (8)	Cu4 - I1 - Cu2"	56.8 (1)
Cu4 ··· Cu2"	2.566 (6)	Cu1 - I5' - Cu3	50.5 (2)
Cu3 - I5'	2.879 (7)	O15 - Li1 - O11	116 (3)

TABLE 101 (Continued)

Li1 - O11	2.12 (6)	O15 - Li1 - O12	124 (3)
Li1 - O12	2.02 (6)	O15 - Li1 - O13	112 (3)
Li1 - O13	2.15 (6)	O15 - Li1 - O14	105 (2)
Li1 - O14	2.09 (6)	O11 - Li1 - O12	79 (2)
Li1 - O15	1.92 (6)	O11 - Li1 - O13	132 (3)
Li2 - O21	1.92 (8)	O11 - Li1 - O14	78 (2)
Li2 - O22	2.00 (7)	O12 - Li1 - O13	81 (2)
Li2 - O23	2.09 (8)	O12 - Li1 - O14	130 (3)
Li2 - O24	2.05 (10)	O13 - Li1 - O14	82 (2)
Li2 - O25	1.97 (7)	O25 - Li2 - O21	109 (3)
O11 - C11	1.43 (5)	O25 - Li2 - O22	125 (4)
O11 - C18	1.47 (5)	O25 - Li2 - O23	112 (4)
C11 - C12	1.39 (6)	O25 - Li2 - O24	108 (4)
C12 - O12	1.40 (5)	O21 - Li2 - O22	86 (3)
O12 - C13	1.40 (6)	O21 - Li2 - O23	138 (4)
C13 - C14	1.42 (6)	O21 - Li2 - O24	83 (4)
C14 - O13	1.50 (5)	O22 - Li2 - O23	73 (3)
O13 - C15	1.41 (7)	O22 - Li2 - O24	126 (4)
C15 - C16	1.57 (8)	O23 - Li2 - O24	80 (4)
C16 - O14	1.48 (6)	Li1 - O11 - C11	106 (2)
O14 - C17	1.41 (6)	O11 - C11 - C12	110 (3)
C17 - C18	1.50 (6)	C11 - C12 - O12	109 (3)
O21 - C21	1.23 (9)	C12 - O12 - C13	110 (3)
O21 - C28	1.43 (6)	O12 - C13 - C14	108 (4)
C21 - C22	1.22 (10)	C13 - C14 - O13	109 (3)
C22 - O22	1.66 (9)	C14 - O13 - C15	117 (3)
O22 - C23	1.24 (6)	O13 - C15 - C16	110 (4)
C23 - C24	1.52 (8)	C15 - C16 - O14	108 (3)

TABLE 101 (Continued)

C24 - O23	1.56 (7)	C16 - O14 - C17	112 (3)
O23 - C25	1.24 (10)	O14 - C17 - C18	103 (3)
C25 - C26	1.58 (12)	C17 - C18 - O11	106 (3)
C26 - O24	1.42 (12)	C18 - O11 - C11	120 (3)
O24 - C27	1.41 (6)	Li1 - O11 - C18	108 (3)
C27 - C28	1.50 (6)	Li1 - O12 - C12	114 (3)
		Li1 - O12 - C13	110 (3)
		Li1 - O13 - C14	104 (3)
		Li1 - O13 - C15	107 (3)
		Li1 - O14 - C16	109 (3)
		Li1 - O14 - C17	112 (3)
		Li2 - O21 - C21	110 (4)
		O21 - C21 - C22	127 (7)
		C21 - C22 - O22	109 (5)
		C22 - O22 - C23	96 (4)
		O22 - C23 - C24	90 (4)
		C23 - C24 - O23	112 (4)
		C24 - O23 - C25	119 (6)
		O23 - C25 - C26	113 (8)
		C25 - C26 - O24	106 (6)
		C26 - O24 - C27	135 (8)
		O24 - C27 - C28	123 (6)
		C27 - C28 - O21	105 (4)
		C28 - O21 - C21	119 (5)
		Li2 - O21 - C28	113 (4)
		Li2 - O22 - C22	100 (3)
		Li2 - O22 - C23	131 (4)
		Li2 - O23 - C24	104 (4)

TABLE 101 (Continued)

	Li2 - O23 - C25	111 (5)
	Li2 - O24 - C26	111 (6)
	Li2 - O24 - C27	113 (7)

Symmetry operations:

' = 1.0-x, -y, 2.0-z.
" = 1.5-x, y, 2.0-z.

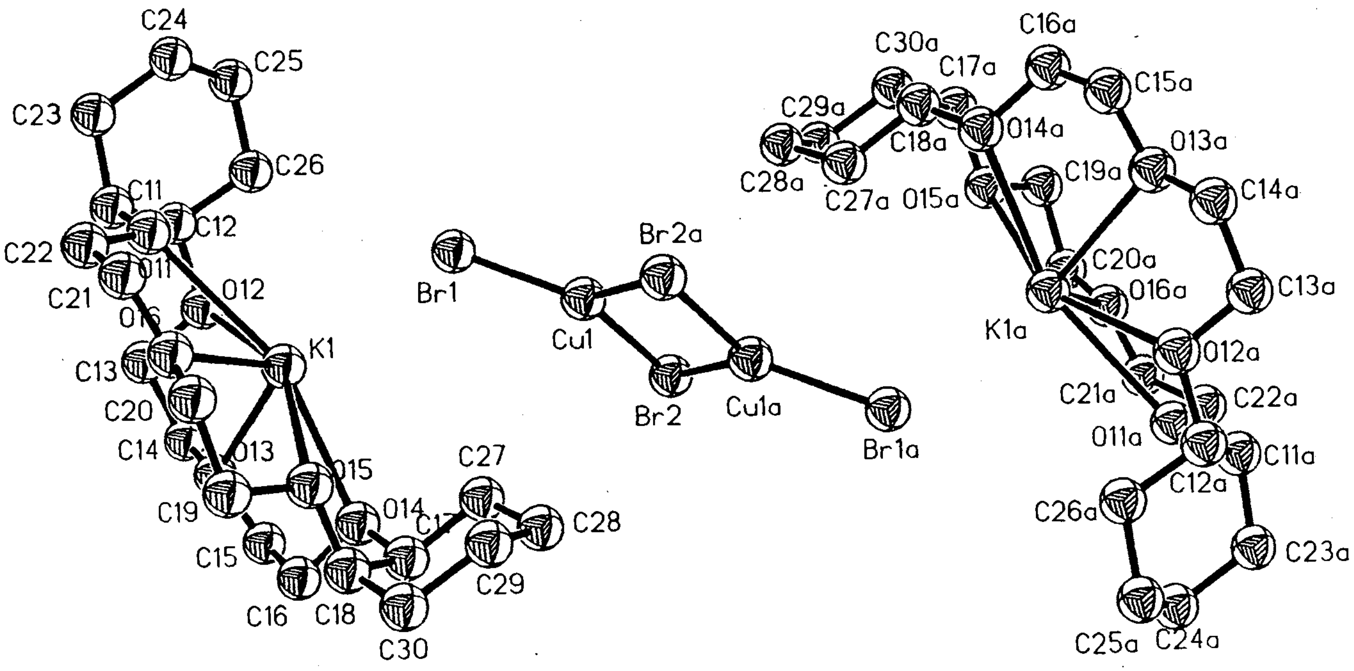

Figure 55. Projection View of $[K\text{-}(DC18\text{-}Crown\text{-}6)]_2[Cu_2Br_4]$.

TABLE 102

CRYSTAL DATA FOR [K-(Dicyclohexano-18-Crown-6)]$_2$[Cu_2Br_4]

Formula	$CuBr_2KC_{20}O_6H_{36}$
MWT	634.95
a	13.678(5) Å
b	15.044(3)
c	13.229(5)
α	90.0°
β	110.74(3)
γ	90.0
V	2545.7(15) Å^3
F (000)	1288
μMoK_α	41.62 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.656 g cm^{-3}
Z	4
Obs. Refl.	7320
Contribut. Refl.	1372
Variab.	272
R/R_w	5.5/6.4%
Space Group	$P2_1/n$
Octants Meas.	±h, +k, +l

TABLE 103

POSITIONAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)]$_2$[Cu$_2$Br$_4$]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cu1	0.4450 (2)	0.4678 (2)	0.5654 (2)
K1	0.4717 (3)	0.2952 (2)	0.8804 (3)
Br1	0.3488 (2)	0.4095 (1)	0.6617 (2)
Br2	0.4644 (2)	0.3912 (1)	0.4110 (2)
O11	0.3376 (8)	0.3314 (8)	1.0092 (8)
O12	0.2995 (8)	0.1893 (7)	0.8682 (9)
O13	0.4913 (8)	0.1087 (8)	0.8943 (9)
O14	0.6198 (9)	0.2122 (8)	0.8107 (9)
O15	0.6914 (8)	0.3474 (8)	0.9641 (8)
O16	0.5537 (8)	0.3674 (8)	1.0810 (9)
C11	0.250 (1)	0.275 (1)	1.000 (1)
C12	0.213 (1)	0.235 (1)	0.888 (1)
C13	0.333 (1)	0.112 (1)	0.929 (1)
C14	0.402 (1)	0.060 (1)	0.880 (1)
C15	0.554 (2)	0.070 (1)	0.840 (2)
C16	0.646 (2)	0.127 (1)	0.859 (2)
C17	0.706 (1)	0.265 (1)	0.813 (1)
C18	0.765 (1)	0.301 (1)	0.929 (1)
C19	0.728 (1)	0.354 (1)	1.079 (1)
C20	0.650 (1)	0.408 (1)	1.110 (1)
C21	0.490 (1)	0.408 (1)	1.129 (1)
C22	0.397 (2)	0.350 (1)	1.115 (2)
C23	0.163 (2)	0.330 (1)	1.011 (2)
C24	0.117 (2)	0.399 (1)	0.923 (2)
C25	0.083 (1)	0.359 (1)	0.816 (1)
C26	0.169 (1)	0.302 (1)	0.800 (1)
C27	0.664 (1)	0.340 (1)	0.734 (1)
C28	0.747 (2)	0.402 (1)	0.732 (1)

TABLE 103 (Continued)

C29	0.811 (1)	0.437 (1)	0.845 (2)
C30	0.852 (1)	0.361 (1)	0.928 (2)

TABLE 104

HYDROGEN POSITIONAL PARAMETERS FOR $[K\text{-}(Dicyclohexano\text{-}18\text{-}Crown\text{-}6)]_2[Cu_2Br_4]$

ATOM	x	y	z
H131	0.3730	0.1286	1.0067
H132	0.2717	0.0781	0.9316
H141	0.4186	0.0012	0.9125
H142	0.3626	0.0518	0.8020
H151	0.5707	0.0088	0.8615
H152	0.5133	0.0703	0.7606
H161	0.6820	0.1340	0.9412
H162	0.6996	0.0965	0.8371
H191	0.7329	0.2943	1.1123
H192	0.7985	0.3800	1.1076
H201	0.6806	0.4221	1.1859
H202	0.6441	0.4653	1.0692
H211	0.5296	0.4252	1.2050
H212	0.4628	0.4657	1.0909
H221	0.4271	0.2914	1.1576
H222	0.3552	0.3738	1.1582
H231	0.1056	0.2919	1.0134
H232	0.1891	0.3620	1.0823
H241	0.0606	0.4294	0.9337
H242	0.1739	0.4420	0.9290
H251	0.0237	0.3217	0.8062
H252	0.0632	0.4069	0.7615
H261	0.1408	0.2722	0.7274
H262	0.2258	0.3423	0.7937
H271	0.6263	0.3149	0.6627
H272	0.6124	0.3745	0.7554
H281	0.7957	0.3684	0.7030
H282	0.7178	0.4501	0.6791

TABLE 104 (Continued)

H291	0.8684	0.4765	0.8431
H292	0.7638	0.4770	0.8691
H301	0.9067	0.3292	0.9119
H302	0.8871	0.3875	1.0026

TABLE 105

ANISOTROPIC THERMAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)]$_2$[Cu$_2$Br$_4$]

ATOM	U11	U22	U33	U12	U13	U23
Cu1	45 (2)	73 (2)	53 (2)	3 (2)	22 (1)	12 (2)
K1	34 (2)	26 (2)	38 (2)	-4 (2)	14 (2)	-8 (2)
Br1	46 (1)	55 (1)	44 (1)	-5 (1)	19 (1)	7 (1)
Br2	65 (1)	52 (1)	60 (1)	-12 (1)	35 (1)	-13 (1)
O11	30 (7)	73 (10)	4 (6)	23 (7)	-4 (5)	11 (6)
O12	32 (7)	28 (8)	56 (8)	9 (6)	24 (6)	2 (6)
O13	19 (7)	33 (8)	68 (9)	-17 (6)	4 (6)	-14 (7)
O14	44 (8)	27 (8)	49 (8)	6 (7)	17 (7)	7 (6)
O15	35 (8)	66 (9)	34 (7)	-22 (7)	15 (6)	-7 (6)
O16	7 (6)	58 (9)	46 (8)	-11 (6)	-4 (6)	-10 (6)
C11	0 (1)	3 (1)	4 (1)	-1 (1)	-1 (1)	0 (1)
C12	2 (1)	3 (1)	3 (1)	1 (1)	0 (1)	0 (1)
C13	4 (1)	4 (1)	7 (1)	2 (1)	4 (1)	2 (1)
C14	3 (1)	2 (1)	5 (1)	1 (1)	0 (1)	0 (1)
C15	5 (1)	2 (1)	10 (2)	1 (1)	4 (1)	1 (1)
C16	5 (1)	6 (2)	8 (2)	-2 (1)	4 (1)	-3 (1)
C17	4 (1)	3 (1)	4 (1)	1 (1)	2 (1)	0 (1)
C18	2 (1)	3 (1)	4 (1)	-2 (1)	2 (1)	0 (1)
C19	2 (1)	8 (2)	4 (1)	0 (1)	1 (1)	2 (1)
C20	4 (1)	5 (1)	3 (1)	2 (1)	1 (1)	-1 (1)
C21	1 (1)	9 (2)	3 (1)	1 (1)	1 (1)	-2 (1)
C22	6 (2)	7 (2)	6 (2)	3 (1)	3 (1)	3 (1)
C23	6 (1)	4 (1)	5 (1)	-2 (1)	3 (1)	0 (1)
C24	5 (1)	7 (2)	11 (2)	0 (1)	5 (1)	-1 (2)
C25	1 (1)	5 (1)	5 (1)	0 (1)	0 (1)	-1 (1)
C26	4 (1)	3 (1)	3 (1)	0 (1)	1 (1)	1 (1)
C27	3 (1)	6 (1)	2 (1)	-1 (1)	-2 (1)	-1 (1)
C28	6 (1)	5 (1)	5 (1)	1 (1)	1 (1)	1 (1)

TABLE 105 (Continued)

C29	4 (1)	6 (2)	10 (2)	-2 (1)	4 (1)	-1 (1)
C30	5 (1)	6 (1)	7 (1)	0 (1)	3 (1)	-2 (1)

The anisotropic displacement exponent takes the form:
$\exp(-2\pi (U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$
$\times 10^3$ for Cu, Br and K, and $\times 10^2$ for O and C.

TABLE 106

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[K\text{-(Dicyclohexano-18-Crown-6)}]_2[Cu_2Br_4]$

Cu1 - Br1	2.304 (4)	Br1 - Cu1 - Br2	122.4 (1)
Cu1 - Br2	2.440 (4)	Br1 - Cu1 - Br2'	128.9 (1)
Cu1 - Br2'	2.420 (4)	Br2 - Cu1 - Br2'	108.6 (1)
Cu1' - Br2	2.420 (4)	Br2 - Cu1' - Br2'	108.6 (1)
Cu1 ··· Cu1'	2.835 (4)	Cu1 - Br2 - Cu1'	71.4 (1)
K1 - O11	2.96 (1)	Cu1 - Br2' - Cu1'	71.3 (1)
K1 - O12	2.80 (1)	Br2 - Cu1' - Br1'	128.9 (1)
K1 - O13	2.82 (1)	Br1' - Cu1' - Br2'	122.4 (1)
K1 - O14	2.80 (1)	O11 - K1 - O12	57.2 (3)
K1 - O15	2.92 (1)	O12 - K1 - O13	59.7 (3)
K1 - O16	2.71 (1)	O13 - K1 - O14	60.7 (4)
C11 - O11	1.44 (2)	O14 - K1 - O15	58.6 (3)
C11 - C12	1.52 (2)	O15 - K1 - O16	60.5 (4)
C11 - C23	1.50 (3)	O11 - K1 - O13	102.1 (4)
C12 - O12	1.47 (2)	O11 - K1 - O15	119.8 (3)
C12 - C26	1.50 (2)	O12 - K1 - O14	114.5 (4)
O12 - C13	1.39 (2)	O12 - K1 - O16	109.4 (4)
C13 - C14	1.53 (3)	O13 - K1 - O15	100.5 (3)
C14 - O13	1.38 (2)	O14 - K1 - O16	113.9 (3)
O13 - C15	1.43 (3)	O12 - K1 - O15	155.1 (3)
C15 - C16	1.46 (3)	O11 - K1 - O14	159.7 (4)
C16 - O14	1.40 (2)	O13 - K1 - O16	109.7 (3)
O14 - C17	1.42 (2)	K1 - O11 - C11	121 (1)
C17 - C18	1.55 (2)	K1 - O11 - C22	111 (1)
C17 - C27	1.51 (2)	O11 - C11 - C12	107 (1)
C18 - O15	1.44 (2)	O11 - C11 - C23	109 (1)
C18 - C30	1.50 (3)	C11 - C12 - O12	110 (1)
O15 - C19	1.43 (3)	C11 - C12 - C26	113 (1)

TABLE 106 (Continued)

C19 - C20	1.51 (3)	K1 - O12 - C12	116 (1)
C20 - O16	1.37 (2)	K1 - O12 - C13	110 (1)
O16 - C21	1.40 (2)	C12 - O12 - C13	114 (1)
C21 - C22	1.50 (3)	O12 - C13 - C14	108 (2)
C22 - O11	1.38 (2)	C13 - C14 - O13	109 (1)
C23 - C24	1.52 (3)	C14 - O13 - C15	113 (1)
C24 - C25	1.46 (3)	K1 - O13 - C14	117 (1)
C25 - C26	1.53 (3)	K1 - O13 - C15	115 (1)
C27 - C28	1.48 (3)	O13 - C15 - C16	108 (2)
C28 - C29	1.53 (3)	C15 - C16 - O14	112 (1)
C29 - C30	1.55 (3)	C16 - O14 - C17	115 (1)
		K1 - O14 - C16	111 (1)
		K1 - O14 - C17	115 (1)
		O14 - C17 - C18	111 (2)
		O14 - C17 - C27	110 (1)
		C17 - C18 - O15	108 (1)
		C17 - C18 - C30	110 (2)
		C18 - O15 - C19	111 (1)
		K1 - O15 - C18	120 (1)
		K1 - O15 - C19	110 (1)
		O15 - C19 - C20	108 (1)
		C19 - C20 - O16	113 (1)
		C20 - O16 - C21	112 (1)
		K1 - O16 - C20	118 (1)
		K1 - O16 - C21	121 (1)
		O16 - C21 - C22	109 (2)
		C21 - C22 - O11	114 (2)
		C22 - O11 - C11	112 (1)
		C12 - C26 - C25	113 (2)

TABLE 106 (Continued)

C23 - C24 - C25	111 (2)
C24 - C25 - C26	112 (1)
C24 - C23 - C11	116 (2)
C17 - C27 - C28	112 (1)
C27 - C28 - C29	112 (2)
C28 - C29 - C30	112 (2)
C29 - C30 - C18	112 (1)
C12 - C11 - C23	108 (1)

Symmetry operation:

' = 1.0-x, 1.0-y, 1.0-z.

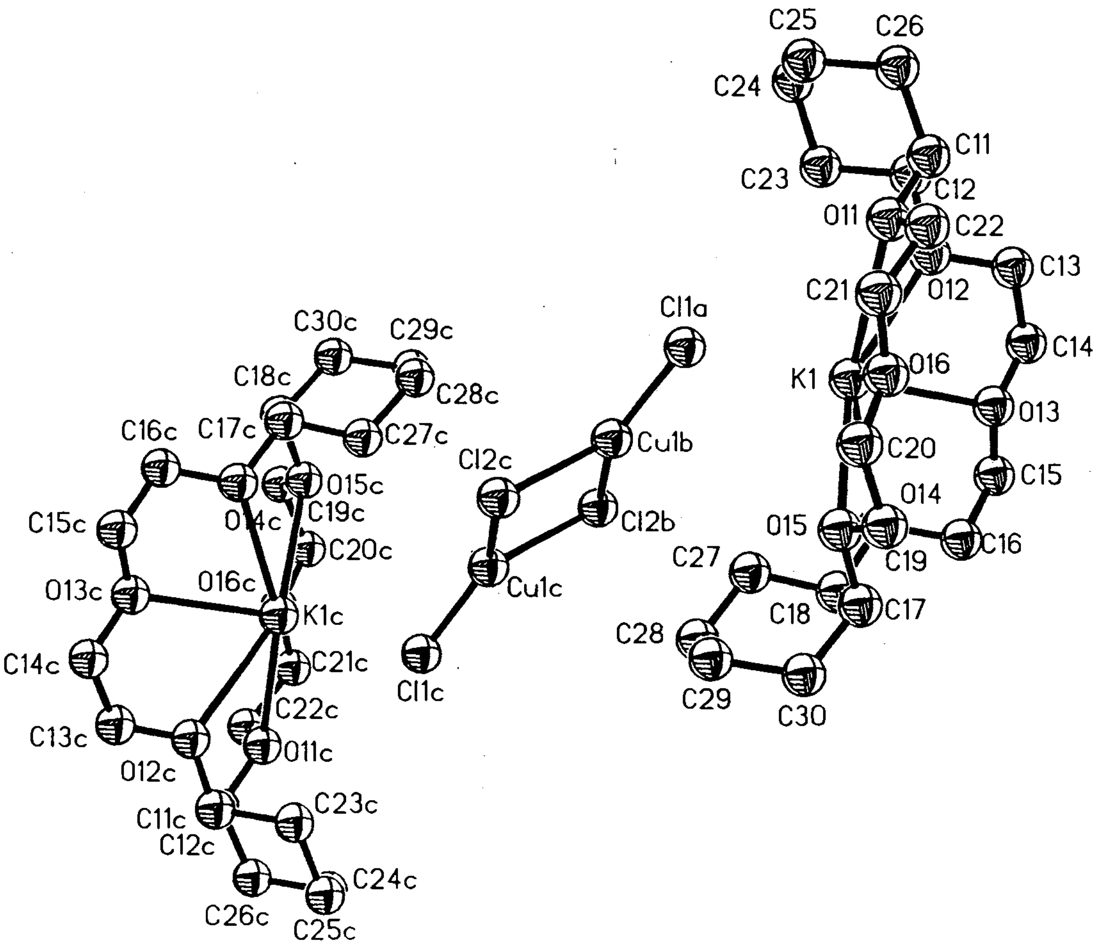

Figure 56. Projection View of $[K\text{-}(DC18\text{-}Crown\text{-}6)]_2[Cu_2Cl_4]$.

TABLE 107

CRYSTAL DATA FOR [K-(Dicyclohexano-18-Crown-6)]$_2$[Cu$_2$Cl$_4$]

Formula	$CuCl_2KC_{20}O_6H_{36}$
MWT	546.05
a	13.612(4) Å
b	14.918(4)
c	12.997(4)
α	90.0°
β	109.94(3)
γ	90.0
V	2481.1(14) Å^3
F (000)	1144
μMoK_α	12.97 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.462 g cm^{-3}
Z	4
Obs. Refl.	7065
Contribut. Refl.	1673
Variab.	272
R/R_w	5.8/6.6%
Space Group	$P2_1/n$
Octants Meas.	±h, +k, +l

TABLE 108

POSITIONAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)]$_2$[Cu_2Cl_4]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cu1	1.0654 (1)	0.4502 (2)	0.4386 (1)
K1	0.5341 (2)	0.2026 (1)	0.6226 (2)
Cl1	1.1466 (2)	0.4094 (2)	0.3344 (2)
Cl2	1.0329 (2)	0.3966 (2)	0.5858 (2)
O11	0.6677 (4)	0.1688 (4)	0.4893 (4)
O12	0.7068 (4)	0.3108 (3)	0.6346 (4)
O13	0.5123 (5)	0.3902 (4)	0.6047 (5)
O14	0.3841 (4)	0.2885 (4)	0.6897 (5)
O15	0.3127 (4)	0.1496 (4)	0.5351 (4)
O16	0.4502 (4)	0.1320 (4)	0.4152 (4)
C11	0.7554 (6)	0.2240 (6)	0.5001 (6)
C12	0.7916 (6)	0.2675 (6)	0.6152 (6)
C13	0.6739 (7)	0.3902 (6)	0.5737 (7)
C14	0.6044 (7)	0.4427 (6)	0.6202 (7)
C15	0.4476 (8)	0.4281 (6)	0.6583 (8)
C16	0.3526 (7)	0.3712 (7)	0.6359 (8)
C17	0.2950 (7)	0.2334 (6)	0.6866 (7)
C18	0.2377 (6)	0.2001 (6)	0.5700 (7)
C19	0.2759 (7)	0.1416 (6)	0.4205 (7)
C20	0.3536 (7)	0.0865 (7)	0.3861 (6)
C21	0.5189 (7)	0.0910 (7)	0.3668 (7)
C22	0.6089 (7)	0.1545 (7)	0.3781 (7)
C23	0.8319 (6)	0.1952 (6)	0.7046 (7)
C24	0.9205 (7)	0.1428 (6)	0.6862 (7)
C25	0.8855 (7)	0.0983 (7)	0.5767 (8)
C26	0.8468 (6)	0.1713 (6)	0.4888 (7)
C27	0.3408 (7)	0.1575 (7)	0.7658 (7)
C28	0.2549 (8)	0.0947 (7)	0.7697 (8)

TABLE 108 (Continued)

C29	0.1935 (8)	0.0568 (7)	0.6574 (8)
C30	0.1527 (7)	0.1341 (7)	0.5751 (8)

TABLE 109

HYDROGEN POSITIONAL PARAMETERS FOR K-(Dicyclohexano-18-Crown-6)]$_2$[Cu$_2$Cl$_4$]

ATOM	x	y	z
H131	0.7367	0.4266	0.5773
H132	0.6382	0.3761	0.4963
H141	0.6407	0.4516	0.6985
H142	0.5861	0.4995	0.5844
H151	0.4853	0.4316	0.7381
H152	0.4292	0.4908	0.6334
H161	0.2992	0.4004	0.6613
H162	0.3183	0.3626	0.5558
H191	0.2059	0.1154	0.3919
H192	0.2709	0.2015	0.3835
H201	0.3619	0.0272	0.4258
H202	0.3262	0.0714	0.3080
H211	0.5492	0.0343	0.4064
H212	0.4826	0.0743	0.2907
H221	0.6521	0.1364	0.3364
H222	0.5776	0.2151	0.3461
H231	0.8522	0.2494	0.7507
H232	0.7867	0.1596	0.7352
H241	0.9786	0.1845	0.6934
H242	0.9474	0.0981	0.7462
H251	0.9418	0.0638	0.5645
H252	0.8278	0.0555	0.5704
H261	0.8994	0.1973	0.4621
H262	0.7875	0.1521	0.4203
H271	0.3902	0.1235	0.7405
H272	0.3787	0.1815	0.8379
H281	0.2827	0.0443	0.8221
H282	0.2045	0.1265	0.7981

TABLE 109 (Continued)

H291	0.2415	0.0197	0.6325
H292	0.1362	0.0185	0.6590
H301	0.1172	0.1103	0.5013
H302	0.0998	0.1681	0.5959

TABLE 110

ANISOTROPIC THERMAL PARAMETERS FOR [K-(Dicyclohexano-18-Crown-6)]$_2$[Cu$_2$Cl$_4$]

ATOM	U11	U22	U33	U12	U13	U23
Cu1	78 (1)	268 (3)	92 (1)	-78 (1)	52 (1)	-101 (2)
K1	38 (1)	27 (1)	40 (1)	-4 (1)	13 (1)	-6 (1)
Cl1	59 (2)	64 (2)	45 (1)	-1 (1)	22 (1)	-8 (1)
Cl2	91 (2)	71 (2)	59 (2)	9 (2)	45 (2)	12 (2)
O11	29 (3)	46 (4)	34 (4)	-5 (3)	12 (3)	-2 (3)
O12	33 (3)	16 (4)	45 (3)	-1 (3)	12 (3)	-1 (3)
O13	43 (4)	26 (4)	66 (4)	-4 (3)	24 (3)	-11 (3)
O14	32 (3)	36 (4)	57 (4)	-6 (3)	18 (3)	-6 (3)
O15	30 (3)	49 (4)	30 (3)	-4 (3)	7 (2)	-8 (3)
O16	37 (4)	53 (4)	38 (3)	-13 (3)	12 (3)	-18 (3)
C11	37 (5)	32 (6)	30 (5)	-9 (4)	16 (4)	-11 (4)
C12	34 (5)	26 (5)	40 (5)	14 (4)	23 (4)	6 (4)
C13	49 (6)	22 (6)	47 (5)	8 (4)	20 (4)	5 (4)
C14	44 (6)	14 (5)	50 (6)	11 (4)	3 (4)	15 (4)
C15	62 (7)	28 (6)	60 (6)	-3 (5)	10 (6)	4 (5)
C16	40 (6)	35 (6)	67 (7)	9 (5)	10 (5)	-2 (5)
C17	40 (5)	36 (6)	42 (5)	-3 (5)	9 (4)	6 (5)
C18	29 (5)	40 (6)	48 (5)	-9 (5)	20 (4)	-4 (5)
C19	36 (5)	44 (6)	48 (6)	-1 (5)	12 (4)	13 (5)
C20	46 (6)	76 (8)	23 (4)	-19 (6)	6 (4)	-12 (5)
C21	38 (6)	75 (8)	34 (5)	12 (6)	-3 (4)	-16 (6)
C22	38 (5)	72 (8)	38 (6)	-7 (6)	18 (4)	-14 (5)
C23	45 (5)	37 (6)	43 (5)	1 (5)	26 (4)	0 (5)
C24	45 (6)	32 (6)	46 (6)	3 (5)	10 (5)	2 (5)
C25	45 (6)	45 (7)	60 (6)	-6 (5)	25 (5)	-9 (5)
C26	39 (5)	47 (6)	42 (5)	-7 (5)	17 (4)	-11 (5)
C27	48 (6)	46 (6)	39 (5)	-5 (5)	17 (4)	-10 (5)
C28	79 (7)	51 (7)	52 (6)	6 (6)	38 (6)	9 (6)

TABLE 110 (Continued)

C29	59 (7)	45 (7)	65 (7)	-18 (6)	32 (5)	-17 (6)
C30	32 (5)	58 (7)	55 (6)	-10 (5)	18 (5)	-17 (6)

The anisotropic displacement exponent takes the form:

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

x 10^3 for Cu, Cl, K, O and C.

TABLE 111

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR [K-(Dicyclohexano-18-Crown-6)]$_2$[Cu$_2$Cl$_4$]

Cu1 - Cl1	2.109 (4)	Cl1 - Cu1 - Cl2	138.0 (2)
Cu1 - Cl2	2.252 (4)	Cl1 - Cu1 - Cl2'	122.1 (1)
Cu1 - Cl2'	2.611 (4)	Cl2 - Cu1' - Cl2'	100.0 (1)
Cu1' - Cl2	2.612 (4)	Cl2' - Cu1 - Cl2	100.0 (1)
Cu1 ··· Cu1'	3.240 (3)	Cu1 - Cl2 - Cu1'	80.0 (1)
K1 - O11	2.952 (7)	Cu1 - Cl2' - Cu1'	80.0 (1)
K1 - O12	2.812 (6)	Cl1' - Cu1' - Cl2'	137.8 (2)
K1 - O13	2.815 (6)	Cl2 - Cu1' - Cl1'	122.2 (1)
K1 - O14	2.790 (7)	O11 - K1 - O12	57.3 (2)
K1 - O15	2.943 (6)	O12 - K1 - O13	59.8 (2)
K1 - O16	2.752 (6)	O13 - K1 - O14	60.1 (2)
C11 - O11	1.42 (1)	O14 - K1 - O15	58.8 (2)
C11 - C12	1.55 (1)	O15 - K1 - O16	59.4 (2)
C11 - C26	1.52 (1)	O11 - K1 - O13	101.0 (2)
C12 - O12	1.42 (1)	O11 - K1 - O15	118.2 (2)
C12 - C23	1.54 (1)	O12 - K1 - O14	114.0 (2)
O12 - C13	1.41 (1)	O12 - K1 - O16	109.5 (2)
C13 - C14	1.50 (1)	O13 - K1 - O15	99.8 (2)
C14 - O13	1.43 (1)	O14 - K1 - O16	112.2 (2)
O13 - C15	1.41 (1)	O12 - K1 - O15	154.4 (2)
C15 - C16	1.49 (1)	O11 - K1 - O14	157.7 (2)
C16 - O14	1.40 (1)	O13 - K1 - O16	107. 6 (2)
O14 - C17	1.45 (1)	K1 - O11 - C11	120.6 (5)
C17 - C18	1.53 (1)	K1 - O11 - C22	112.3 (5)
C17 - C27	1.51 (1)	O11 - C11 - C12	108.6 (7)
C18 - O15	1.46 (1)	O11 - C11 - C26	112.3 (7)
C18 - C30	1.54 (1)	C11 - C12 - O12	110.6 (6)
O15 - C19	1.40 (1)	C11 - C12 - C23	110.4 (7)

TABLE 111 (Continued)

C19 - C20	1.52 (1)	K1 - O12 - C12	116.4 (4)
C20 - O16	1.41 (1)	K1 - O12 - C13	110.6 (4)
O16 - C21	1.43 (1)	C12 - O12 - C13	113.9 (7)
C21 - C22	1.52 (1)	O12 - C13 - C14	109.5 (8)
C22 - O11	1.41 (1)	C13 - C14 - O13	107.4 (7)
C23 - C24	1.52 (1)	C14 - O13 - C15	112.0 (7)
C24 - C25	1.49 (1)	K1 - O13 - C14	118.0 (5)
C25 - C26	1.54 (1)	K1 - O13 - C15	115.0 (5)
C27 - C28	1.51 (2)	O13 - C15 - C16	108.8 (8)
C28 - C29	1.52 (1)	C15 - C16 - O14	107.7 (7)
C29 - C30	1.54 (1)	C16 - O14 - C17	111.8 (6)
C14 - O13	1.43 (1)	K1 - O14 - C16	112.2 (6)
		K1 - O14 - C17	115.1 (5)
		O14 - C17 - C18	110.4 (8)
		O14 - C17 - C27	105.0 (6)
		C17 - C18 - O15	107.6 (6)
		C17 - C18 - C30	107.5 (8)
		C18 - O15 - C19	109.8 (6)
		K1 - O15 - C18	118.2 (4)
		K1 - O15 - C19	112.4 (5)
		O15 - C19 - C20	108.9 (6)
		C19 - C20 - O16	109.8 (8)
		C20 - O16 - C21	111.4 (7)
		K1 - O16 - C20	119.0 (5)
		K1 - O16 - C21	118.6 (4)
		O16 - C21 - C22	108.5 (8)
		C21 - C22 - O11	110.6 (8)
		C22 - O11 - C11	111.7 (7)
		C12 - C23 - C24	109.7 (8)
		C23 - C24 - C25	111.4 (7)
		C24 - C25 - C26	108.1 (8)

TABLE 111 (Continued)

	C25 - C26 - C11	112.3 (8)
	C17 - C27 - C28	109.9 (7)
	C27 - C28 - C29	112.0 (9)
	C28 - C29 - C30	109.8 (8)
	C29 - C30 - C18	114.2 (7)

Symmetry operation:

' = 2.0-x, 1.0-y, 1.0-z.

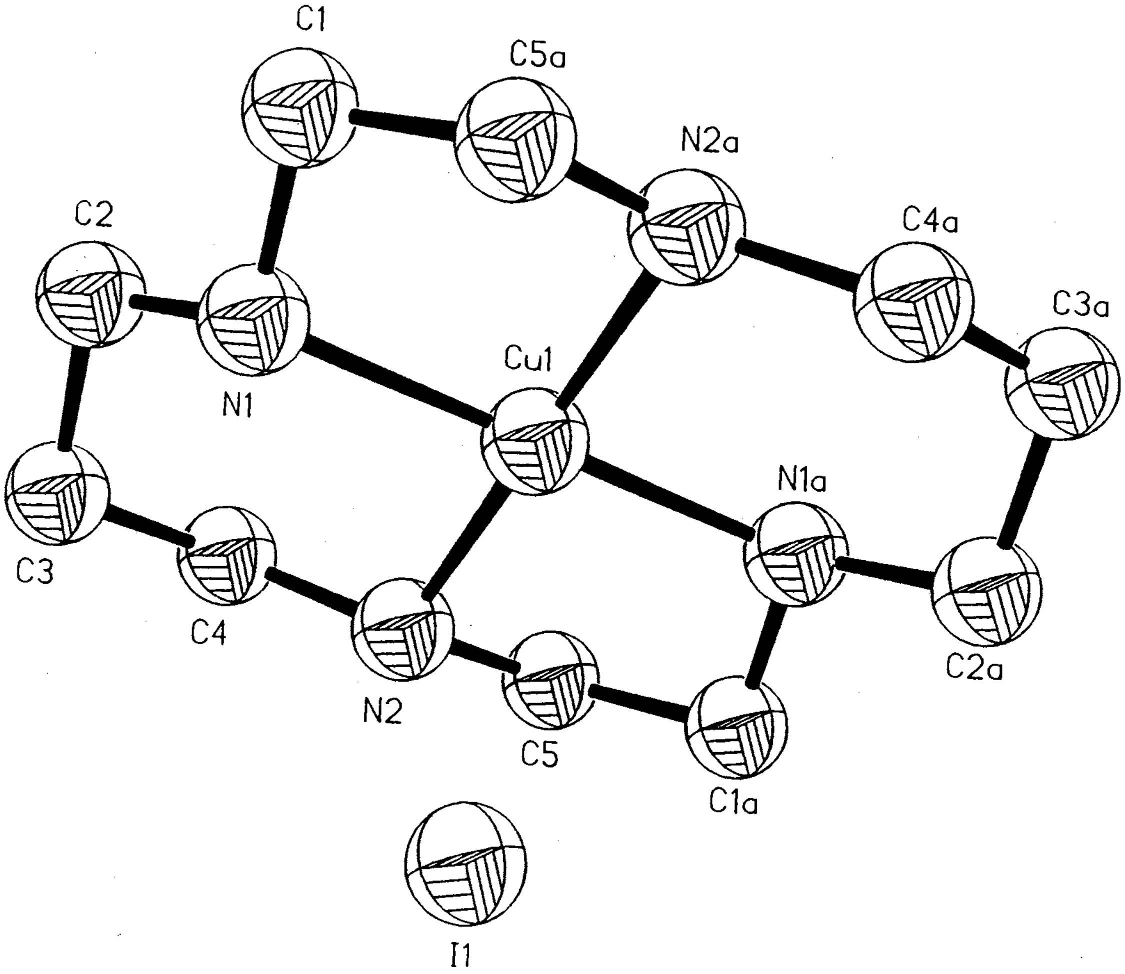

Figure 57. Projection View of [1,4,8,11-Tetraazacyclotetradecane][CuI].

TABLE 112

CRYSTAL DATA FOR [1,4,8,11-Tetraazacyclotetradecane][CuI]

Formula	$CuIN_4C_{10}H_{20}$
MWT	386.74
a	7.488(3) Å
b	12.972(7)
c	8.846(1)
α	90.0°
β	111.24(3)
γ	90.0
V	800.9(6) $Å^3$
F (000)	380
μMoK_α	32.60 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.604 g cm^{-3}
Z	2
Obs. Refl.	2316
Contribut. Refl.	1334
Variab.	79
R/R_w	5.9/7.5%
Space Group	$P2_1/c$
Octants Meas.	±h, +k, +l

TABLE 113

POSITIONAL PARAMETERS FOR [1,4,8,11-Tetraazacyclotetradecane][CuI]

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	1.2311 (1)	0.0230 (1)	0.7611 (1)
Cu1	1.0000	0.0000	1.0000
N1	1.260 (1)	-0.022 (1)	1.178 (1)
N2	0.965 (1)	-0.149 (1)	0.923 (1)
C1	1.300 (2)	0.068 (1)	1.283 (2)
C2	1.292 (2)	-0.120 (1)	1.270 (2)
C3	1.249 (2)	-0.214 (1)	1.155 (2)
C4	1.042 (2)	-0.230 (1)	1.051 (2)
C5	0.764 (2)	-0.162 (1)	0.823 (2)

TABLE 114

HYDROGEN POSITIONAL PARAMETERS FOR [1,4,8,11-Tetraazacyclotetradecane][CuI]

ATOM	x	y	z
H11	1.4428	0.0722	1.3450
H12	1.2395	0.0638	1.3613
H21	1.4269	-0.1212	1.3461
H22	1.2109	-0.1210	1.3346
H31	1.3198	-0.2059	1.0895
H32	1.2975	-0.2768	1.2184
H41	1.0217	-0.2976	1.0021
H42	0.9664	-0.2262	1.1238
H51	0.7455	-0.2238	0.7549
H52	0.6869	-0.1700	0.8909

TABLE 115

ANISOTROPIC THERMAL PARAMETERS FOR [1,4,8,11-Tetraazacyclotetradecane][CuI]

ATOM	U11	U22	U33	U12	U13	U23
I1	364 (4)	367 (4)	439 (4)	5 (3)	209 (3)	42 (3)
Cu1	346 (10)	187 (9)	341 (10)	-25 (6)	80 (8)	-6 (7)
N1	39 (5)	21 (4)	30 (4)	0 (4)	15 (4)	0 (4)
N2	36 (5)	28 (5)	34 (5)	-5 (4)	17 (4)	-3 (4)
C1	34 (6)	39 (7)	46 (7)	7 (5)	11 (6)	-12 (5)
C2	40 (7)	44 (7)	49 (8)	8 (6)	18 (6)	25 (6)
C3	47 (8)	36 (7)	63 (9)	2 (6)	20 (7)	8 (6)
C4	58 (8)	23 (6)	52 (8)	-2 (5)	25 (7)	-6 (6)
C5	36 (6)	28 (6)	50 (7)	-7 (4)	21 (6)	-17 (5)

The anisotropic displacement exponent takes the form:

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

x 10^4 for I and Cu, and x 10^3 for N and C.

TABLE 116

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR [1,4,8,11-Tetraazacyclotetradecane][CuI]

Cu1 - I1	3.193 (2)	N1 - Cu1 - N2	95.4 (3)
Cu1 - I1'	3.193 (2)	N1 - Cu1 - N2'	84.6 (3)
Cu1 - N1	2.033 (8)	N2 - Cu1 - N1'	84.6 (3)
Cu1 - N2	2.034 (10)	N1' - Cu1 - N2'	95.4 (3)
Cu1 - C1	2.83 (1)	Cu1 - N1 - C1	107.2 (6)
Cu1 - C2	3.02 (1)	Cu1 - N1 - C2	117.9 (7)
Cu1 - C5	2.83 (1)	Cu1 - N2 -C4	116.2 (7)
N1 - C1	1.46 (2)	Cu1 - N2 - C5	107.2 (7)
N1 - C2	1.48 (2)	N1 - C2 - C3	111 (1)
C1 - C5'	1.52 (2)	C2 - C3 - C4	116 (1)
C2 - C3	1.48 (2)	C3 - C4 - N2	113 (1)
C3 - C4	1.50 (2)	C4 - N2 - C5	114 (1)
C4 - N2	1.50 (2)	N1 - C1 - C5'	108 (1)
N2 - C5	1.46 (1)	C1 - N1 - C2	112 (1)
C5 - C1'	1.52 (2)	N2 - C5 - C1'	108 (1)

Symmetry operation:

' = 2.0-x, -y, 2.0-z.

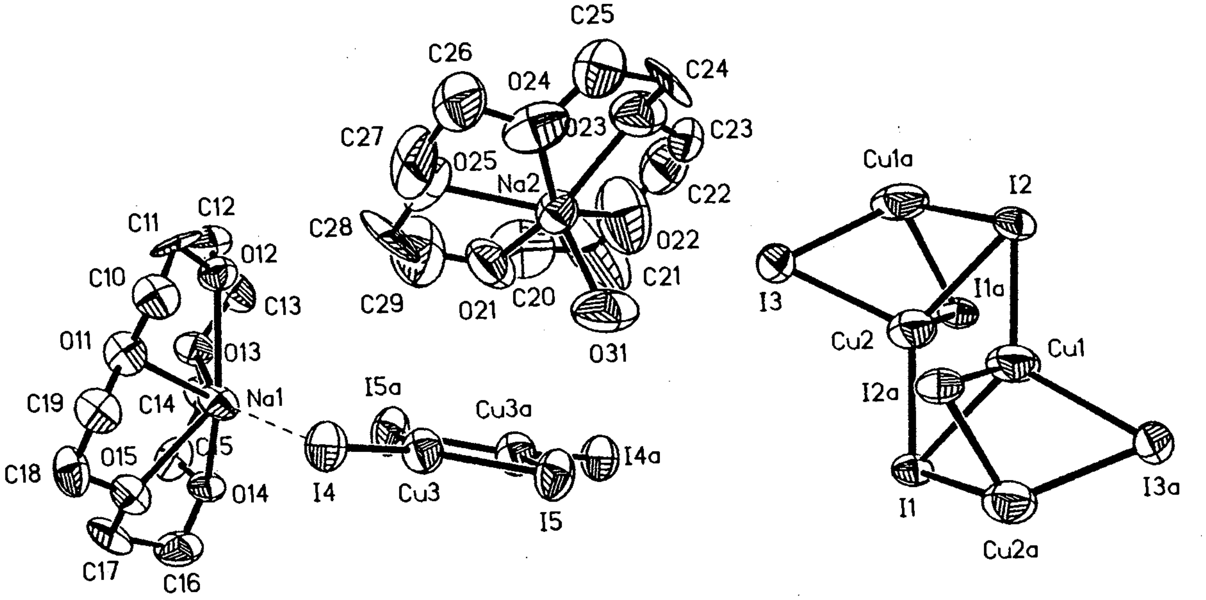

Figure 58. Projection View of $[Na\text{-}(15\text{-}Crown\text{-}5)]_2$
$[Na\text{-}(15\text{-}Crown\text{-}5)\text{-}H_2O]_2[Cu_2I_4][Cu_2I_3]_2$.

TABLE 117

CRYSTAL DATA FOR $[Na\text{-}(15\text{-}Crown\text{-}5)]_2$-$[Na\text{-}(15\text{-}Crown\text{-}5)\text{-}H_2O]_2\ [Cu_2I_4][Cu_2I_3]_2$

Formula	$Cu_6I_{10}Na_4C_{40}O_{22}H_{84}$
MWT	2659.36
a	14.046(3) Å
b	33.013(7)
c	8.425(2)
α	90.0°
β	96.11(3)
γ	90.0
V	3884.5(15) $Å^3$
F (000)	2496
μMoK_α	56.31 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	2.273 g cm^{-3}
Z	2
Independent Refl.	6778
Obs. Refl. ($F > 4.0\sigma(F)$)	1887
Variab.	370
R/R_w	6.9%
Space Group	$P2_1/c$
Octants Meas.	±h, +k, +l

TABLE 118

POSITIONAL PARAMETERS FOR $[Na\text{-}(15\text{-}Crown\text{-}5)]_2$-$[Na\text{-}(15\text{-}Crown\text{-}5)\text{-}H_2O]_2[Cu_2I_4][Cu_2I_3]_2$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	0.3005 (1)	0.7313 (1)	0.0456 (2)
I2	0.5668 (1)	0.7759 (1)	0.3699 (2)
I3	0.4424 (1)	0.6581 (1)	0.4338 (2)
I4	0.1389 (1)	0.4202 (1)	0.2899 (2)
I5	0.0553 (1)	0.5482 (1)	0.3552 (2)
Cu1	0.4753 (2)	0.7733 (1)	0.0948 (4)
Cu2	0.3996 (2)	0.7311 (1)	0.3167 (3)
Cu3	0.0496 (2)	0.4728 (1)	0.4241 (4)
Na1	0.0670 (5)	0.3534 (2)	0.5288 (10)
Na2	0.3481 (6)	0.5424 (3)	0.7462 (10)
O11	0.1873 (9)	0.3045 (5)	0.484 (2)
O12	0.1988 (9)	0.3497 (4)	0.744 (2)
O13	0.0158 (9)	0.3326 (5)	0.786 (2)
O14	-0.1054 (8)	0.3446 (4)	0.512 (2)
O15	0.009 (1)	0.3080 (5)	0.306 (2)
O21	0.207 (2)	0.5076 (7)	0.812 (2)
O22	0.255 (2)	0.5826 (8)	0.902 (3)
O23	0.450 (1)	0.5851 (7)	0.916 (2)
O24	0.515 (2)	0.5293 (8)	0.725 (2)
O25	0.376 (2)	0.4707 (6)	0.778 (3)
O31	0.300 (1)	0.5693 (7)	0.500 (2)
C10	0.274 (1)	0.3228 (7)	0.529 (3)
C11	0.278 (2)	0.3286 (7)	0.699 (2)
C12	0.177 (2)	0.3420 (8)	0.895 (3)
C13	0.073 (1)	0.3553 (7)	0.906 (2)
C14	-0.084 (1)	0.3385 (7)	0.788 (3)
C15	-0.135 (1)	0.3210 (7)	0.640 (3)
C16	-0.141 (3)	0.3313 (8)	0.360 (3)
C17	-0.082 (1)	0.2947 (7)	0.300 (3)

TABLE 118 (Continued)

C18	0.079 (1)	0.2783 (7)	0.268 (3)
C19	0.176 (1)	0.2942 (8)	0.309 (2)
C20	0.150 (3)	0.525 (2)	0.900 (7)
C21	0.169 (3)	0.564 (2)	0.944 (6)
C22	0.301 (3)	0.604 (1)	1.013 (4)
C23	0.403 (3)	0.619 (1)	0.957 (3)
C24	0.534 (2)	0.593 (1)	0.851 (4)
C25	0.580 (2)	0.551 (2)	0.811 (5)
C26	0.537 (2)	0.488 (1)	0.739 (4)
C27	0.463 (3)	0.464 (1)	0.685 (4)
C28	0.296 (3)	0.451 (1)	0.740 (6)
C29	0.216 (2)	0.466 (1)	0.815 (6)

TABLE 119

HYDROGEN POSITIONAL PARAMETERS FOR $[Na\text{-}(15\text{-}Crown\text{-}5)]_2$-$[Na\text{-}(15\text{-}Crown\text{-}5)\text{-}H_2O]_2[Cu_2I_4][Cu_2I_3]_2$

ATOM	x	y	z
H10A	0.2766	0.3474	0.4785
H10B	0.3234	0.3069	0.5027
H11A	0.2818	0.3027	0.7511
H11B	0.3361	0.3432	0.7340
H12A	0.2183	0.3568	0.9731
H12B	0.1841	0.3136	0.9174
H13A	0.0530	0.3511	1.0096
H13B	0.0669	0.3836	0.8801
H14A	-0.0994	0.3668	0.7936
H14B	-0.1061	0.3250	0.8781
H15A	-0.1143	0.2935	0.6310
H15B	-0.2033	0.3210	0.6408
H16A	-0.1333	0.3535	0.2889
H16B	-0.2079	0.3247	0.3537
H17A	-0.0847	0.2728	0.3744
H17B	-0.1056	0.2856	0.1953
H18A	0.0698	0.2709	0.1573
H18B	0.0726	0.2543	0.3305
H19A	0.2231	0.2749	0.2846
H19B	0.1833	0.3184	0.2490
H20A	0.1309	0.5078	0.9607
H20B	0.0936	0.5299	0.8049
H21A	0.1200	0.5795	0.8831
H21B	0.1611	0.5683	1.0547
H22A	0.3197	0.5882	1.1059
H22B	0.2647	0.6269	1.0442
H23A	0.3864	0.6337	0.8597
H23B	0.4399	0.6363	1.0315

TABLE 119 (Continued)

H24A	0.5762	0.6100	0.9188
H24B	0.5156	0.6069	0.7519
H25A	0.6368	0.5550	0.7576
H25B	0.5989	0.5390	0.9122
H26A	0.5540	0.4821	0.8500
H26B	0.5917	0.4822	0.6822
H27A	0.4486	0.4706	0.5744
H27B	0.4804	0.4360	0.6924
H28A	0.3087	0.4231	0.7722
H28B	0.2754	0.4508	0.6282
H29A	0.1574	0.4525	0.7769
H29B	0.2300	0.4595	0.9267

TABLE 120

ANISOTROPIC THERMAL PARAMETERS FOR $[Na\text{-}(15\text{-}Crown\text{-}5)]_2\text{-}[Na\text{-}(15\text{-}Crown\text{-}5)\text{-}H_2O]_2[Cu_2I_4][Cu_2I_3]_2$

ATOM	U11	U22	U33	U12	U13	U23
I1	36 (1)	66 (1)	47 (1)	4 (1)	4 (1)	-3 (1)
I2	40 (1)	70 (1)	51 (1)	1 (1)	2 (1)	-9 (1)
I3	58 (1)	55 (1)	73 (1)	-2 (1)	-1 (1)	2 (1)
I4	85 (1)	71 (1)	86 (1)	-1 (1)	21 (1)	2 (1)
I5	77 (1)	66 (1)	112 (2)	15 (1)	24 (1)	-5 (1)
Cu1	105 (3)	109 (3)	64 (3)	19 (2)	-26 (2)	-30 (2)
Cu2	86 (3)	89 (2)	63 (2)	8 (2)	-11 (2)	-6 (2)
Cu3	71 (2)	71 (2)	92 (3)	-4 (2)	11 (2)	4 (2)
Na1	40 (4)	78 (6)	70 (6)	-20 (5)	8 (4)	-9 (4)
Na2	76 (5)	70 (6)	71 (6)	-3 (5)	15 (5)	7 (5)
O11	6 (1)	8 (1)	7 (1)	0 (1)	2 (1)	0 (1)
O12	6 (1)	6 (1)	6 (1)	1 (1)	0 (1)	0 (1)
O13	5 (1)	8 (1)	7 (1)	-1 (1)	1 (1)	0 (1)
O14	4 (1)	6 (1)	8 (1)	-1 (1)	-1 (1)	0 (1)
O15	8 (1)	8 (1)	6 (1)	-2 (1)	0 (1)	-1 (1)
O21	12 (2)	10 (2)	10 (2)	-2 (1)	0 (1)	-4 (1)
O22	19 (3)	15 (2)	13 (2)	-5 (2)	5 (2)	-2 (2)
O23	8 (1)	12 (2)	13 (2)	2 (1)	2 (1)	0 (1)
O24	9 (1)	16 (2)	11 (2)	4 (2)	4 (1)	7 (2)
O25	11 (1)	9 (1)	14 (2)	2 (1)	0 (1)	2 (1)
O31	7 (1)	16 (2)	11 (1)	4 (1)	-2 (1)	-1 (1)
C10	4 (1)	8 (2)	10 (2)	0 (2)	2 (1)	-1 (1)
C11	7 (1)	10 (2)	5 (1)	5 (1)	-1 (1)	3 (1)
C12	8 (2)	8 (2)	7 (2)	0 (1)	-2 (1)	1 (1)
C13	7 (1)	9 (2)	5 (1)	-3 (1)	2 (1)	-1 (1)
C14	4 (1)	9 (2)	8 (2)	0 (2)	2 (1)	0 (1)
C15	5 (1)	7 (2)	9 (2)	0 (1)	2 (1)	0 (1)
C16	4 (1)	11 (2)	10 (2)	2 (2)	-1 (1)	-1 (1)
C17	5 (1)	9 (2)	6 (2)	-1 (1)	0 (1)	-5 (1)

TABLE 120 (Continued)

C18	6 (1)	6 (2)	11 (2)	-1 (1)	2 (1)	0 (1)
C19	6 (1)	9 (2)	6 (2)	-1 (1)	2 (1)	-1 (1)
C20	13 (3)	22 (6)	34 (7)	-5 (5)	15 (4)	-6 (4)
C21	11 (3)	29 (8)	27 (6)	-9 (6)	6 (3)	-11 (4)
C22	15 (3)	12 (3)	12 (3)	0 (2)	3 (3)	6 (3)
C23	26 (4)	5 (2)	8 (2)	-1 (2)	-8 (3)	4 (2)
C24	8 (2)	14 (3)	15 (3)	5 (3)	-2 (2)	-5 (2)
C25	6 (2)	36 (8)	14 (4)	0 (4)	0 (2)	-2 (4)
C26	13 (3)	15 (3)	12 (3)	2 (2)	5 (2)	4 (3)
C27	19 (4)	8 (2)	16 (4)	-4 (2)	6 (3)	6 (2)
C28	22 (4)	10 (3)	26 (6)	-2 (4)	-14 (4)	-4 (4)
C29	9 (2)	15 (4)	26 (5)	1 (3)	-1 (3)	-6 (2)

The anisotropic displacement exponent takes the form:

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

$\times 10^3$ for I, Cu and Na, and $\times 10^2$ for O and C.

TABLE 121

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[Na\text{-}(15\text{-}Crown\text{-}5)]_2\text{-}[Na\text{-}(15\text{-}Crown\text{-}5)\text{-}H_2O]_2[Cu_2I_4][Cu_2I_3]_2$

I1 - Cu2	2.545 (3)	Cu2 - I1 - Cu2'	110.9 (1)
I1 - Cu2'	2.787 (3)	Cu2 - I1 - Cu1	58.9 (1)
I1 - Cu1	2.811 (3)	Cu2 - I1 - Cu1'	52.4 (1)
I2 - Cu1	2.530 (3)	Cu1 - I2 - Cu2	59.6 (1)
I2 - Cu2	2.771 (3)	Cu1 - I2 - Cu1"	111.3 (1)
I2 - Cu1"	2.897 (4)	Cu2 - I2 - Cu1"	51.7 (1)
I3 - Cu2	2.649 (4)	Cu2 - I3 - Cu1"	55.6 (1)
I3 - Cu1"	2.655 (4)	Cu3 - I4 - Na1	89.3 (2)
I4 - Cu3	2.484 (3)	Cu3 - I5 - Cu3'''	62.7 (1)
I4 ··· Na1	3.220 (8)	Cu2 - Cu1 - I2	174.8 (2)
I5 - Cu3	2.557 (4)	Cu2 - Cu1 - Cu2'	118.3 (2)
I5 - Cu3'''	2.587 (3)	I2 - Cu1 - Cu2	64.7 (1)
Cu1 ··· Cu2'	2.472 (4)	Cu2 - Cu1' - I3'	62.1 (1)
Cu1 ··· Cu2	2.643 (4)	I2 - Cu1 - I3'	118.9 (1)
Cu3 ··· Cu3'''	2.678 (6)	Cu2 - Cu1 - I3'	138.5 (2)
Na1 - O11	2.40 (2)	Cu2 - Cu1 - I1'	63.3 (1)
Na1 - O14	2.43 (1)	I2 - Cu1 - I1	120.2 (1)
Na1 - O12	2.45 (2)	Cu2 - Cu1 - I1	55.5 (1)
Na1 - O13	2.45 (2)	I3 - Cu1 - I1'	104.0 (1)
Na1 - O15	2.48 (2)	Cu2 - Cu1 - I2'	61.5 (1)
O11 - C10	1.37 (2)	I2 - Cu1 - I2'	113.6 (1)
O11 - C19	1.50 (2)	Cu2 - Cu1 - I2'	114.1 (2)
O12 - C12	1.36 (2)	I3 - Cu1' - I2'	102.1 (1)
O12 - C11	1.41 (2)	I1 - Cu1 - I2'	94.0 (1)
O13 - C13	1.44 (2)	Cu1 - Cu2 - I1"	171.8 (2)
O13 - C14	1.42 (2)	Cu1 - Cu2 - Cu1"	122.4 (2)
O14 - C16	1.40 (3)	I1 - Cu2 - Cu1	65.6 (1)
O14 - C15	1.43 (2)	Cu1 - Cu2 - I3"	62.3 (1)

TABLE 121 (Continued)

O15 - C17	1.34 (2)	I1 - Cu2 - I3	114.7 (1)
O15 - C18	1.45 (2)	Cu1 - Cu2 - I3	130.5 (2)
C10 - C11	1.44 (3)	Cu1 - Cu2 - I2"	66.8 (1)
C12 - C13	1.54 (3)	I1 - Cu2 - I2	121.2 (1)
C14 - C15	1.48 (3)	Cu1 - Cu2 - I2	55.7 (1)
C16 - C17	1.58 (3)	I3 - Cu2 - I2	105.7 (1)
C18 - C19	1.46 (3)	Cu1 - Cu2" - I1"	64.30 (1)
Na2 - O31	2.29 (2)	I1 - Cu2 - I1"	110.7 (1)
Na2 - O22	2.36 (3)	Cu1 - Cu2 - I1"	121.6 (2)
Na2 - O23	2.37 (2)	I3 - Cu2 - I1"	104.9 (1)
Na2 - O24	2.41 (2)	I2 - Cu2 - I1"	97.4 (1)
Na2 - O25	2.41 (2)	I4 - Cu3 - I5	123.2 (1)
Na2 - O21	2.40 (2)	I4 - Cu3 - I5'''	119.6 (1)
O21 - C20	1.29 (4)	I5 - Cu3 - I5'''	117.3 (1)
O21 - C29	1.39 (4)	I4 - Cu3 - Cu3'''	177.7 (2)
O22 - C22	1.29 (4)	I5 - Cu3 - Cu3'''	59.2 (1)
O22 - C21	1.43 (4)	I5 - Cu3' - Cu3'''	58.1 (1)
O23 - C23	1.35 (3)	O11 - Na1 - O14	128.8 (6)
O23 - C24	1.38 (3)	O11 - Na1 - O12	66.1 (5)
O24 - C25	1.32 (4)	O14 - Na1 - O12	134.8 (6)
O24 - C26	1.41 (4)	O11 - Na1 - O13	103.2 (6)
O25 - C28	1.31 (4)	O14 - Na1 - O13	68.4 (5)
O25 - C27	1.54 (3)	O12 - Na1 - O13	66.5 (5)
C20 - C21	1.37 (6)	O11 - Na1 - O15	69.7 (5)
C22 - C23	1.63 (4)	O14 - Na1 - O15	68.8 (5)
C24 - C25	1.58 (5)	O12 - Na1 - O15	133.9 (6)
C26 - C27	1.34 (4)	O13 - Na1 - O15	113.4 (6)
C28 - C29	1.43 (5)	O11 - Na1 - I4	95.1 (4)
		O14 - Na1 - I4	115.1 (5)

TABLE 121 (Continued)

O12 - Na1 - I4	103.6 (4)
O13 - Na1 - I4	152.3 (5)
O15 - Na1 - I4	92.3 (4)
C10 - O11 - C19	112 (2)
C10 - O11 - Na1	106 (1)
C19 - O11 - Na1	108 (1)
C12 - O12 - C11	115 (2)
C12 - O12 - Na1	118 (1)
C11 - O12 - Na1	113 (1)
C13 - O13 - C14	114 (2)
C13 - O13 - Na1	106 (1)
C14 - O13 - Na1	111 (1)
C16 - O14 - C15	115 (2)
C16 - O14 - Na1	110 (1)
C15 - O14 - Na1	113 (1)
C17 - O15 - C18	116 (2)
C17 - O15 - Na1	117 (1)
C18 - O15 - Na1	113 (1)
O11 - C10 - C11	106 (2)
O11 - C10 - Na1	49 (1)
C11 - C10 - Na1	84 (1)
O12 - C11 - C10	112 (2)
O12 - C12 - C13	108 (2)
O13 - C13 - C12	106 (2)
O13 - C14 - C15	109 (2)
O14 - C15 - C14	106 (2)
O14 - C16 - C17	113 (2)
O15 - C17 - C16	106 (2)
O15 - C18 - C19	110 (2)

TABLE 121 (Continued)

	C18 - C19 - O11	108 (2)
	O31 - Na2 - O22	99.0 (9)
	O31 - Na2 - O23	114.6 (8)
	O22 - Na2 - O23	70.2 (9)
	O31 - Na2 - O24	101.4 (7)
	O22 - Na2 - O24	138 (1)
	O23 - Na2 - O24	68.0 (9)
	O31 - Na2 - O25	120.7 (8)
	O22 - Na2 - O25	125.9 (9)
	O23 - Na2 - O25	115.9 (8)
	O24 - Na2 - O25	71.6 (8)
	O31 - Na2 - O21	102.9 (7)
	O22 - Na2 - O21	67.8 (9)
	O23 - Na2 - O21	126.9 (8)
	O24 - Na2 - O21	139.8 (10)
	O25 - Na2 - O21	68.6 (8)
	C20 - O21 - C29	120 (3)
	C20 - O21 - Na2	120 (3)
	C29 - O21 - Na2	114 (2)
	C22 - O22 - C21	115 (3)
	C22 - O22 - Na2	116 (2)
	C21 - O22 - Na2	116 (3)
	C23 - O23 - C24	113 (3)
	C23 - O23 - Na2	112 (2)
	C24 - O23 - Na2	111 (2)
	C25 - O24 - C26	111 (3)
	C25 - O24 - Na2	119 (2)
	C26 - O24 - Na2	112 (2)
	C28 - O25 - C27	121 (3)
	C28 - O25 - Na2	110 (2)

TABLE 121 (Continued)

C27 - O25 - Na2	102 (2)
O21 - C20 - C21	118 (4)
C20 - C21 - O22	119 (4)
O22 - C22 - C23	110 (3)
O23 - C23 - C22	107 (2)
O23 - C24 - C25	108 (3)
O24 - C25 - C24	109 (3)
C27 - C26 - O24	112 (3)
C26 - C27 - O25	112 (3)
C26 - C27 - Na2	82 (2)
O25 - C27 - Na2	49 (1)
O25 - C28 - C29	114 (4)
O21 - C29 - C28	114 (3)

Symmetry operations:

' = x, 1.5-y, -0.5+z.
" = x, 1.5-y, 0.5+z.
''' = -x, 1.0-y, 1.0-z.

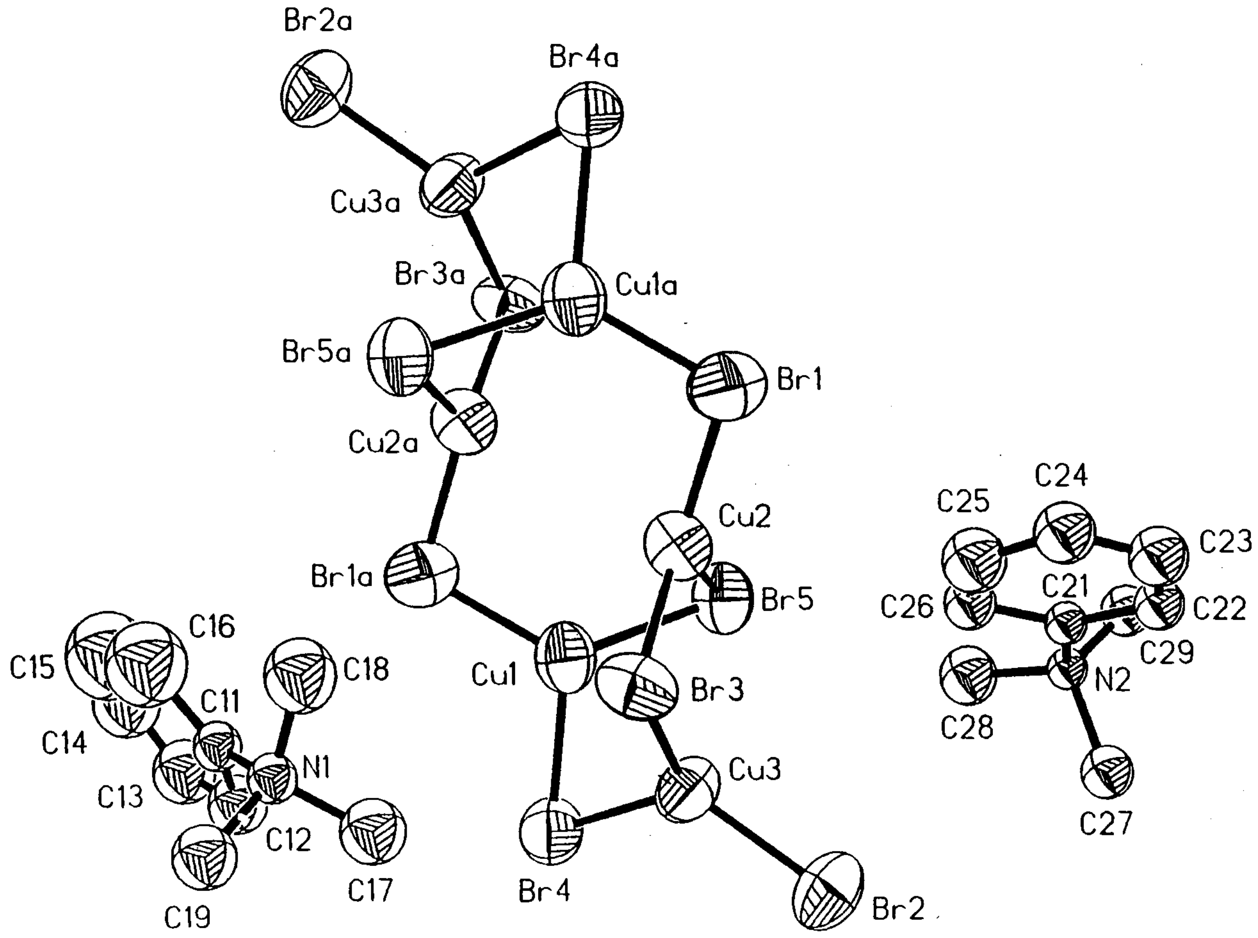

Figure 59. Projection View of $[PhMe_3N][Cu_6Br_{10}]$.

TABLE 122

CRYSTAL DATA FOR $[PhMe_3N]_4[Cu_6Br_{10}]$

Formula	$Cu_3Br_5C_{18}H_{28}N_2$
MWT	862.6
a	9.477(2) Å
b	21.712(4)
c	12.683(3)
a	90.00°
b	94.43(3)
g	90.00
V	2601.9(13) Å^3
F (000)	1648
μMoK_α	101.16 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	2.202 g cm^{-3}
Z	4
Independent Refl.	2086
Obs. Refl. $(F > 4.0\sigma(F))$	1019
Variab.	172
R/R_w	5.8%
Space Group	$P2_1/n$
Octants Meas.	+h, +k, ±l

TABLE 123

POSITIONAL PARAMETERS FOR $[PhMe_3N]_4[Cu_6Br_{10}]$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cu1	0.3462 (3)	0.0561 (2)	0.3444 (2)
Cu1	0.3462 (3)	0.0561 (2)	0.3444 (2)
Cu2	0.4096 (3)	0.0598 (2)	0.5560 (2)
Cu3	0.2784 (3)	0.1684 (2)	0.4082 (2)
Br1	0.4779 (3)	0.0068 (2)	0.7065 (2)
Br2	0.1242 (3)	0.2434 (14)	0.4536 (2)
Br3	0.5071 (3)	0.1545 (1)	0.5079 (2)
Br4	0.2753 (3)	0.1350 (1)	0.2213 (2)
Br5	0.1779 (3)	0.0396 (1)	0.4738 (2)
N1	0.798 (2)	0.1430 (7)	0.221 (1)
C11	0.780 (2)	0.092 (1)	0.143 (1)
C12	0.664 (2)	0.097 (1)	0.068 (2)
C13	0.653 (3)	0.045 (1)	-0.010 (2)
C14	0.736 (3)	0.001 (1)	-0.010 (2)
C15	0.835 (4)	0.002 (2)	0.055 (2)
C16	0.873 (3)	0.043 (1)	0.138 (2)
C17	0.667 (2)	0.175 (1)	0.243 (2)
C18	0.852 (2)	0.116 (1)	0.324 (1)
C19	0.895 (2)	0.192 (1)	0.185 (2)
N2	-0.114 (1)	0.150 (1)	0.712 (1)
C21	0.022 (2)	0.157 (1)	0.780 (2)
C22	0.014 (2)	0.180 (1)	0.879 (1)
C23	0.144 (1)	0.185 (1)	0.941 (2)
C24	0.273 (2)	0.171 (1)	0.906 (2)
C25	0.269 (2)	0.151 (1)	0.806 (2)
C26	0.150 (2)	0.141 (1)	0.738 (2)
C27	-0.168 (3)	0.212 (1)	0.689 (3)
C28	-0.092 (4)	0.120 (2)	0.609 (2)

TABLE 123 (Continued)

C29	-0.217 (3)	0.114 (2)	0.765 (2)
C27'	-0.130 (6)	0.088 (1)	0.669 (4)
C28'	-0.243 (3)	0.163 (2)	0.770 (3)
C29'	-0.120 (5)	0.194 (2)	0.622 (3)

TABLE 124

HYDROGEN POSITIONAL PARAMETERS FOR $[PhMe_3N]_4[Cu_6Br_{10}]$

ATOM	x	y	z
H11A	-0.7217	0.2121	0.2174
H11B	-0.6607	0.1414	0.1240
H12	0.6017	0.1296	0.0669
H13	0.5773	0.0467	-0.0611
H14	0.7209	-0.0312	-0.0578
H15	0.8997	-0.0305	0.0508
H16	0.9520	0.0392	0.1862
H17A	0.6754	0.1906	0.3142
H17B	0.5894	0.1470	0.2344
H17C	0.6517	0.2090	0.1946
H18A	0.8395	0.1459	0.3787
H18B	0.9508	0.1070	0.3220
H18C	0.8009	0.0795	0.3375
H19A	0.9093	0.2230	0.2381
H19B	0.8541	0.2101	0.1205
H19C	0.9846	0.1736	0.1719
H22	-0.0714	0.1917	0.9046
H23	0.1429	0.1985	1.0110
H24	0.3578	0.1756	0.9481
H25	0.3559	0.1428	0.7796
H26	0.1551	0.1258	0.6697
H27A	-0.1767	0.2336	0.7539
H27B	-0.2594	0.2090	0.6506
H27C	-0.1042	0.2334	0.6470
H28A	-0.1368	0.1435	0.5522
H28B	-0.1321	0.0790	0.6078
H28C	0.0078	0.1167	0.6003
H29A	-0.2411	0.1351	0.8275

TABLE 124 (Continued)

H29B	-0.1768	0.0743	0.7846
H29C	-0.3003	0.1080	0.7183
H27D	-0.0554	0.0790	0.6245
H27E	-0.2199	0.0843	0.6283
H27F	-0.1270	0.0583	0.7260
H28D	-0.2263	0.1507	0.8424
H28E	-0.3221	0.1400	0.7377
H28F	-0.2642	0.2061	0.7661
H29D	-0.0331	0.1932	0.5888
H29E	-0.1352	0.2352	0.6486
H29F	-0.1972	0.1836	0.5719

TABLE 125

ANISOTROPIC THERMAL PARAMETERS FOR $[PhMe_3N]_4[Cu_6Br_{10}]$

ATOM	U11	U22	U33	U12	U13	U23
Cu1	89 (2)	89 (2)	73 (2)	-14 (2)	11 (2)	-2 (2)
Cu2	73 (2)	91 (3)	75 (2)	-1 (2)	1 (2)	-10 (2)
Cu3	79 (2)	80 (2)	82 (2)	-7 (2)	1 (2)	19 (2)
Br1	105 (2)	101 (3)	112 (2)	15 (2)	7 (2)	14 (2)
Br2	95 (2)	91 (2)	106 (2)	-30 (2)	-4 (2)	12 (2)
Br3	70 (2)	93 (2)	80 (2)	20 (2)	-191 (14)	-19 (2)
Br4	79 (2)	115 (3)	72 (2)	5 (2)	-14 (15)	21 (2)
Br5	59 (2)	90 (2)	89 (2)	-9 (2)	104 (14)	17 (2)
N1	42 (4)					
C11	42 (5)					
C12	67 (7)					
C13	81 (8)					
C14	96 (9)					
C15	140 (12)					
C16	122 (10)					
C17	75 (7)					
C18	86 (8)					
C19	67 (7)					
N2	32 (4)					
C21	32 (5)					
C22	44 (5)					
C23	59 (6)					
C24	60 (6)					
C25	70 (7)					
C26	48 (6)					
C27	54 (12)					
C28	67 (14)					
C29	51 (12)					

TABLE 125 (Continued)

C27'	96 (26)
C28'	45 (17)
C29'	59 (19)

The anisotropic displacement exponent takes the form:
$\exp(-2\pi (U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^{*}b^{*}+2U_{13}hla^{*}c^{*}+2U_{23}klb^{*}c^{*}))$
x 10^3 for Cu, Br, N and C (N and C are isotropic).

TABLE 126

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[PhMe_3N]_4[Cu_6Br_{10}]$

Cu1- Br1	2.287 (4)	Br1 - Cu1 - Br4	114.8 (2)
Cu1 - Br4	2.380 (4)	Br1 - Cu1 - Br5	129.9 (2)
Cu1 - Br5	2.402 (4)	Br4 - Cu1 - Br5	112.8 (2)
Cu1 ··· Cu3	2.664 (4)	Br1 - Cu1 - Cu3	146.2 (2)
Cu1 ··· Cu2	2.706 (4)	Br4 - Cu1 - Cu3	58.5 (1)
Cu2 - Br1	2.279 (4)	Br5 - Cu1 - Cu3	75.0 (1)
Cu2 - Br3	2.354 (4)	Br1 - Cu1 - Cu2	100.8 (2)
Cu2 - Br5	2.397 (4)	Br4 - Cu1 - Cu2	131.2 (2)
Cu3 - Br2	2.290 (4)	Br5 - Cu1 - Cu2	55.6 (1)
Cu3 - Br3	2.442 (4)	Cu3 - Cu1 - Cu2	73.2 (1)
Cu3 - Br4	2.477 (4)	Br1 - Cu2 - Br3	124.5 (2)
Br1 - Cu1	2.287 (4)	Br1 - Cu2 - Br5	117.6 (2)
N1 - C17	1.47 (2)	Br3 - Cu2 - Br5	114.3 (2)
N1 - C11	1.48 (2)	Br1 - Cu2 - Cu1	147.4 (2)
N1 - C18	1.48 (2)	Br3 - Cu2 - Cu1	80.3 (1)
N1 - C19	1.50 (2)	Br5 - Cu2 - Cu1	55.8 (1)
C11 - C16	1.39 (3)	Br2 - Cu3 - Br3	121.0 (2)
C11 - C12	1.40 (2)	Br2 - Cu3 - Br4	119.2 (2)
C12 - C13	1.49 (3)	Br3 - Cu3 - Br4	113.8 (1)
C13 - C14	1.24 (3)	Br2 - Cu3 - Cu1	154.2 (2)
C14 - C15	1.20 (3)	Br3 - Cu3 - Cu1	79.6 (1)
C15 - C16	1.40 (3)	Br4 - Cu3 - Cu1	55.0 (1)
N2 - C29	1.46 (2)	Cu2 - Br1 - Cu1	103.4 (2)
N2 - C27'	1.46 (2)	Cu2 - Br3 - Cu3	83.8 (1)
N2 - C27	1.46 (2)	Cu1 - Br4 - Cu3	66.5 (1)
N2 - C29'	1.49 (2)	Cu2 - Br5 - Cu1	68.6 (1)
N2 - C28	1.49 (2)	C17 - N1 - C11	115 (2)
N2 - C21	1.50 (2)	C17 - N1 - C18	105 (2)
N2 - C28'	1.50 (2)	C11 - N1 - C18	108 (2)
C21 - C22	1.36 (2)	C17 - N1 - C19	106 (2)

TABLE 126 (Continued)

C21 - C26	1.40 (2)	C11 - N1 - C19	112 (1)
C22 - C23	1.42 (2)	C18 - N1 - C19	112 (2)
C23 - C24	1.36 (2)	C16 - C11 - C12	119 (2)
C24 - C25	1.35 (2)	C16 - C11 - N1	124 (2)
C25 - C26	1.39 (2)	C12 - C11 - N1	116 (2)
		C11 - C12 - C13	114 (2)
		C14 - C13 - C12	125 (3)
		C15 - C14 - C13	117 (3)
		C14 - C15 - C16	131 (4)
		C11 - C16 - C15	114 (3)
		C29 - N2 - C27	110 (2)
		C27' - N2 - C29'	109 (2)
		C29 - N2 - C28	108 (2)
		C27 - N2 - C28	108 (1)
		C29 - N2 - C21	111 (2)
		C27' - N2 - C21	112 (2)
		C27 - N2 - C21	107 (2)
		C29' - N2 - C21	111 (2)
		C28 - N2 - C21	112 (2)
		C27' - N2 - C28'	107 (2)
		C29' - N2 - C28'	105 (2)
		C21 - N2 - C28'	113 (2)
		C22 - C21 - C26	123 (2)
		C22 - C21 - N2	118 (2)
		C26 - C21 - N2	119 (2)
		C21 - C22 - C23	116 (2)
		C24 - C23 - C22	124 (2)
		C25 - C24 - C23	115 (2)
		C24 - C25 - C26	127 (2)
		C25 - C26 - C21	114 (2)

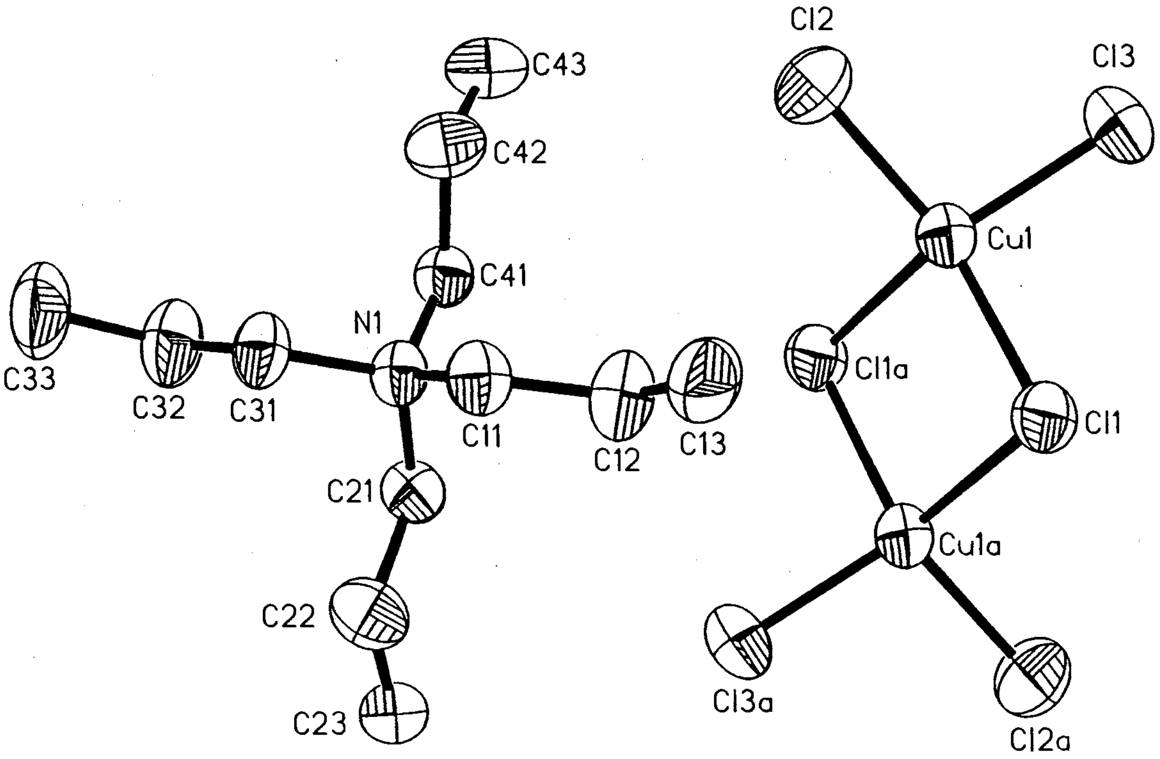

Figure 60. Projection View of $[(n\text{-Propyl})_4N]_2[Cu(II)_2Cl_6]$.

TABLE 127
CRYSTAL DATA FOR $[(n\text{-Propyl})_4N]_2[Cu(II)_2Cl_6]$

Formula	$Cu_2Cl_6C_{48}H_{56}N_2$
MWT	500.35
a	9.368 (2) Å
b	9.382(2)
c	11.881(3)
α	100.12(1)°
β	106.37(1)
γ	113.0(1)
V	2609.7(13) $Å^3$
F (000)	518
μMoK_α	5.77 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	1.274 g cm^{-3}
Z	2
Independent Refl.	3992
Obs. Refl. (F > 4.0σ(F))	2512
Variab.	370
R/R_w	3.7/4.6%
Space Group	P1bar
Octants Meas.	±h, +k, ±l

TABLE 128

POSITIONAL PARAMETERS FOR $[(n\text{-Propyl})_4N]_2[Cu(II)_2Cl_6]$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cu1	0.0524 (1)	0.4474 (1)	0.3790 (1)
Cl1	0.0812 (1)	0.6836 (1)	0.5034 (1)
Cl2	-0.0922 (1)	0.2429 (1)	0.2030 (1)
Cl3	0.2914 (1)	0.5649 (1)	0.3549 (1)
N1	-0.7028 (3)	0.0096 (3)	0.2414 (2)
C11	-0.6471 (4)	0.1680 (4)	0.2094 (3)
C12	-0.4696 (5)	0.3002 (5)	0.2869 (4)
C13	-0.4232 (6)	0.4392 (5)	0.2345 (4)
C21	-0.6936 (4)	0.0410 (4)	0.3741 (3)
C22	-0.8030 (5)	0.1129 (5)	0.4045 (4)
C23	-0.7736 (5)	0.1388 (5)	0.5400 (3)
C31	-0.8824 (4)	-0.1042 (4)	0.1472 (3)
C32	-0.9675 (5)	-0.2728 (5)	0.1595 (4)
C33	-1.1373 (5)	-0.3733 (6)	0.0551 (4)
C41	-0.5866 (4)	-0.0642 (4)	0.2363 (3)
C42	-0.5661 (6)	-0.1035 (5)	0.1151 (3)
C43	-0.4519 (6)	-0.1797 (5)	0.1234 (4)

TABLE 129

HYDROGEN POSITIONAL PARAMETERS FOR $[(n\text{-Propyl})_4N]_2[Cu(II)_2Cl_6]$

ATOM	x	y	z
H11A	-0.7217	0.2121	0.2174
H11B	-0.6607	0.1414	0.1240
H12A	-0.3940	0.2547	0.2875
H12B	-0.4581	0.3401	0.3707
H13A	-0.3092	0.5224	0.2843
H13B	-0.4337	0.3990	0.1509
H13C	-0.4984	0.4851	0.2349
H21A	-0.5787	0.1152	0.4293
H21B	-0.7242	-0.0608	0.3914
H22A	-0.9196	0.0384	0.3536
H22B	-0.7747	0.2155	0.3886
H23A	-0.8420	0.1835	0.5617
H23B	-0.8024	0.0354	0.5546
H23C	-0.6567	0.2135	0.5897
H31A	-0.8824	-0.1182	0.0652
H31B	-0.9506	-0.0518	0.1550
H32A	-0.9796	-0.2626	0.2377
H32B	-0.8988	-0.3255	0.1562
H33A	-1.1917	-0.4806	0.0614
H33B	-1.2051	-0.3197	0.0595
H33C	-1.1238	-0.3830	-0.0226
H41A	-0.6285	-0.1644	0.2553
H41B	-0.4771	0.0096	0.3001
H42A	-0.5183	-0.0039	0.0964
H42B	-0.6743	-0.1767	0.0496
H43A	-0.4381	-0.2039	0.0464
H43B	-0.3439	-0.1054	0.1887
H43C	-0.5010	-0.2794	0.1417

TABLE 130

ANISOTROPIC THERMAL PARAMETERS FOR $[(n\text{-Propyl})_4N]_2[Cu(II)_2Cl_6]$

ATOM	U11	U22	U33	U12	U13	U23
Cu1	43 (1)	48 (1)	48 (1)	19 (1)	16 (1)	18 (1)
Cl1	67 (1)	44 (1)	72 (1)	24 (1)	36 (1)	26 (1)
Cl2	73 (1)	83 (1)	52 (1)	22 (1)	8 (1)	0 (1)
Cl3	55 (1)	77 (1)	79 (1)	26 (1)	37 (1)	32 (1)
N1	39 (1)	44 (2)	39 (1)	16 (1)	11 (1)	18 (1)
C11	49 (2)	47 (2)	51 (2)	20 (2)	18 (2)	25 (2)
C12	54 (2)	54 (2)	70 (3)	11 (2)	11 (2)	18 (2)
C13	83 (3)	51 (2)	81 (3)	8 (2)	40 (3)	11 (2)
C21	48 (2)	57 (2)	42 (2)	27 (2)	18 (2)	22 (2)
C22	65 (2)	75 (3)	70 (3)	44 (2)	31 (2)	32 (2)
C23	60 (2)	61 (2)	60 (2)	27 (2)	27 (2)	8 (2)
C31	40 (2)	49 (2)	45 (2)	12 (2)	5 (1)	16 (2)
C32	58 (2)	57 (3)	68 (3)	8 (2)	13 (2)	24 (2)
C33	54 (2)	72 (3)	91 (3)	-2 (2)	14 (2)	13 (3)
C41	46 (2)	47 (2)	44 (2)	21 (2)	15 (2)	16 (2)
C42	82 (3)	76 (3)	46 (2)	40 (2)	27 (2)	21 (2)
C43	91 (3)	79 (3)	58 (2)	48 (3)	38 (2)	22 (2)

The anisotropic displacement exponent takes the form:

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

x 10^3 for Cu, Cl, N and C.

TABLE 131
BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[(n\text{-Propyl})_4N]_2[Cu(II)_2Cl_6]$

Cu1 - Cl1	2.306 (1)	Cl1 - Cu1 - Cl2	147.7 (1)
Cu1 - Cl2	2.197 (1)	Cl1 - Cu1 - Cl3	96.1 (1)
Cu1 - Cl3	2.197 (1)	Cl2 - Cu1 - Cl3	98.8 (1)
Cu1 - Cl1'	2.325 (1)	Cl1 - Cu1 - Cl1'	85.5 (1)
N1 - C11	1.524 (5)	Cl2 - Cu1 - Cl1'	97.4 (1)
N1 - C21	1.522 (5)	Cl3 - Cu1 - Cl1'	146.1 (1)
N1 - C31	1.524 (3)	Cu1 - Cl1 - Cu1'	94.5 (1)
N1 - C41	1.513 (6)	C11 - N1 - C21	111.1 (3)
C11 - C12	1.502 (4)	C11 - N1 - C31	105.6 (3)
C12 - C13	1.506 (7)	C21 - N1 - C31	111.9 (3)
C21 - C22	1.519 (8)	C11 - N1 - C41	111.3 (3)
C22 - C23	1.512 (6)	C21 - N1 - C41	105.0 (3)
C31 - C32	1.519 (6)	C31 - N1 - C41	111.9 (3)
C32 - C33	1.499 (5)	N1 - C11 - C12	116.3 (3)
C41 - C42	1.507 (6)	C11 - C12 - C13	110.7 (4)
C42 - C43	1.495 (9)	N1 - C21 - C22	116.1 (3)
		C21 - C22 - C23	108.2 (4)
		N1 - C31 - C32	115.9 (3)
		C31 - C32 - C33	109.3 (4)
		N1 - C41 - C42	116.9 (3)
		C41 - C42 - C43	110.6 (4)

Symmetry operation:

' = -x, 1.0-y, 1.0-z.

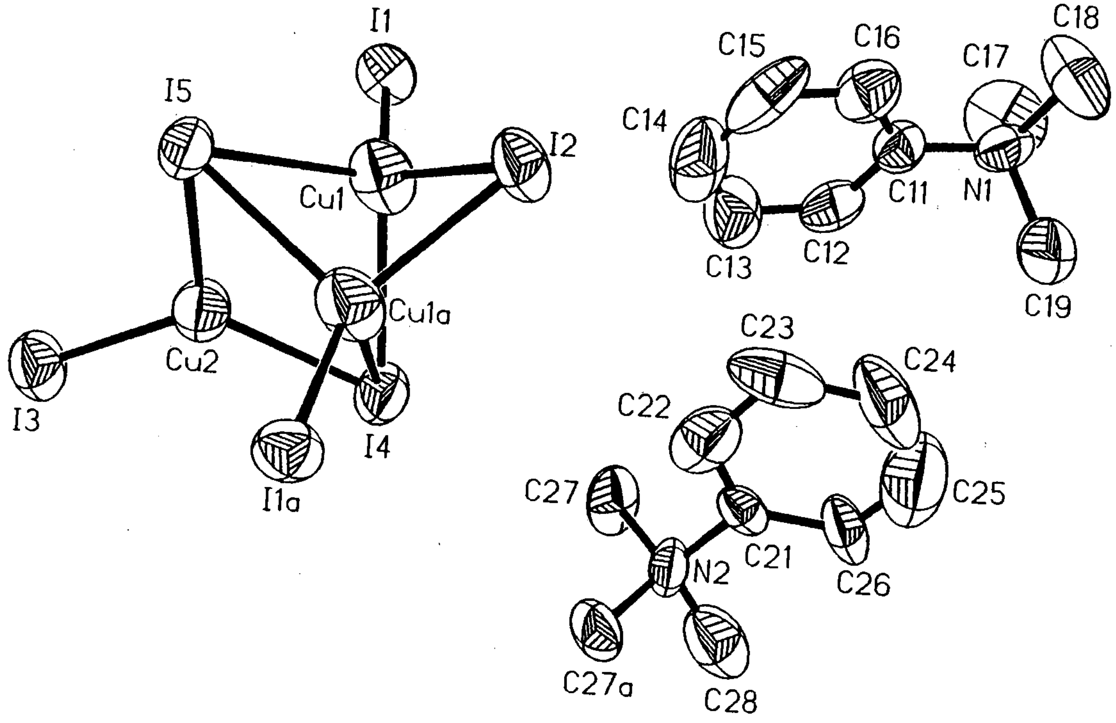

Figure 61. Projection View of $[PhMe_3N]_3[Cu_3I_6]$.

TABLE 132

CRYSTAL DATA FOR $[PhMe_3N]_3[Cu_3I_6]$

Formula	$C_{27}H_{42}Cu_3I_6N_3$
MWT	1360.7
a	26.364(2) Å
b	15.055(2)
c	10.027(1)
α	90.0°
β	90.0
γ	90.0
V	3979.7(6) $Å^3$
F (000)	2520
μMoK_α	62.63 cm^{-1}
λMoK_α	0.71073 Å
D_{calc}	2.271 g cm^{-3}
Z	4
Independent Refl.	3639
Obs. Refl. $(F > 4.0\sigma(F))$	1759
Variab.	197
R/R_w	4.2/4.5%
Space Group	Pnma
Octants Meas.	+h, +k, +l

TABLE 133

POSITIONAL PARAMETERS FOR $[PhMe_3N]_3[Cu_3I_6]$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cu1	0.1233 (1)	0.1642 (1)	0.2266 (2)
Cu2	0.0463 (1)	0.2500	0.3808 (3)
I1	0.1114 (1)	-0.0003 (1)	0.2458 (1)
I2	0.1909 (1)	0.2500	0.0802 (2)
I3	-0.0338 (1)	0.2500	0.5160 (2)
I4	0.1363 (1)	0.2500	0.4801 (1)
I5	0.0369 (1)	0.2500	0.1255 (1)
N1	0.4287 (4)	-0.0257 (8)	0.253 (1)
N2	0.2910 (5)	0.2500	0.722 (2)
C11	0.3740 (8)	0.0013 (9)	0.247 (2)
C12	0.3476 (6)	-0.0040 (9)	0.366 (2)
C13	0.2975 (7)	0.021 (1)	0.370 (2)
C14	0.2753 (3)	0.051 (1)	0.258 (3)
C15	0.3021 (7)	0.054 (1)	0.136 (2)
C16	0.3512 (6)	0.029 (1)	0.135 (2)
C17	0.4348 (6)	-0.118 (1)	0.304 (2)
C18	0.4538 (6)	-0.020 (1)	0.119 (2)
C19	0.4575 (5)	0.035 (1)	0.346 (2)
C21	0.3218 (7)	0.2500	0.596 (2)
C22	0.2970 (9)	0.2500	0.480 (3)
C23	0.324 (1)	0.2500	0.359 (2)
C24	0.377 (1)	0.2500	0.372 (4)
C25	0.400 (1)	0.2500	0.496 (4)
C26	0.3735 (7)	0.2500	0.604 (3)
C27	0.2581 (4)	0.1681 (9)	0.730 (1)
C28	0.3247 (7)	0.2500	0.848 (2)

TABLE 134

HYDROGEN POSITIONAL PARAMETERS FOR $[PhMe_3N]_3[Cu_3I_6]$

ATOM	x	y	z
H12A	0.3643	-0.0244	0.4452
H13A	0.2790	0.0233	0.4526
H14A	0.2407	0.0709	0.2598
H15A	0.2872	0.0791	0.0573
H16A	0.3697	0.0289	0.0528
H17A	0.4181	-0.1595	0.2462
H17B	0.4704	-0.1316	0.3081
H17C	0.4205	-0.1222	0.3921
H18A	0.4408	-0.0686	0.0659
H18B	0.4437	0.0350	0.0798
H18C	0.4901	-0.0238	0.1215
H19A	0.4457	-0.0351	0.4371
H19B	0.4938	0.0306	0.3454
H19C	0.4473	0.0894	0.3037
H22A	0.2607	0.2500	0.4746
H23A	0.3093	0.2500	0.2721
H24A	0.3965	0.2500	0.2910
H25A	0.4367	0.2500	0.4935
H26A	0.3900	0.2500	0.6896
H27A	0.2393	0.1649	0.8122
H27B	0.2351	0.1695	0.6564
H27C	0.2798	0.1171	0.7230
H28A	0.3467	0.3008	0.8487
H28B	0.3025	0.2525	0.9239

TABLE 135

ANISOTROPIC THERMAL PARAMETERS FOR $[PhMe_3N]_3[Cu_3I_6]$

ATOM	U11	U22	U33	U12	U13	U23
Cu1	78 (1)	53 (1)	111 (2)	2 (1)	20 (1)	7 (1)
Cu2	55 (1)	73 (2)	70 (2)	0	0 (1)	0
I1	70 (1)	52 (1)	67 (1)	6 (1)	5 (1)	6 (1)
I2	57 (1)	70 (1)	83 (1)	0	29 (1)	0
I3	57 (1)	85 (1)	87 (1)	0	15 (1)	0
I4	50 (1)	88 (1)	56 (1)	0	-6 (1)	0
I5	44 (1)	64 (1)	62 (1)	0	-7 (1)	0
N1	65 (7)	58 (8)	61 (8)	-10 (6)	-9 (7)	-15 (7)
N2	27 (7)	56 (11)	77 (13)	0	5 (8)	0
C11	5 (1)	5 (1)	7 (1)	-1 (1)	0 (1)	-1 (1)
C12	6 (1)	6 (1)	8 (1)	-1 (1)	-1 (1)	0 (1)
C13	8 (1)	10 (2)	11 (2)	-2 (1)	3 (1)	0 (1)
C14	6 (1)	6 (1)	18 (2)	-2 (1)	1 (2)	-1 (2)
C15	10 (1)	7 (1)	11 (2)	-2 (1)	-7 (1)	2 (1)
C16	7 (1)	7 (1)	7 (1)	0 (1)	-2 (1)	0 (1)
C17	14 (2)	8 (1)	10 (2)	2 (1)	0 (1)	3 (1)
C18	9 (1)	14 (2)	8 (1)	5 (1)	2 (1)	2 (1)
C19	5 (1)	19 (2)	12 (2)	2 (1)	-1 (1)	-6 (2)
C21	5 (1)	3 (1)	5 (1)	0	2 (1)	0
C22	8 (2)	5 (2)	12 (2)	0	-2 (2)	0
C23	16 (3)	8 (2)	4 (2)	0	3 (2)	0
C24	11 (3)	9 (2)	15 (3)	0	8 (2)	0
C25	7 (2)	13 (3)	20 (4)	0	0 (3)	0
C26	5 (1)	5 (1)	12 (2)	0	4 (1)	0
C27	6 (1)	5 (1)	12 (1)	-1 (1)	2 (1)	2 (1)

TABLE 135 (Continued)

C28	8 (2)	10 (2)	8 (2)	0	2 (1)	0

The anisotropic displacement exponent takes the form:

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

$\times 10^3$ for I, Cu and N, $\times 10^2$ for C.

TABLE 136

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[PhMe_3N]_3[Cu_3I_6]$

Cu1 ··· Cu2	2.861 (3)	Cu2 - Cu1 - I1	108.4 (1)
Cu1 - I1	2.504 (2)	Cu2 - Cu1 - I2	123.9 (1)
Cu1 - I2	2.646 (2)	I1 - Cu1 - I2	127.6 (1)
Cu1 - I4	2.871 (2)	Cu2 - Cu1 - I4	53.3 (1)
Cu1 - I5	2.808 (2)	I1 - Cu1 - I4	113.1 (1)
Cu1 ··· Cu1'	2.584 (4)	I2 - Cu1 - I4	101.0 (1)
Cu2 - I3	2.507 (3)	Cu2 - Cu1 - I5	54.0 (1)
Cu2 - I4	2.573 (3)	I1 - Cu1 - I5	112.4 (1)
Cu2 - I5	2.572 (3)	I2 - Cu 1- I5	97.0 (1)
Cu2 ··· Cu1'	2.861 (3)	I4 - Cu1 - I5	102.1 (1)
I2 - Cu1'	2.646 (2)	Cu2 - Cu1 - Cu1'	63.2 (1)
I4 - Cu1'	2.871 (2)	I1 - Cu1 - Cu1'	171.5 (1)
I5 - Cu1'	2.808 (2)	I2 - Cu1 - Cu1'	60.8 (1)
N1 - C11	1.50 (2)	I4 - Cu1 - Cu1'	63.3 (1)
N1 - C17	1.49 (2)	I5 - Cu1 - Cu1'	62.6 (1)
N1 - C18	1.50 (2)	Cu1 - Cu2 - I3	152.8 (1)
N1 - C19	1.51 (2)	Cu1 - Cu2 - I4	63.5 (1)
N2 - C21	1.50 (2)	I3 - Cu2 - I4	124.5 (1)
N2 - C27	1.51 (1)	Cu1 - Cu2 - I5	62.0 (1)
N2 - C28	1.55 (2)	I3 - Cu2 - I5	117.2 (1)
N2 - C27'	1.51 (1)	I4 - Cu2 - I5	118.2 (1)
C11 - C12	1.38 (2)	Cu1 - Cu2 - Cu1'	53.7 (1)
C11 - C16	1.34 (2)	I3 - Cu2 - Cu1'	152.8 (1)
C12 - C13	1.37 (2)	I4 - Cu2 - Cu1'	63.5 (1)
C13 - C14	1.35 (3)	I5 - Cu2 - Cu1'	62.0 (1)
C14 - C15	1.41 (3)	Cu1 - I2 - Cu1'	58.5 (1)
C15 - C16	1.35 (2)	Cu1' - I4 - Cu2	63.1 (1)
C21 - C22	1.34 (3)	Cu1 - I4 - Cu1'	53.5 (1)
C21 - C26	1.37 (3)	Cu2 - I4 - Cu1'	63.1 (1)

TABLE 136 (Continued)

C22 - C23	1.41 (4)	Cu1 - I5 - Cu2	64.1 (1)
C23 - C24	1.40 (4)	Cu1 - I5 - Cu1'	54.8 (1)
C24 - C25	1.38 (6)	Cu2 - I5 - Cu1'	64.1 (1)
C25 - C26	1.29 (5)	C11 - N1 - C17	112 (1)
Br1' - Cu1	2.224 (1)	C11 - N1 - C18	112 (1)
K1 ··· Cl1	3.400 (2)	C17 - N1 - C18	108 (1)
K1 - O1	2.791 (7)	C11 - N1 - C19	110 (1)
K1 - O2	2.793 (8)	C17 - N1 - C19	107 (1)
K1 - O3	2.821 (8)	C18 - N1 - C19	108 (1)
K1 - O1'	2.791 (7)	C21 - N2 - C27	111 (1)
K1 - O2'	2.793 (8)	C21 - N2 - C28	112 (1)
K1 - O3'	2.821 (8)	C27 - N2 - C28	106 (1)
O1 - C1	1.42 (2)	C21 - N2 - C27'	111 (1)
O1 - C2	1.41 (2)	C27 - N2 - C27'	109 (1)
O2 - C3	1.39 (1)	C28 - N2 - C27'	106 (1)
O2 - C4	1.46 (2)	N1 - C11 - C12	116 (1)
O3 - C5	1.40 (2)	N1 - C11 - C16	123 (1)
O3 - C6	1.38 (2)	C12 - C11 - C16	121 (1)
C1 - C6'	1.65 (2)	C11 - C12 - C13	120 (2)
C2 - C3	1.47 (2)	C12 - C13 - C14	119 (2)
C4 - C5	1.47 (2)	C13 - C14 - C15	121 (2)
C6 - C1'	1.65 (2)	C14 - C15 - C16	119 (2)
		C11 - C16 - C15	121 (2)
		N2 - C21 - C22	118 (2)
		N2 - C21 - C26	120 (2)
		C22 - C21 - C26	123 (2)
		C21 - C22 - C23	120 (2)
		C22 - C23 - C24	115 (2)
		C23 - C24 - C25	121 (3)
		C24 - C25 - C26	121 (3)

TABLE 136 (Continued)

	C21 - C26 - C25	120 (3)

Symmetry operation:

' = x, 1/2-y, z.

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