CORRELATION OF STRUCTURAL AND EMISSION PROPERTIES OF NEW CUPROUS IODIDE COMPLEXES

By

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CHAPTER I

INTRODUCTION

It was first observed(1) in 1938 that Cu(I)Cl fluoresced differently at room temperature than at low temperature. No further detailed investigation into this interesting phenomenon seems to have been undertaken until the early 70's. Since 1970, because of the pioneering synthetic work of H. D. Hardt and his group, numerous Cu(I) complexes have been synthesized, some of which fluoresce independent of temperature, whereas others emit at different wave lengths at different temperatures.

Most of the work done by Hardt and coworkers is synthetic in nature, however they have also identified many compounds amongst their synthesized materials to be temperature dependent or temperature independent fluorescent materials. Their early work dealt with carboxylates and other oxygen ligands whereas later, emphasis shifted towards nitrogen donor Lewis base ligands. Hardt and DeAhna (2,3) observed that reduction of cupric acetate by hydrazine forms cuprous acetate which fluoresces under UV light.

They reported(4) that, adding acetyl halide to a solution of Cu(I)acetate in a mixture of acetonitrile and acetic acid, resulted in highly pure Cu(I)X which, with ligands like pyridine and alkylpyridine, formed yellow or greenish yellow compounds of the formula CuL_3X. Colorless compounds of formula CuXL can be obtained by thermal decomposition of these compounds. All of the compounds exhibit intense fluorescence of different colors, however, some of the CuLX compounds emit different color at different temperatures. For this phenomenon of reversible change in emission wave length of the solid state compound with temperature, the term "fluorescent thermochromism" was proposed by DeAhna and Hardt. The compounds, Cu(4-picoline)Cl, CuLBr (L=2-picoline and 2,4-lutidine) and CuIL (L= 3-picoline and 2,4-lutidine) have been shown to exhibit fluorescent thermochromism. In another publication (5), Hardt and Gechnizdjani synthesized and noted the fluorescence of Cu(I)I with ethylpyridine and amino pyridines. Of the series of compounds synthesized, the following compounds have been reported to show fluorescent thermochromism: CuXL where L = 4-aminopyridine, X=Cl, Br, I and with X=I, L= 2 and 3-ethylpyridine. Compounds of the type CuL_2X where X=Cl and L=4-aminopyridine; X=I, L=2-ethylpyridine have also been reported to exhibit thermochromic fluorescence. Hardt and Pierre(6) have been able to identify three different compounds of CuI and pyridine with different stoichiometries; $CuIL_n$ where n= 1,2,3. The tripyridino compound is not obtainable at room temperature and normal pressures. All three compounds have different structures (determined by comparison of X-ray powder diffraction patterns) and show different emission color in UV light. The dipyridine compound did not show fluorescent thermochromism; the tripyridine compound did not fluoresce at room temperature but fluoresced bright yellow at liquid nitrogen temperature. The monopyridine compound which fluoresced yellow at room temperature, was reported to change its emission to orange at -163 ^{o}C, to red at -188 ^{o}C and to violet at liquid nitrogen temperature under UV light. Contrary to other published observations, (7-9), these authors reported that macrocrystalline, pure Cu(I)I was nonfluorescent at any temperature. However, when CuI was crystallized from KI_{aq} solution or acetonitrile, the product fluoresced. These fluorescent CuI samples did not show fluorescence when heated above 200^{o} or cooled to liq. nitrogen temperature but fluoresced when brought back to room temperature. The cause for this fluorescence has been attributed to lattice disturbance in CuIL crystals. The loss of fluorescence at high and low temperatures has been explained as due to the destruction of the electron states necessary for the phenomenon. Fluorescence and fluorescent thermochromism of solids like Cu(Py)I was attributed to the fact that pyridine molecules are fixed in a less restrictive manner to the solid state structure of CuI and have a certain ability to twist, thus altering the energy of the emitting states with temperature. Thus steric crowding was viewed as antagonistic to thermochromism.

The thermochromic fluorescence of the nitrogen base complexes of CuI has been exploited as an analytical method for identifying the particular nitrogen base by use of CuI impregnated spot test papers (10,6,11) with the base dissolved in acetonitrile or aqueous KI. Hardt and Gechnizdjani(5) further synthesized Cu(I) complexes with ethers, amides and nitrile derivatives of nicotinic acid as well as with quinoline, isoquinoline and quinaldine, all of which are strongly fluorescent, however, only in one case, i.e. in the case of the hexyl ester of nicotinic acid, did the CuIL compound showed a change in emission with temperature. With only limited powder diffraction data available to give information about the structure of these compounds, Hardt(12) noted that there was no difference in the crystal structure of samples at low temperature and at room temperature. He also observed that CuI reacts independently with pyridine and hexamethylene tetraamine to give to thermochromic compounds, however, the mixed ligand complex with the same two ligands gave rise to a nonthermochromic but merely fluorescent compound. Hardt and Pierre(13) have been able to isolate and measure the powder diffraction patterns of two isomeric forms of Cu(I) acetate, one synthesized at room temperature and the other one at higher temperature. Of the two forms, the room temperature compound is the only one to exhibit thermochromic fluorescence. From the study of CuX compounds with 2,4-lutidine and esters of nicotinic acid, authors, Goher and Dratovsky(14,15), have concluded that the 1:1:1 compounds of CuX, i.e. CuXL are fluorescent irrespective of the anion present. They further pointed out that all Cu(I) complexes that are red, orange or brown, are not fluorescent at room temperature, e.g. the red-orange CuI(isonicotinic acid) does not emit at room temperature but the colorless form does.

By studying the fluorescent properties of the hexamethylenetetraamine(HMTA) complexes of Cu(I)I, Hardt and Gechnizdjani (16) observed that, depending on the method of preparation and solvent used, the compound showed different fluorescent behavior and color, e.g. when methanol or ethanol were used as the solvent, the compounds obtained displayed fluorescent thermochromism, with the yellow room temperature emission changing to red and violet respectively at 77 K. But if the structure was 'tightened' by inclusion of additional HMTA or the presence of a second nitrogen base in the solid state, then thermochromism was not present. They also synthesized a mixed ligand CuI complex with L=HMTA and pyridine which was reported to be phosphorescent. A hypothesis called the "framework hypothesis" suggested that a solid state Cu(I) complex in which the Cu atom has at least 1.33 nitrogen functions available, making it a 'tight structure', will not display thermochromism due to limited mobility in the lattice.

Next, Hardt and Pierre(17) attempted to correlate the symmetry of Cu(I) complexes with their thermochromism. They assigned the fluorescence of the monomeric complexes Cu(pyridine)$_4$ClO$_4$ to $3d^{10} \rightarrow 3d^9pi^*$ transitions on Cu$^+$ centers. Further, they have concluded that the extent of the red shift of the emission peak for the thermochromic complexes depends more upon the symmetry of the cluster than on the Cu-Cu distance. The higher the symmetry of the cluster, the less the red shift. The reason for the red shift at lower temperatures was presumed due to an increase in electronic interaction between adjacent Cu ions (caused by short metal-metal distances) in the excited state.

Hardt and Stoll(18) explored the synthesis of thermochromic Cu(I) complexes by the reaction of CuI with acetonitrile in the presence of the crown ether, dibenzo-18-crown-6. They have reported that the compounds CuI-acetonitrile and CuIacetonitrile dibenzo-18-crown-6 both exhibited thermochromic fluorescence. The red shifted emission in the compound with the crown ether was attributed to interaction between crown and CuIacetonitrile.

Hardt and Weber (19) have synthesized and studied the fluorescent properties of some Cu(I) carboxylates. All of the complexes involving carboxylates were fluorescent. They have inferred that the fluorescence stems from the presence of the oxygen atoms which are strong donors compared with nitrogen. They observed that most of these compounds exhibit no thermochromism, particularly the ones with tetragonal structure. The only carboxylate compound which they found to be thermochromic is the compound with 3-hydroxybenzoate. This was suggested to be due to lower symmetry of the molecule.

Eitel and Oelkrug(20) synthesized a second modification of 1:1:1 CuI(pyridine), i.e. polymeric $(\mathrm{CuIpyridine})_x$, and have determined the single crystal X-ray structure. They have studied the fluorescent properties of this compound and made comparisons with the emission properties of the tetramer, $\mathrm{Cu_4I_4pyridine_4}$, the tetramer being thermochromic and the polymer being simply fluorescent. They have attributed the difference in behavior of the two compounds to the metal-metal separation and number of I atoms bonded to the copper atoms.

Hardt and Stoll(21) investigated fluorescent properties of some phosphine complexes, sesqui-, bis-, and tris(triphenylphosphine)Cu(I)X. They inferred that the fluorescence is independent of the halide ion whereas excitation depends on the anion present. Furthermore they have observed that solvate molecules do not change the fluorescent emission in this series. Dimeric sesqui-compounds show a red shift in emission when cooled whereas monomeric bis- and tris- complexes undergo a blue shift of emission upon cooling. They synthesized mixed ligand complexes(22) of the type $CuX(Ph_3P)(Py-R)$ and attempted a correlation between the fluorescence and the mesomeric, inductive properties of the substituents and anions. All of these compounds exhibit intense solid state fluorescence. Weber and Hardt(23) synthesized and studied the emission properties of a series of aliphatic Cu(I) carboxylates. They have reported that of the series of compounds synthesized, only Cu(I)valerate shows a blue shift of its emission maxima whereas the all others show a red shift on cooling to liquid nitrogen temperature. The greatest red shift of the emission maxima was shown by Cu(I)capronate.

Lewis base adducts of Cu(I)X have recently been of much focus, structurally. Nitrogen base complexes are less fully characterized compared with the phosphine and arsine base compounds (24). For phosphine base ligands the tetrameric 1:1:1 (metal:halide:ligand) complexes, $M_4X_4L_4$ clusters with pseudo 'cubane' stereochemistry, may be topologically transformed into chair or step structures by suitably unfolding the cube. By separating the opposite faces of the cube or severing the step, independent dimeric species are possible. Monomeric species such as $CuXL_3$, $CuXL_2$; dimeric species such as

$Cu_2X_2L_4$ and $Cu_2X_2L_3$ are known whereas trinuclear species $Cu_3X_3L_2$ where L=bidentate ligand $((CH_2)(PPh_2)_2)$ has been reported.

The earlier literature has numerous reports of the synthesis of N-donor Lewis base complexes, even though, structurally, this class of componds is less extensively studied. Again, 'cubane' is the most commonly encounterd structural motif for those of stoichiometry 1:1:1 (metal:halide:ligand). Two independent research groups, led by A. H. White and V. Schramm, have carried out investigations into the solid state structures of Cu(I)X systems involving N-donor ligands. The thermochromic tetrameric complex $(CuIL)_4$, where L=morpholine (25) and the temperature independent fluorescent complex with L=piperidine (26) have been structurally characterized by Schramm and co-workers. Both of these compounds have the cubane geometry and display an inner tetrahedron of four Cu atoms surrounded by a concentric and opposed larger I_4 tetrahedron with each I attached to three Cu atoms. The fourth coordination site of each copper atom is occupied by the appropriate ligand (L). One of the cubic tetramers with pyridine(Py) as the ligand, $(CuIPy)_4$, which exhibits thermochromism, was structurally characterized by Raston and White (27). The L=2-picoline adduct of CuBr, $(CuBrL)_4$ also has a cubane structure (28). There is no step structure known of 1:1:1 stoichiometry with N-donor ligands. The compound $(CuBrPPh_3)_4$, with P-donor ligand has the step structure (29).

A series of polymeric structures are known with 1:1:1 stoichiometry which are also referred to as 'ribbon' or 'stair' or 'pleated sheet' polymers. A second polymorph of CuI and Py, $(CuI(Py))_x$ (20) and the adducts of CuCl and CuBr with acetonitrile (30-32), benzonitrile (33), and azomethane(33) are also of this form. A 'displaced stair polymer' structure has been observed for $(CuIMeNC)_x$ (34). A third polymeric form, the 'split stair polymer' has been observed with bulky ligands such as 2,4,6,-trimethyl pyridine compound of CuI (30).

A complex, $Cu_4I_4L_6$, with stoichiometry 1:1:1.5 was isolated and characterized with 2-picoline as the ligand (24). This compound exhibits a chair structure with two diferent types of copper cooridination, the copper at the corners of the chair being tetra-coordinate and the coppers in the shared edges of the rhombs being tri-coordinate.

For compounds with the stoichiometry 1:1:2, the most common structural motif encountered is an isolated rhombohedron of Cu_2I_2 with Cu and I atoms alternating. Each Cu atom is bonded to two ligands and two I atoms making it tetracoordinate. Examples of $(CuIL_2)$ show L= Py(35), 2-picoline, 3,5-lutidine (36); and L=2,4-lutidine (37). A quinoline compound with a molecule of the solvent trapped in the crystal lattice has also been reported to exhibit a rhombohedral structure. (36)

The 3-picoline compound of CuI, of the type $CuIL_3$ with the stoichiometry 1:1:3, has been reported recently (38). The monomeric adduct $CuI(3\text{-picoline})_3$ exists as an isolated tetrahedron with the Cu and I on a three fold axis.

A stoichiometry of 2:2:1, metal:halide:ligand, has been observed for the adduct of CuI with 2-picoline; $(Cu_2I_2)(2\text{-picoline})$ (39). The compound has a double ribbon structure with alternating Cu and I atoms. The Cu atoms are tetrahedrally coordinated by four I atoms or by three I atoms and a molecule of picoline respectively.

When a solid absorbs energy a number of energy conversion processes are possible, most of which involve the promotion of electrons to an excited state followed by decay of these electrons back to their ground state with the excited state energy given off in the form of heat or radiation of various wave lengths, one of these processes being luminescence. Luminescence can be defined as (40) the absorption of photons or charged particles by a substance which is then followed by a photoemission (energy also being lost to thermal agitation) and which is strongly dependent upon the nature of the emitting substance (unlike losses in the form of heat). Like most solid state properties, the luminescent characteristics depend upon such factors as composition of the material, the level of purity, temperature, and the specific arrangement of bonds.

Excited state transition metal complexes are receiving increasing attention because they may be viewed as (41) highly reactive reagents, often differing dramatically in reactivity from their ground state precursors. A further impetus for the investigation of these systems stems from the possibility that they may find application in solar energy conversion schemes. Spectral sensitization of wide band gap semiconductors has been studied. Cu(I) complexes with 2,9-diphenyl-1,10-phenanthroline (dpp) or 2,4,7,9- tetraphenyl-1,10-phenanthroline (tpp) having low lying MLCT excited states have been shown to act as sensitizers(42) of semiconducters, absorbing at one wavelength and emitting at a wavelength suitable to cause current flow in the semiconductor. Breddels and Blasse(43) have made use of magnesium tetraphenylporphyrine as a spectral sensitizer of $SrTiO_3$ electrodes. These complexes provide a means to use a wavelength present in the solar spectrum, which is converted to a wavelength appropriate for semiconductor function.

In solid state materials, excitation mechanism generally involve three phenomena: charge transfer(CT), metal centered(MC) and ligand centered(LC)(44).

Charge transfer photochemistry of Cu(I) (45) complexes is due to a. charge transfer to solvent (CTTS); or b. charge transfer from metal to ligand (MLCT).

a. Charge transfer to solvent: The UV irradiation of Cu(I) complexes with halides or pseudohalides induces the photogeneration of solvated electrons. One example of this behavior is found in photochemistry of $CuCl_3^{2-}$ and $CuBr_3^{2-}$ (46). It is possible to find photoactive CTTS states in Cu(I) complexes with ligands different from the halides and pseudohalides.

b. The photochemistry of a large number of Cu(I) complexes, e.g., the tetramers $(CuIPy)_4$, and $(CuI(3\text{-}picoline))_4$ can be explained on the basis of charge transfer to ligand or metal to ligand charge transfer (MLCT). Besides Cu(I), the other common oxidation state for copper is Cu(II). Normally the two oxidation states exhibit different structures. Despite the fact that Cu(I) has the larger ionic radius, Cu(II) is a more powerful electrophile and tends to exhibit a higher coordination number. Thus whilst a coordination number of four with tetrahedral geometry is common for Cu(I), coordination numbers of five and six are more prevalent with square pyramidal or octahedral geometries for Cu(II). Such structural considerations and the electronic character of the ligands are important factors determining the relative energies of the two oxidation states.

Metal to ligand charge transfer emissions have been identified in Cu(I) systems. From work on glassy Cu(I) complexes, $Cu(PPh_3)_2(2,2'\text{-bipyridyl})^+$, Cu-(cis-bis(1,2-diphenylphosphino)ethylene$^+$ and Cu(2,9-dimethyl-

1,10-phenanthroline)$^+$, McMillin (41,47) and coworkers concluded that the broad featureless emission bands observed (λ abs 356, 398, 454 nm respectively; λ_{max}610, 612, 710 nm respectively were derived from more than a single MLCT state. Further work(48) on solid state $Cu(PPh_3)_2$(phenanthroline)$^+$ BF_4^- showed the emission spectrum and decay time to be temperature dependent. These features suggested a three level system (48,49) consisting of two excited states and a ground state, the higher excited state emitting green, decaying rapidly and coexisting at room temperature with a lower energy excited state which emits yellow and is of longer decay time. This latter excited state is chiefly responsible for the low temperature emission. Metal centered transitions were considered less likely in these systems because the expected lifetimes for low lying tetrahedral $3d^94s^1$ states were longer than those observed. Work on powder samples of similar structure ($Cu(R_3P)_2L$ where L= bidentate nitrogen donor aromatic ligands (50), showed similar broad emission envelopes whose maxima were blue shifted at lower temperatures. Correlation of excitation intensities and decay times with temperature, suggested that a splitting of the lower excited state of the model into singlet and triplet levels with differing decay times would better explain the observed phenomenon. Single crystal X-ray studies(51) revealed the solid state materials to consist of isolated Cu atoms tetrahedrally coordinated to two phosphorous donor ligands and one bidentate nitrogen donor system of extended aromatic character. The low lying pi* levels of these extended aromatic systems are accessible to the metal for MLCT interactions.

Emissions due to metal centered transitions have been observed for Cu(I) doped into a $RbMgF_3$ matrix. (λ 450 and 575 nm). The associated λ_{ex} = 295 nm was assigned to a $3d^{10} \longrightarrow 3d^9 4s^1$ transition and the appearance of two emission bands believed due to two different Cu(I) sites in the crystal. Since the concentration of Cu in the crystal was at the ppm level, only isolated metal centers were involved(52).

Industrial research interest has been focused on the study of the fluorescence of transition metals doped into host lattices in less than stoichiometric quantities such that the electronic states of the isolated metal centers are modified by the host matrices causing emission. Examples are Cu^+ doped into ZnS or Cr^{+3} in Al_2O_3 (ruby). These have attracted much attention because of their use as phosphors(40) and laser materials.

Attempts have been made to correlate interactive metal-metal distances in d^{10} systems with the electronic states. MO calculations based on Cu(I) model systems (53) have shown that $Cu_4{}^{4+}$ clusters with Cu-Cu distances of 2.83 Å have overlap population 0.32 (binding energy -0.417 eV) and that binding strength increases as the Cu-Cu distance is diminished (overlap 0.08, binding energy -0.984 eV at Cu-Cu separation of 2.57 Å). Inclusion of a ligand in a dimeric model produced a computed Cu-Cu optimum distance of 2.7 Å with Cu-Cu orbital overlap population increasing as Cu-Cu separation diminished. The identification of Cu-Cu distance of 2.8 Å or less as indication of interaction is also supported by the maintenance of Cu-Cu distance averaging close to 2.82 Å in a series of Cu_8S_{12} species(54), despite fundamentally different demands of ligand geometry. All the tetrameric complexes showing λem,max of 550 to 628 nm also show Cu-Cu separation of 2.8 Å or less despite the range of ligands attached with them. The assignment of emission in this range to a metal-metal interaction is supported by the absence of this absorption in the polymeric structure, $(cuIPy)_x$.

Ligand centered emission has been studied(55) in transition metal complexes. These studies have shown that ligand centered emission due to coordinated ligands is shifted by less than 1000 cm^{-1} form that of the uncoordinated ligand. The spectrum exhibits all of the fine structures seen in the spectrum of the ligand alone.

The Cu-I bond is another potential source of excitation leading to emissions. Donor-acceptor pairs (DAP)(56) have been cited as the source of the emission. λ_{max}=420 nm in crystalline CuI when excited at 337 nm using nitrogen laser. In this excitation unshared pair of electrons on I is accepted into empty orbitals on Cu. In the solid state CuI also displays a series of narrow band emissions at lower and higher wavelengths attributed to unknown excitation phenomena.

Based on the synthetic and lumunescence studies by Hardt and coworkers, many CuIL complexes were identified to be thermochromic. The availablity of the limited powder diffraction data, to which was later added single crystal X-ray structural results, led authors such as Hardt, Schramm, Oelkrug _et al_ to attempt to find correlation between the structure and fluorescence thermochromism of these compounds.

With the single crystal X-ray structural data and the fluorescence data for three tetramers of the type $M_4X_4L_4$ where X=I and L=Py(27), morpholine(25) and piperidine (26) in hand, Schramm proposed a correlation between the symmetry and fluorescence thermochromism. In a cube there can be various symmetry elements present: (a) there can be a $\bar{4}$ symmetry element present which makes all Cu-L bonds equivalent to each other (b) there can be a two fold symmetry axis passing through the opposite sides of the cube making Cu-L bonds equivalent to each other in pairs or (c) there may be no symmetry element present in the molecule and hence all the Cu-L bonds are independent of each other. According to this author, thermochromic fluorescence can be correlated with the absence of the $\bar{4}$ symmetry element. Of the three tetramers named, the first two exhibit fluorescent thermochromism and they do not have a $\bar{4}$ symmetry element present, although the morpholine compound has a two fold axis. The piperidine compound is merely fluorescent and structurally was observed to have a $\bar{4}$ symmetry element in the molecule making all Cu-N bonds equivalent to each other. From the results of these three compounds, Schramm proposed a working hypothesis (26)that " a tetrameric complex between CuI and N bases does not show a marked phenomenon of 'fluorescence thermochromism' if the point symmetry of the cluster molecule is at least of fourfold order, i.e. the Cu-N bond lengths involved are equal by symmetry". He has also pointed out that earlier workers believed that the 'necessary precondition' for the possibility of fluorescence thermochromism in complexes of CuI with organic ligands is the presence of an electron donating bond from ligand to Cu. Hardt and Pierre(17) attempted to correlate symmetry of the cluster and the fluorescence thermochromism . By studying fluorescence of a series of $CuXL_n$ complexes and by comparision with the structural data from the literature, the authors have concluded that the extent of red shift of the emission peak with temperature depends more on the symmetry of the cluster than on the Cu-Cu distance. The higher the symmetry of the cluster, the less the red shift. They have furher inferred that at low temperature, higher excited states are preferentially populated (they have assigned the transition in case of $CuPy_4ClO_4$ to be $3d^{10} \rightarrow 3d^9$ pi*).

A combination of metal centered and charge(20) transfer phenomena were suggested responsible for emissions observed for the complexs of CuI and pyridine. The spectrum of $(CuIPy)_x$ shows a single band in the blue region (B-band), the position of which is independent of the excitation and temperature. The Stokes shift between luminescence and excitation maxima is 5200 cm^{-1} and the band is assigned to a ($3d^{10} \rightarrow 3d^9$pi*) transition (MLCT). The tetrameric complex, $(CuPy)_4$, also shows the B-band, which first appears on excitation between 25,500 and 27,000 cm^{-1} with a Stokes shift of about 4100 cm^{-1} between the excitation and emission maxima. The second luminescence band appears in the red region (R-band) with excitation at 30,000 cm^{-1} and has been assigned to a $3d^{10} \rightarrow 3d^9 4s^1$ transition. This is a metal centered transition, the assignment of which is substantiated by the fact that the $(CuIpip)_4$ complex, which does not have an aromatic ligand also shows this transition.

Upon lowering the temperature, the authors have found that, the B-band totally disappears at 50 K leaving only the R-band. This phenomenon occurs at frequencies below 27,000 cm^{-1} at which R-luminescence is not directly excited. The temperature dependent luminescence shift have been attributed to the dynamics of the excited states rather than to a structural change of the crystal lattice. If both the emitting states have similar energy, cross over phenomena could appear in the region of the energy minima. If the $3d^9pi^*$ state is reached energetically (i.e., with 27,000 cm^{-1} excitation, B-band), then only B-luminescence is possible at low temperature. If the excitation energy allows attainment of $3d^94s^1$ state (i.e., with 30,000 cm^{-1} excitation, R-band), then the potential minimum of $3d^9pi^*$ can be reached from $3d^94s^1$ through radiationless relaxation. Thus B and R luminescence are to be observed. At higher temperatures, the $3d^9s^1$ minimum can also be reached from d^9pi^* minimum which is possible via a thermal reaction or through energy transmission (overlapping of the R-absorption band with the B-emission band). Since the rate of the two processes increase with increasing temperature, an alteration of the luminescence is observed untill finally at temperatures above 100 K the R-luminescence becomes the only luminescence process. The authors(3) discuss their observation in terms of transitions at a single metal atom. However, it was noted that $(CuIPy)_4$ which displays MLCT and metal-centered transitions, has a Cu-Cu distance of 2.691 Å(av.) whereas the polymer $(CuIPy)_x$ has a longer Cu-Cu distance of 2.875(2) Å. The smaller metal-metal distance within the tetramer together with the higher coordination of the 4s orbital reduces its energy strongly and therefore the $3d^94s^1$ state is stabilized.

This suggests that the state $3d^9 4s^1$ in the tetramer is of lower energy than the $3d^9 4s^1$ in the polymer.

Workers in allied fields have used the emission properties of Cu(I) to study oxidation reduction reactions including H_2 formation (57). They state(41) that CT states are prone to undergo redox reactions while MC states are likely to undergo ligand-substitution reactions. In many systems, the nature of the lowest energy excited state can be affected by chemical modification of ligands or by judicious choice of solvents. On the other hand, the photophysical and photochemical properties of some metal complexes are more complex and reflect two or more participating excited states. In such systems, the rate of interconversion among levels dictates the response to light. However, the factors which determine how rapidly excited states equilibriate are not fully understood. Of interest in this regard are systems where unusually slow interconversions can be identified e.g., by emission spectroscopy.

Recently the solution photochemistry of (Cu(I) systems has been of interest, Until the mid 70's, Cu(I) complexes were known to fluoresce only in the solid state(16). In the late '70's, some Cu(I) complexes (46,58) have been synthesized which luminesce in solution. Since the metal ions interact strongly with the solvents, very few inorganic salts of Cu(I) in solution are observed to luminesce(59) because strong solutesolvent interactions provides a radiationless mode of degrading the energy of a molecular or atomic excited states via collision deactivation.

So from the pertinent literature, one does not arrive at a clear overall view of the factors responsible for fluorescent thermochromism of the Cu(I) complexes. The results of the investigations have been viewed in an emperical fashion and there are very few instances where synthetic and fluorescence results have been supported by structural studies in order to draw conclusive theories or hypotheses. Fluorescence results are mostly confined to noting change of visible emission with temperature for those compounds previously identified as displaying fluorescent thermochromism. The detailed investigation of the compounds displaying temperature dependent fluorescence is of interest because of the possibility of materials whose emission is in a useful range and can be controlled by the temperature. In order to be able to correlate the emission properties of the material with the structure so that specific useful systems can be designed and their emission properties can be predicted, the need of extensive synthetic and structural studies became obvious. Such studies could provide insight into the exciting and interesting structural chemistry of Cu(I) complexes. The working hypotheses or correlations in the literature seemed insufficient and inconclusive at this point, because of the lack of structural data for the compounds known to exhibit fluorescent thermochromism. Therefore, a project was undertaken to synthesize and characterize structurally compounds of this class and to study their emission properties so that the phenomenon of fluorescent thermochromism can be better understood. During the course of this investigation, the main focus was on Lewis bases with nitrogen donor atoms and studies were restricted to the complexes of CuI.

CHAPTER II

X-RAY CRYSTALLOGRAPHY

For single crystal x-ray structure determination, either the crystal was (a) mounted on a glass fiber, if it proved stable towards oxygen, moisture etc. and did not deteriorate with time or (b) sealed in a glass capillary tube along with a drop of the mother liquor from which it was crystallized. Because of the unstable nature of many of the compounds studied, method (b) was used more frequently than method (a). The mounted crystal was afixed to a brass nib, which was mounted on a goniometer head. The goniometer with the mounted crystal was placed on a four-circle Syntex P3 automated diffractometer. The physical centering of the crystal was adjusted visually. A rotation photograph was taken to ascertain crystal quality and to provide starting information. A reflection of $\chi = 90^{o}$ and 2θ less than 20^{o} was selected and used to precisely adjust the height of the crystal. Fifteen independent reflections chosen from the poloroid film were centered. An indexing routine(60) provided possible cell edges from which a set was chosen with maximum symmetry and minimum cell volume. A least-squares fitting of the diffractometer centered angles for the fifteen reflections to the cell parameters gave the final cell parameters, their associated errors and an orientation matrix to be used for data collection(60). If the errors (standard deviations) of the cell parameters were high, a fast data scan was used to find fifteen independent reflections with higher 2θ values (2θ greater than 15°) and the cell determination procedure was repeated, usually to give a better cell.

Depending on the crystal class, data were collected such that the diffraction symmetry of the cell generated a complete sphere of data(61). The details of data collected for each compound are shown in crystal data tables.

The diffractometer records the intensity data, I_{hkl}, associated with each reflection and recorded in the format(60):

Sequence number, h, k, l, (negative for standard reflections), 2θ , ω , ϕ, χ , 2θ scan range, scan speed, peak profile, left-background, peak count, right-background, scaled net count on 1°/minute basis, standard deviation, crystal exposure hours.

The diffraction data is reduced by a computer program, DATRDN(62), which reduces the data by applying the corrections (i) background correction, (ii) Lorentz effect, (iii) polarization correction and (iv) decomposition correction.

Background Correction:

Correction for left and right-background is done by simple subtraction :

$$I_{int} = (I_{meas}-Lbg-Rbg)\ \text{X Scan rate.} \qquad (1)$$

$$I_{int} = (I_{meas}+Lbg-Rbg)^{1/2}\ \text{X Scan rate} \qquad (2)$$

where I_{int} = Integrated intensity

I_{meas} = Measured intensity

Lbg = Left-Background

Rbg = Right-Background

I_{int} = Standard deviation in integrated intensity

The reflection is considered to be observed if :

$$I_{int} > 3\sigma I_{int} \qquad (3)$$

The data must also be corrected for polarization and Lorentz effect(61) such that :

$$(KI_{hkl} \,/\, Lp) = I_{cor} \qquad (4)$$

where K = Constant, depends on crystal size, beam intensity and machine constants.

L = Lorentz factor

p = Polarization factor

The polarization term (p) arises because of the nature of the x-ray beam and the manner in which its reflection efficiency varies with the reflection angle. The unpolarized electric vector of the x-ray beam has two components, $I_{\parallel}$ and $I_{\perp}$; parallel and perpendicular to the surface of reflecting planes. Because of the greater efficiency of reflection of $I_{\parallel}$, it will be represented to a greater extent in the reflected beam than is $I_{\perp}$, and so the beam is partially polarized. The correction for the polarization is done by the equation :

$$p = (1+\cos^2 2\theta) / 2 \tag{5}$$

p is a simple function of 2θ and is independent of the method for collecting data.

The Lorentz factor is a geometrical factor, which takes into account the fact that the average intensity of reflections depends upon the magnitude of 2θ. When the crystal is rotated at a constant angular velocity, reflections with low 2θ spend more time in the beam than reflections with high 2θ. The Lorentz factor (L) is given by:

$$L = 1 / \sin 2\theta \tag{6}$$

Therefore, Lp correction is given by :

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

and

$$I_{cor} = I_{int} / Lp \tag{8}$$

A correction has to be applied due to the decomposition of the crystal. The decomposition correction assumes that decomposition is a linear effect, occurring between any two measurments of the standards. Thus, the decomposition correction is given by :

$$I_{orig} / I_{ave} \tag{9}$$

where I_{orig} = Original intensity of the standard reflection.

I_{ave} = Average current intensity of the standard reflection.

Final corrected intensity, I_{cor} is given by :

$$I_{cor} = I_{int} \times (1 / Lp) \times (I_{orig} / I_{ave}) \qquad (10)$$

Then the structure factor $|F|$ is determined as the square root of I_{cor}.

$$| F_{hkl} | = (I_{cor})^{1/2} \qquad (11)$$

The error in F_{hkl} ,σF is calculated according to the equation(61):

$$\sigma F = (1/2)(k/(Lp)^{1/2})((N_t+N_{rbg}+N_{lbg}+(0.01Npk)^2)/(N_t-N_{lbg}-N_{rbg}))^{1/2} \qquad (12)$$

where N_t = number of total counts

N_{lbg} = number of left-background counts

N_{rbg} = number of right-background counts

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

Thus $|F|$, the structure factor may be derived directly from the measurments made on the diffractometer. But, the measurment contains no information about the phase (α)(61), because phases cannot be measured. Phase is defined as the difference in period, expressed as an angle, between the wave resulting from a specific set of planes and a wave resulting from scatering at the origin. To find the atomic positions in a model, we have to have information about the phase, at least for enough reflections, so that a Fourier transformation of the αF, we will generate an interpretable electron density map and hence show the atomic positional parameters.

The structure factor, $| F_{hkl}|$,without phase can still be used to find the coordinates of atoms by two procedures, Patterson mapping and Direct methods. A

Patterson map is the Fourier Transform of $|F|^2$, for which phase is eliminated. The Patterson map locates the positions of ends of vectors between the atoms, translated to the origin. Because the vectors between heavy atoms are most visible in the maps, use of the knowledge of the space group general equivalent positions, allows calculation of Harker planes and lines, from which positional parameters for the heavy atoms can be determined. This method of obtaining a solution is known as the "Heavy atom method"(62).

The second method used to obtain positional parameters for the atoms is the "Direct methods". The principle behind these methods is the idea that the relationships between the intensities themselves can give indication of phases of enough reflections to allow a Fourier transform of a limited set of phased structure factors to display the molecule. Using the Harker-Kasper inequalities(61), intensities and phases can be correlated. Normalized structure factors, E_{hkl} are calculated by the equation :

$$E^2_{hkl} = (F_{hkl})^2 / \Sigma f_i \qquad (13)$$

By use of the Sigma1, Sigma2 relationships and the Symbolic addition procedures, calculational programs(63) determine the phase associated with sufficient number of reflections.

Once the heavy atoms are positioned by the Heavy atom method or the Direct method, structure factors

(F_{cal}) can be calculated and compared with those measured (F_{obs}). The correctness of the model is indicated by the 'Residual factor', R_f, defined as :

$$R_f = (\Sigma||F_{obs}|-|F_{cal}||) / (\Sigma|F_{obs}|) \qquad (14)$$

As the model approaches completion, the difference between the F_{obs} and F_{cal} is reduced and hence the R_f is also reduced.

When some atoms are correctly placed and thus the phases(α) are nearly correct, a Fourier transform of F gives rise to an electron density map which shows only the positions of missing atoms. A least-squares refinement of the positional parameters, x,y,z, and the thermal parameter, U(isotropic), is carried out. The magnitude of the thermal parameter is an indication of the correctness of the identity of the atom. After least-squares refinement of the positional parameters for the complete set of atoms and anisotropic thermal parameters (U11, U22, U33, U12, U13, U23), final R_f value should be less than 10%. The bond angles, bond distances and the number of atoms in the model should be chemically reasonable. The anisotropic thermal parameters and the refined positional parameters are used to obtain a three-dimensional pictorial representation of the molecule, in which the the atoms are drawn as spheres of 90% probability of electron enclosure(64).

CHAPTER III

EXPERIMENTAL

All the chemicals used in the syntheses were freshly opened and were of Aldrich reagent quality. The chemicals were used without further purification. Mainly, three different types of synthetic procedure were adopted : (1) Use of acetonitrile solution of CuI (2) Use of saturated aqueous KI to dissolve CuI and then the resulting solution was reacted with the desired ligand (3) Use of the ligand as the solvent. The synthetic procedures for the individual compounds are discussed in detail in the following sections.

$(Cu_4I_4(\text{p-Toluidine})_2(\text{Acetonitrile})_2)$ (I):

To a mixture of 0.475 g (2.5 mmole) of CuI in 25 mL acetonitrile, excess (0.48 g, 5 mmole) of p-toluidine was added with stirring. The resulting mixture was refluxed for twelve hours under inert atmosphere and then cooled to room temperature under nitrogen. Crystallization, i.e. the formation of a light brown colored wedge shaped crystals was observed. The reaction mixture was cooled to 5 ^{o}C to complete the crystallization. The compound luminesced light yellow at room temperature and no change in emission color was detected upon cooling to liq. nitrogen temperature. A single crystal of suitable size was chosen and was mounted in a sealed capillary tube in an atmosphere of its own mother liquor to be used for collection of X-ray diffraction data.

$(Cu_2I_2$(p-Chloroaniline)(Acetonitrile)$)_2$(II):

To 50 mL acetonitrile in a 250 mL beaker, 1.27 g (0.01 mole) of CuI and 0.95 g(0.005 mole) of p-chloroaniline was added. The mixture was stirred for three hours and then was allowed to react at room temperature. After forty-eight hours, formation of the crystals was observed. The process of crystallization was completed at 5°C. The compound crystallized as light brown needle shaped crystals. These luminesced yellow at room temperature as well as at liq. nitrogen temperature. Beacuse of the relatively stable nature of the compound, a single crystal mounted on a glass fiber was used to collect the X-ray diffraction data.

$(CuI(CH_3CN))_x$(III):

0.76 g(4 mmole) of CuI was mixed with 50 mL of acetonitrile in a 250 mL beaker and allowed to react slowly at room temperature until formation of crystals was observed (forty-eight hours). Then the crystallization was completed at 5 °C. The compound formed colorless cubic crystals, unstable in air, which luminesced bright yellow under UV light at room tempertature. No change in luminescence was observed for the dry crystal upon cooling to liq. nitrogen temperature although the wet crystal luminesces yellow green at the liq. nitrogen temperture. X-ray diffraction data were collected using a single crystal sealed in a capillary tube in an atmosphere of its own mother liquor.

(18-crown-6(Acetonitrile)2)(IV):

0.38 g (2 mmole) of CuI was dissolved in 30 mL acetonitrile and 0.52g (2 mmole) of 18-crown-6 was added. The mixture was heated to boiling and then allowed to crystallize at room temperature. After about seventy-two hours, chunky,colorless, crystals were obtained. The dry crystals did not respond the qualitative tests for I or Cu. The compound was highly unstable in air, giving off solvent. So a crystal had to be selected under its own mother liquor and was sealed off in a capillary tube, pre-saturated with the vapour of the mother liquor and x-ray diffraction data was collected on it.

(Dicyclohexano-18-crown-6(Acetonitrile)2)(V):

To 0.38 g (2 mmole) of CuI in 30 mL of acetonitrile, 0.75 g (2 mmole) dicyclohexano-18-crown-6 was added and the mixture was heated to boiling. The resulting mixture was allowed to crystallize at room temperature whereupon colorless crystals were formed after about forty-eight hours. The compound did not show the presence of either I or Cu. Due to the unstable nature of the crystals, for the x-ray diffraction data collection a crystal of the appropriate dimensions had to be selected under its own mother liquor and was sealed off in a capillary tube which was pre-saturated with the vapour of the mother liquor.

$(CuI(Quinoline)_2)_2$(VI):

0.38 g (2 mmole) of CuI was suspended in 50 mL of acetone and excess (1.1 g, 8 mmole) of quinoline was added to the refluxing CuI suspension. To the refluxing mixture, 5 mL of saturated aqueous KI solution was added whereupon a light yellow colored solution was formed. The mixture was refluxed for twentyfour hours and cooled to room temperature. After three days, yellow, needle shaped crystals were formed. The dry crystals luminesced bright yellow at room temperature as well as at liquid nitrogen temperature.

$(Cu_4I_4(quinoline)_4)$(VII):

To a refluxing mixture of CuI(1.14 g, 6 mmole) suspended in 100 mL acetone and 0.4 g (6 mmole) of quinoline, 5 g of KI saturated solution in water was added and the reflux continued for twenty-four hours. The resulting yellow reaction mixture was maintained at 55 °C. After three days light brown, chunky, diamond shaped crystals were formed. The dry crystal luminesced orange-red at room temperature and light green at liq. nitrogen temperature. The X-ray diffraction data were collected on a single crystal mounted on a glass fiber.

$(CuI(2\text{-}Picoline))_x$(VIII):

To a warm, 25 mL acetone suspension of 0.95 g (5 mmole) of CuI, saturated aqueous KI solution was added until a clear solution was obtained. To this solution, excess of 2-picoline (0.93 g, 10 mmole) was added in 20 mL acetone and the mixture was refluxed for twenty-four hours. The resulting solution was set aside at room temperature to crystallize. Colorless long needle shaped crystals were formed after forty-eight hours, which were collected by filtration. The dry crystal luminesced blue-white at room temperature and blue at liq. nitrogen temperature.

Cu_2I_2(3-Picoline)$_4$(IX):

To a 25 mL warm acetone suspension of 0.95 g (5 mmole) of CuI, saturated aqueous KI solution was added with stirring until a clear solution was obtained. To this solution, 0.93 g (10 mmole) of 3-picoline was added in 20 mL of acetone. The resulting mixture was for twelve hours and then left to crystallize at room temperature. Yellow, needle shaped crystals were formed after twenty-four hours. The dry crystals luminesced yellow at room temperature. Little change in emission color was observed upon cooling to liq. nitrogen temperature.

(CuI(2,4-Lutidine))$_x$(X):

To a 25 mL suspension of CuI (0.76 g, 4 mmole) in acetone, saturated aqueous KI solution was added with stirring to obtain a clear solution. To the resulting solution, 0.43 g (4 mmole) of 2,4-lutidine was added in 20 mL acetone and stirring continued for twelve hours whereupon white, needle shaped crystals started to form. crystallization was completed at room temperature. The dry crystals luminesced white-blue at room temperature and blue at liq. nitrogen temperature.

$((Cu_4I_6)(Cu_8I_{13})K_7(12\text{-crown-}4)_6)$(XI):

To 0.38 g (2 mmole) of CuI, saturated aqueous KI solution was added until a clear solution was obtained. The solution was filtered to remove any undissolved particles and to the resulting solution, 20 mL of acetone was added followed by excess 12-crown-4 (1ml) in 20 mL of acetone. The resulting mixture was refluxed for six hours with stirring. After about forty-eight hours, white needle shaped crystals formed which were filtered and redissolved in boiling acetone. The compond was allowed to crystallize from the acetone solution at room temperature yielding light yellow colored, needle shaped crystals Both the crude and the recrystallized compound luminesced yellow at room temperature and green-red at liq. nitrogen temperature.

$((CU_4I_6)K_2(15\text{-crown-}5)_2)$(XII):

To 0.38 g (2 mmole) of CuI, saturated aqueous KI solution was added until a solution was formed. after filteration to remove any undissolved particles and addition of 20 mL of acetone, excess 15-crown-5 (1 mL) was added and the solution was refluxed for six hours. On cooling the reaction mixture, white crystals were formed, which were collected by filtration and was recrystallized from boiling acetone. After most of the solvent was evoporated, light yellow colored, needle shaped crystals were obtained. The dry crystals luminesced bright yellow at room temperature and green at liq. nitrogen temperature.

((Cu_3I_4)K(Dibenzo-24-crown-8))(XIII):

0.38 g (2 mmole) of CuI was dissolved in saturated aqueous KI solution and 20 mL of acetone. To the refluxing solution, approximately 0.5g of dibenzo-24-crown-8 in 20 mL of acetone was added and reflux continued for twenty-four hours. The reaction mixture was cooled slowly to room temperature. After about twenty-four hours, colorless, needle shaped, crystals were formed. The dry crystal luminesced yellow at room temperature and orange red at at liq. nitrogen temperature.

(CuI_2)K(18-crown-6))(VIV):

To a solution of 0.38 g (2 mmole) of CuI in saturated aqueous KI, 20 mL of acetone was added followed by 0.72 g (1 mmole) of 18-crown-6 in 20 mL of acetone. The resulting mixture was refluxed for three hours and then cooled slowly to room temperature. After half of the mother liquor was evoporated, colorless, chunky, diamond shaped crystals were formed. The dry crystal luminesced light purple at room temperature and at liq. nitrogen temperature.

((CuI_2)K(dicyclohexano-18-crown-6))(XV):

0.38 g (2 mmole) of CuI was dissolved in saturated aqueous KI solution and 20 mL of acetone was added, 0.75 g (2 mmole) of dicyclohexano-18-crown-6 in 20 mL of acetone was added to the above refluxing solution. Reflux was continued for three hours. The reaction mixture was cooled slowly to room temperture and after about forty-eight hours, colorless, needle shaped crystals were formed. The dry crystal luminesced sky-blue at room temperature and at liq. nitrogen temperature.

(CuI (Cyclam))(XVI):

To a 20 mL acetone suspenssion of CuI (0.38 g, 2 mmole), an aqueous solution (in 30 mL of water) 0.20 g (1 mmole) of cyclam (1,4,8,11-teteazacyclo-tetradecane) was added dropwise with stirring when a light purple color started to develope and CuI slowly reacted. The mixture was stirred for one hour and filtered. The filtrate was allowed to crystallize at room temperature, whereupon after about twenty-four hours purple colored, needle shaped crystals were obtained. The dry crystal did not luminesce under UV light. A crystal of the right size was selected and was mounted on a glass fiber for collecting x-ray diffraction data.

CHAPTER IV

RESULTS AND DISCUSSIONS

To elucidate the structural factors that lead to components of the emission spectra of Cu(I)IL$_n$, where L= a nitrogen donor ligand and in particular to find correlations between structure and thermochromic emission behaviour, a number of compounds of formula CuIL$_n$ where n= 1, 1.5, 2, were synthesized. Emission spectral measurements have been carried out at room temperature as well as at liquid nitrogen temperature along with single crystal X-ray structure determination at room temperature. From this investigation, it has been posssible to make tentative identification of specific structural motifs leading to excited states populated at low temperature. The investigation has led to confirmation of certain ideas prevailing in literature and it has been possible to refute a number of hypotheses which were put forth without significant structural and emission data.

To identify the role of a crystallographic symmetry element in the temperature dependent luminescence of cubic systems, mixed ligand complexes of the type $Cu_4I_4L_2L'_2$ were prepared and their single crystal X-ray structures determined; the emission characteristics at room temperature and low temperature were studied. It has been observed that when acetonitrile is used as the solvent for reactions of CuI, the solvent often ends up coordinated as a ligand. This behavior was used to advantage in preparing mixed ligand systems. The mixed ligand complexes were synthesized by partial ligand substitution reaction of CuI(acetonitrile), by a suitable second ligand L'. Mixed ligand systems eliminate the possibility of a $\bar{4}$ symmetry element relating all Cu-L bonds. The second ligands, L', were aniline derivatives, p-toluidine(p-tld) and p-chloroaniline(p-ClAn). Attempts to prepare compounds with L' having electron withdrawing groups on the aromatic ring were not successful under similar synthetic conditions, probably due to the reduced electron donating capability of the nitrogen donor atom. An electron withdrawing group at the para position of the ring, acts by resonance to attenuate the presence of the electron pair at the donor nitrogen atom and thus its ability to coordinate to the metal atom.

The compound $Cu_4I_4(CH_3CN)_2(p\text{-tld})_2$ (I) crystallizes in a distorted cubic format in the triclinic space group $P\bar{1}$ (Table I). The projection view of the molecule is shown in Figure 1. The molecule does not have any internal crystallographic symmetry element relating Cu-N bonds. Coordination at the copper atoms is tetrahedral with each copper bonded to three iodide atoms and a molecule of ligand, either CH_3CN or p-tld. The repetition of the most common motif observed for CuI

TABLE I

CRYSTAL DATA FOR $(Cu_4I_4(\text{p-toluidine})_2(\text{acetonitrile})_2)$ (I)

Formula	$Cu_4I_4C_{18}H_{24}N_4$
M.W.	1058.22 g $mole^{-1}$
<u>a</u>	14.274(5) Å
<u>b</u>	7.587(2)
<u>c</u>	14.239(5)
α	88.612(25)°
β	110.067(25)
γ	88.704(25)
V	1447.12(77) $Å^3$
F(000)	976
μMoK_α	71.478 cm^{-1}
λMoK_α	0.71069 Å
D_{cal}	2.428 g cm^{-3}
Z	2
Meas refl	7665
Obs refl	3643
R	5.8%
R_w	7.5%
Space group	$P\bar{1}$ (Triclinic)
Octants measr	±h, ±k, +l

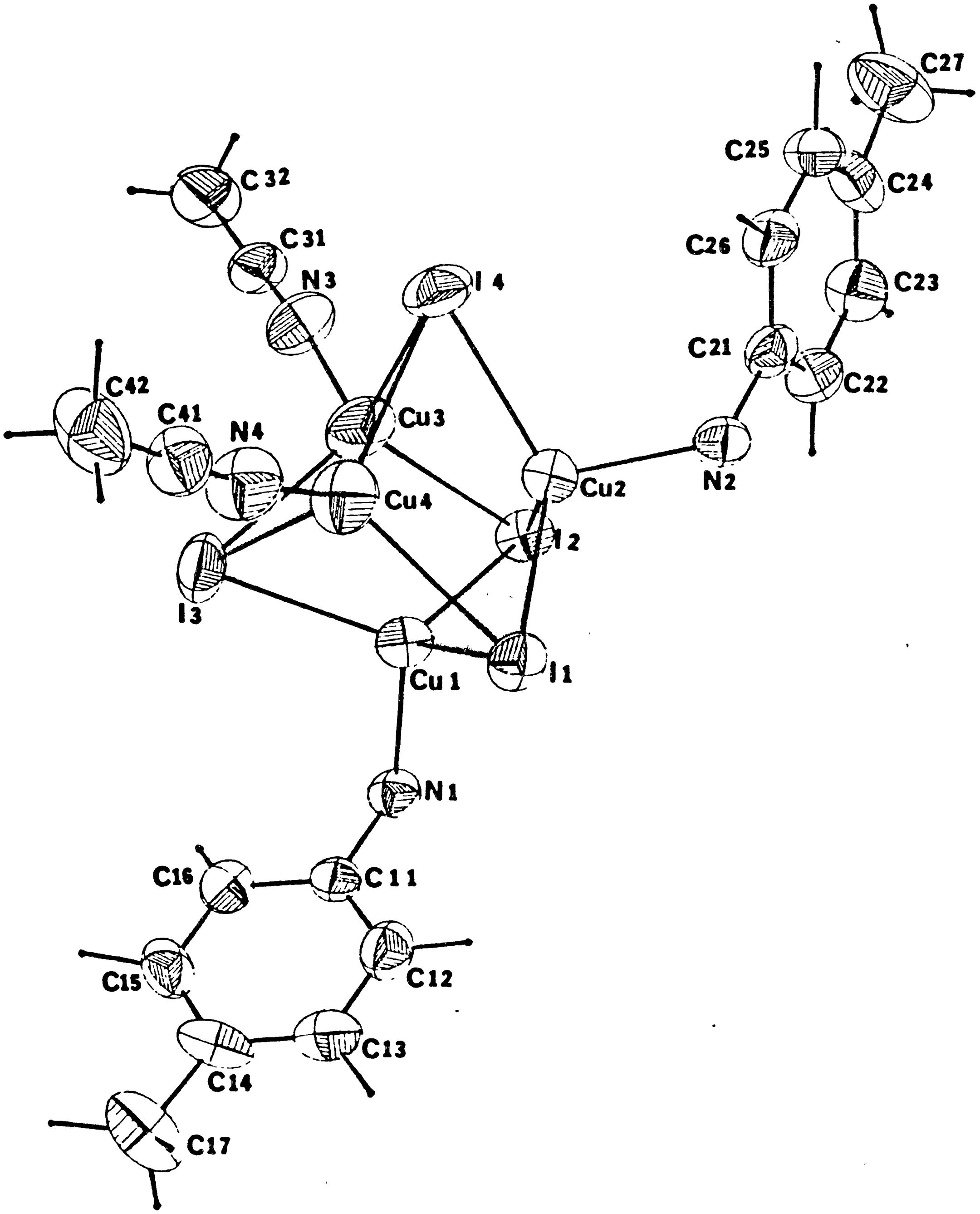

Figure 1. Projection View of I

compounds, the Cu_2I_2 rhomb, can be seen in Figure 1. Two of the rhombs share all edges to form the distorted cube. The compound shows a Cu-I separation of 2.657(2) Å to 2.726(2) Å and a Cu-Cu separation of 2.664(3) to 2.730(3) Å. The angles, I-Cu-I vary from 110.51(7)° to 117.38(8)° and the angles Cu-I-Cu average 60.24(7)°. Each copper is bonded to a nitrogen atom at a distance of 2.09(1) (for the p-tld) and 1.96(2) Å (for CH_3CN). The complete listings of bond distances and angles, positional parameters, and anisotropic thermal parameters are presented in Table numbers II , III and IV respectively.

The mixed ligand complex with L=p-ClAn and L'= CH_3CN, $(Cu_2I_2(p\text{-}ClAn)(CH_3CN))_2$ (II), also has a distorted cubic structure (Figure 2). The compound crystallizes in the orthorhombic space group C2/c (Table V). Unlike the p-tld compound (I), this molecule has a two fold rotation axis passing through opposite faces of the cube, relating the two halves of the cubic cluster. The crystallographic two fold symmetry element makes the copper-ligand bonds equivalent in pairs, that is, acetonitrile bound copper atoms are equivalent to each other, so also the bonds between the second pair of copper atoms and the ligated p-ClAn ligands. Cu-L bond distances average 2.13(3) Å for the p-ClAn ligand and 1.99(2) Å for the CH_3CN ligand. Cu-Cu and Cu-I average distances are 2.682(7) Å and 2.690(6) Å respectively. Tables VI, VII and VIII summarize bond distances and angles, positional parameters, and an-

TABLE II

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR (Cu_4I_4 (p-toluidine)$_2$(acetonitrile)$_2$) (I)

Cu1-I1	2.657(2)	I1-Cu1-I2	110.51(7)
Cu1-I2	2.726(2)	I1-Cu2-I2	110.56(6)
Cu2-I1	2.726(2)	I3-Cu3-I4	115.18(9)
Cu2-I2	2.656(2)	I3-Cu4-I4	115.30(9)
Cu3-I3	2.662(3)	I1-Cu1-I3	117.38(8)
Cu3-I4	2.717(3)	I2-Cu1-I3	112.30(8)
Cu4-I3	2.715(3)	I1-Cu2-I4	112.08(8)
Cu4-I4	2.659(2)	I2-Cu2-I4	117.27(8)
Cu1-I3	2.625(3)	I2-Cu3-I4	110.86(10)
Cu2-I4	2.620(3)	I2-Cu3-I3	110.28(8)
Cu3-I2	2.754(3)	I1-Cu4-I3	111.12(10)
Cu4-I1	2.756(3)	I1-Cu4-I4	109.91(9)
Cu1-Cu2	2.730(2)	Cu1-I1-Cu2	60.93(6)
Cu3-Cu4	2.664(3)	Cu1-I2-Cu2	60.95(5)
Cu1-Cu3	2.721(3)	Cu3-I3-Cu4	59.39(7)
Cu1-Cu4	2.672(3)	Cu3-I4-Cu4	59.40(7)
Cu2-Cu3	2.679(3)	Cu1-I1-Cu4	59.12(7)
Cu2-Cu4	2.730(3)	Cu1-I2-Cu3	59.53(6)
Cu1-N1	2.09(1)	Cu2-I1-Cu4	59.74(7)
Cu2-N2	2.09(1)	Cu2-I2-Cu3	59.32(7)
Cu3-N3	1.96(2)	Cu1-I3-Cu3	61.95(8)
Cu4-N4	1.95(2)	Cu1-I3-Cu4	60.03(7)
N1-C11	1.43(2)	Cu2-I4-Cu3	60.23(7)

TABLE II (Continued)

N2-C21	1.44(2)	Cu2-I4-Cu4	62.28(8)
C11-C12	1.38(2)	Cu1-N1-C11	118.0(9)
C11-C16	1.38(2)	Cu2-N2-C21	116.6(9)
C21-C22	1.40(2)	Cu3-N3-C31	172(2)
C21-C26	1.38(2)	Cu4-N4-C41	171(2)
C12-C13	1.38(2)	N3-C31-C32	179(2)
C15-C16	1.40(2)	N4-C41-C42	179(2)
C22-C23	1.37(2)		
C25-C26	1.40(2)		
C13-C14	1.38(3)		
C14-C15	1.38(2)		
C23-C24	1.37(2)		
C24-C25	1.37(2)		
C14-C17	1.49(2)		
C24-C27	1.51(2)		
N3-C31	1.11(2)		
N4-C41	1.15(2)		
C31-C32	1.45(3)		
C41-C42	1.44(3)		

TABLE III

POSITIONAL PARAMETERS FOR $(Cu_4I_4(\text{p-toluidine})_2(\text{Acetonitrile})_2)$ (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.8091(1)	0.0413(1)	0.4994(1)
I2	1.0005(1)	0.4584(1)	0.6809(1)
I3	0.6743(1)	0.4661(2)	0.6249(1)
I4	0.8750(1)	0.0341(2)	0.8256(1)
Cu1	0.8161(1)	0.3718(2)	0.5563(1)
Cu2	0.9438(1)	0.1279(2)	0.6839(1)
Cu3	0.8531(2)	0.3752(3)	0.7569(2)
Cu4	0.7430(2)	0.1255(3)	0.6468(2)
N1	0.7996(8)	0.5482(15)	0.4362(8)
N2	1.0625(9)	-0.0503(16)	0.6994(8)
N3	0.8711(12)	0.5097(20)	0.8777(11)
N4	0.6224(12)	-0.0070(21)	0.6282(12)
C11	0.7098(10)	0.5441(17)	0.3506(10)
C12	0.7044(12)	0.4306(20)	0.275)(11)
C13	0.6168(4)	0.4221(23)	0.1952(12)
C14	0.5318(14)	0.5191(22)	0.1904(11)
C15	0.5385(12)	0.6321(21)	0.2666(13)
C16	0.6268(11)	0.6441(18)	0.3480(11)
C17	0.4340(16)	0.5006(32)	0.1090(19)
C21	1.1480(11)	-0.0418(17)	0.7899(10)
C22	1.2255(12)	0.0718(21)	0.7947(12)

TABLE III (Continued)

C23	1.3047(11)	0.0752(22)	0.8832(11)
C24	1.3091(13)	-0.0190(21)	0.9677(13)
C25	1.2331(13)	-0.1320(21)	0.9615(11)
C26	1.1515(12)	-0.1442(18)	0.8733(12)
C27	1.3924(19)	-0.0018(32)	1.0674(15)
C31	0.8700(13)	0.5827(21)	0.9438(11)
C32	0.8702(18)	0.6763(31)	1.0309(13)
C41	0.5545(12)	-0.0833(22)	0.6296(13)
C42	0.4686(14)	-0.1769(21)	0.6314(18)
H121	0.7629	0.3510	0.2797
H131	0.6161	0.3372	0.1396
H151	0.4786	0.7034	0.2833
H161	0.6359	0.7386	0.3924
H171	0.3614	0.5408	0.1168
H172	0.4342	0.5678	0.0468
H173	0.4266	0.3755	0.0888
H221	1.2230	0.1458	0.7358
H231	1.3630	0.1564	0.8826
H251	1.2374	-0.2096	1.0223
H261	1.0973	-0.2279	0.8692
H271	1.3785	-0.0664	1.1244
H272	1.4588	-0.0434	1.0641
H273	1.4037	0.1278	1.0839
H321	0.8994	0.7906	1.0303
H322	0.8029	0.6938	1.0321

TABLE III (Continued)

H323	0.9056	0.6128	1.0808
H421	0.4766	-0.2773	0.6864
H422	0.4181	-0.0925	0.6374
H423	0.4415	-0.2322	0.5668

TABLE IV

ANISOTROPIC THERMAL PARAMETERS FOR (Cu$_4$I$_4$(p-Toluidine)$_2$ (Acetonitrile)$_2$) (I)

ATOM	U11	U22	U33	U12	U13	U23
I1	493(5)	476(5)	388(4)	-65(4)	130(4)	-179(3)
I2	459(5)	472(5)	430(5)	-181(4)	139(4)	-64(3)
I3	575(6)	662(6)	759(7)	138(5)	387(5)	4(5)
I4	832(8)	655(6)	523(6)	2(5)	397(5)	138(5)
Cu1	524(10)	529(10)	418(9)	-7(8)	167(8)	14(7)
Cu2	476(10)	529(10)	457(9)	21(7)	163(8)	3(7)
Cu3	903(16)	708(13)	475(11)	-35(11)	275(10)	-233(9)
Cu4	535(11)	716(13)	824(15)	-277(10)	284(10)	-23(11)
N1	42(6)	46(6)	40(6)	-8(4)	16(5)	1(4)
N2	44(6)	52(7)	31(6)	-2(5)	9(5)	-8(5)
N3	90(11)	66(9)	56(8)	-11(8)	35(8)	-24(7)
N4	68(10)	69(9)	77(10)	-24(7)	32(8)	2(7)
C11	47(8)	39(7)	36(7)	2(6)	17(6)	9(5)
C12	59(9)	48(8)	57(8)	8(6)	28(7)	1(6)
C13	67(11)	70(10)	38(8)	-7(8)	15(8)	-2(7)
C14	71(10)	57(9)	36(8)	-5(8)	-4(7)	9(6)
C15	49(8)	54(9)	66(10)	15(7)	21(7)	24(8)
C16	55(8)	39(7)	49(8)	1(6)	24(7)	1(5)
C17	64(12)	95(15)	92(16)	5(10)	-6(11)	6(12)
C21	53(8)	41(7)	39(7)	0(6)	21(6)	-8(5)
C22	55(9)	62(9)	56(9)	1(7)	30(7)	13(7)

TABLE IV (Continued)

C23	45(8)	62(9)	60(9)	-13(6)	12(7)	-4(7)
C24	57(10)	48(8)	57(10)	16(7)	3(8)	0(7)
C25	71(10)	54(9)	36(7)	12(7)	21(7)	8(6)
C26	61(9)	37(7)	60(9)	-13(6)	12(7)	-4(7)
C27	105(17)	94(15)	55(11)	13(12)	-20(11)	-3(10)
C31	73(11)	54(9)	36(7)	12(7)	21(7)	8(6)
C32	107(16)	90(14)	42(9)	29(12)	13(10)	-22(9)
C41	53(9)	53(9)	67(10)	-5(7)	24(8)	5(7)
C42	44(10)	91(14)	99(16)	-13(9)	9(10)	26(12)

Anisotropic thermal parametrs in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^*$$

$$+2U13hla^*c^*+2U23klb^*c^*) \times 10^4 \text{ for Cu and I}$$

$$\times 10^3 \text{ for C and N.}$$

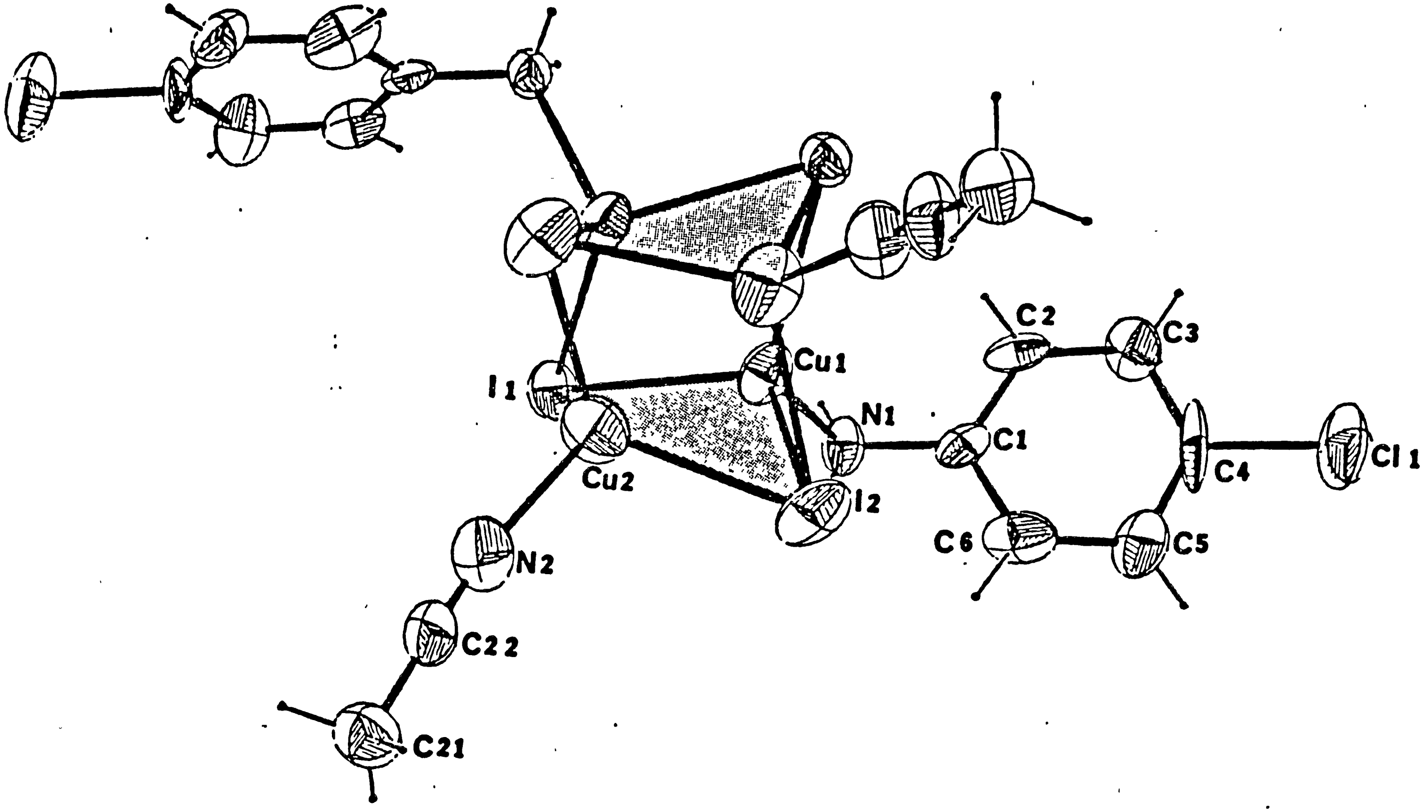

Figure 2. Projection View of II

TABLE V

CRYSTAL DATA FOR $(Cu_2I_2$(p-chloroaniline) (acetonitrile)$)_2$ (II)

Formula	$Cu_2I_2C_8H_9N_2Cl$
M.W.	549.526 g $mole^{-1}$
<u>a</u>	15.952(6) Å
<u>b</u>	23.714(11)
<u>c</u>	7.596(3)
$\alpha = \gamma$	90.0°
β	88.00(3)
V	2871.8(22) $Å^3$
F(000)	2016
μ MoK_{α}	73.91 cm^{-1}
λ MoK_{α}	0.71069 Å
D_{cal}	2.54 g cm^{-3}
Z	8
Measr refl	3107
Obs refl	1315
R	7.3%
R_w	9.5%
Space group	C2/c (Monoclinic)
Octants measr	±h, +k, +l

TABLE VI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR (Cu_2I_2 (p-chloroaniline)(acetonitrile)) (II)

Cu1-I1	2.657(5)	I1-Cu1-I1'	110.2(2)
Cu1-I1'	2.737(5)	I2-Cu2-I2'	115.4(2)
Cu2-I2	2.676(6)	I2-Cu1-I1	117.3(2)
Cu2-I2'	2.679(6)	I2-Cu1-I1'	113.7(2)
Cu1-I2	2.615(5)	I1-Cu2-I2	110.8(2)
Cu2-I1	2.775(6)	I1-Cu2-I2'	110.5(2)
Cu1-Cu1'	2.716(6)	Cu1-I1-Cu1'	60.4(1)
Cu2-Cu2'	2.650(8)	Cu2-I2-Cu2'	59.1(2)
Cu1-Cu2	2.656(7)	Cu1-I1-Cu2	58.5(2)
Cu1-Cu2'	2.708(7)	Cu1-I1-Cu2	60.0(2)
Cu1-N1	2.13(3)	Cu1-N1-C1	115(2)
Cu2-N2	1.99(4)	Cu2-N2-C22	169(3)
N1-C1	1.44(4)	N2-C22-C21	178(4)
C1-C2	1.45(4)		
C1-C6	1.41(5)		
C2-C3	1.36(5)		
C5-C6	1.41(6)		
C3-C4	1.45(6)		
C4-C5	1.42(6)		
C4-Cl1	1.75(3)		
N2-C22	1.16(6)		
C22-C21	1.38(6)		

TABLE VII

POSITIONAL PARAMETERS FOR (Cu_2I_2(p-Chloroaniline) (Acetonitrile)) (II)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.4061(1)	0.4115(1)	0.5425(3)
I2	0.3960(2)	0.2773(1)	0.9622(4)
Cu1	0.4352(3)	0.3806(2)	0.8709(6)
Cu2	0.4436(3)	0.3006(2)	0.6260(7)
Cl1	-0.0033(6)	0.4161(6)	1.0005(18)
N1	0.3680(15)	0.4315(11)	1.0584(35)
N2	0.3739(21)	0.2490(16)	0.4853(47)
C1	0.2778(19)	0.4298(13)	1.0465(38)
C2	0.2337(23)	0.4656(13)	0.9254(41)
C3	0.1492(24)	0.4629(15)	0.9091(52)
C4	0.1055(20)	0.4211(19)	1.0176(59)
C5	0.1443(23)	0.3859(16)	1.1417(50)
C6	0.2324(25)	0.3892(15)	1.1474(47)
C21	0.3095(24)	0.1692(16)	0.3136(52)
C22	0.3435(24)	0.2131(18)	0.4062(56)
H2	0.2680	0.4920	0.8572
H3	0.1199	0.4883	0.8363
H5	0.1098	0.3602	1.2121
H6	0.2638	0.3630	1.2150
H11	0.3861	0.4705	1.0370
H12	0.3825	0.4197	1.1728

TABLE VII (Continued)

H211	0.3144	0.1767	0.1893
H212	0.2490	0.1653	0.3522
H213	0.3369	0.1315	0.3467

TABLE VIII

ANISOTROPIC THERMAL PARAMETERS FOR(Cu_2I_2 (p-Chloroaniline)(Acetonitrile)) (II)

ATOM	U11	U22	U33	U12	U13	U23
I1	39(1)	44(1)	51(1)	2(1)	-7(1)	9(1)
I2	71(2)	36(1)	80(2)	-9(1)	21(1)	12(1)
Cu1	40(3)	42(2)	61(3)	2(2)	10(2)	-3(2)
Cu2	66(4)	56(3)	85(4)	-18(2)	-4(3)	-21(3)
Cl1	30(6)	120(11)	119(10)	6(6)	10(5)	4(9)
N1	3(2)	4(2)	5(2)	0(1)	0(1)	-1(1)
N2	5(2)	8(2)	7(2)	0(2)	-1(2)	0(2)
C1	4(2)	4(2)	2(2)	-1(1)	1(1)	-1(1)
C2	6(2)	3(2)	3(2)	0(2)	1(2)	1(1)
C3	4(2)	4(2)	8(3)	1(2)	0(2)	1(2)
C4	1(2)	10(4)	10(3)	1(2)	0(2)	-6(3)
C5	4(2)	6(2)	6(2)	1(2)	1(2)	-1(2)
C6	8(3)	4(2)	5(2)	2(2)	1(2)	1(2)
C21	8(3)	5(2)	6(2)	-1(2)	-1(2)	-1(2)
C22	4(2)	8(3)	8(3)	1(2)	-1(2)	-2(2)

Anisotropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^*+2U13hla^*c^*+2U23klb^*c^*)) \times 10^3$$

for Cu, I and Cl; X 10^2 for C and N.

isotropic thermal parameters.

Both compounds I and II show distorted cubic format, however, one has no element of symmetry present in the molecule whereas the other has an internal two fold rotation axis. Neither of them has a $\bar{4}$ symmetry element. The copper ligand separations are comparable in I and II and comparable to those found in other nitrogen donor cubic $(CuIL)_4$ systems like L= py(27), piperidine (26), morpholine(25), but shorter than those in the $(CuX(Et_3P)_4$ series, where X=Cl, 3.211(2) Å; X=Br, 3.184(2) Å (66,65) X=I, 2.927(2) Å (66). These Cu-Cu distances are indicative of only weak interactions. The Cu-I distances are relatively unchanging in $(CuIL)_4$ systems. The angle at the Cu remains constant despite variations in the space filling character of the ligand and variation in the hybridization of the nitrogen donor atom, e.g., sp for acetonitrile sp^2 for pyridine and sp^3 for aniline derivatives.

Emission spectera of I and II were measured by exciting the compounds at λ= 365 and 370 nm respectively. Emission was broad and featureless over the range 259.5 to 14.9 K as seen from the spectra (Figures 3 and 4). The emission maxima were at 586 nm for I and 630 nm for II and a minor shoulder in the 420-450 nm range at low temperature in each case. On cooling, increase in emission intensity and sharpening of the λem,max peaks were noted. In both the cases, the emission maximum was strongly

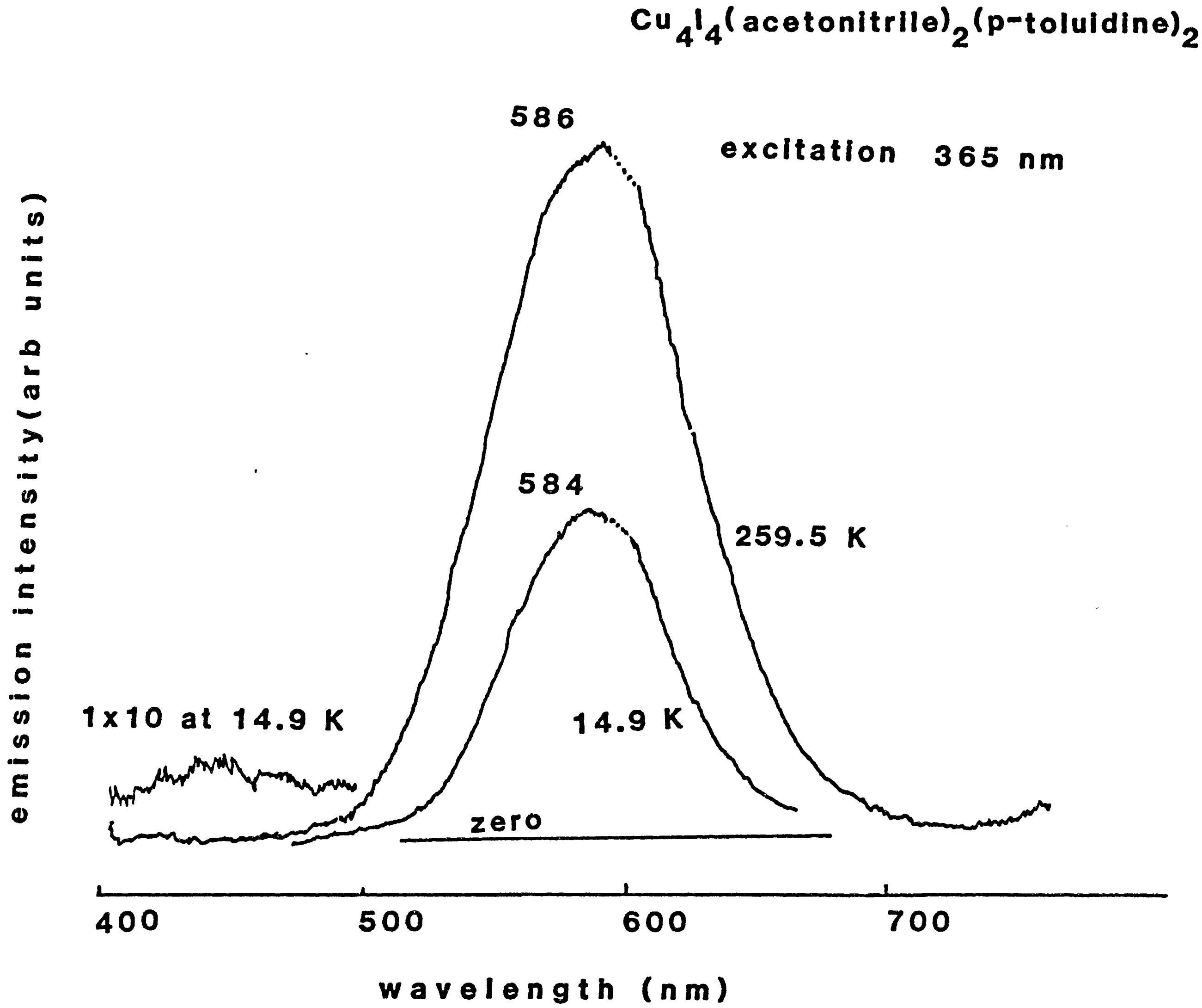

Figure 3. Emission Spectra of I

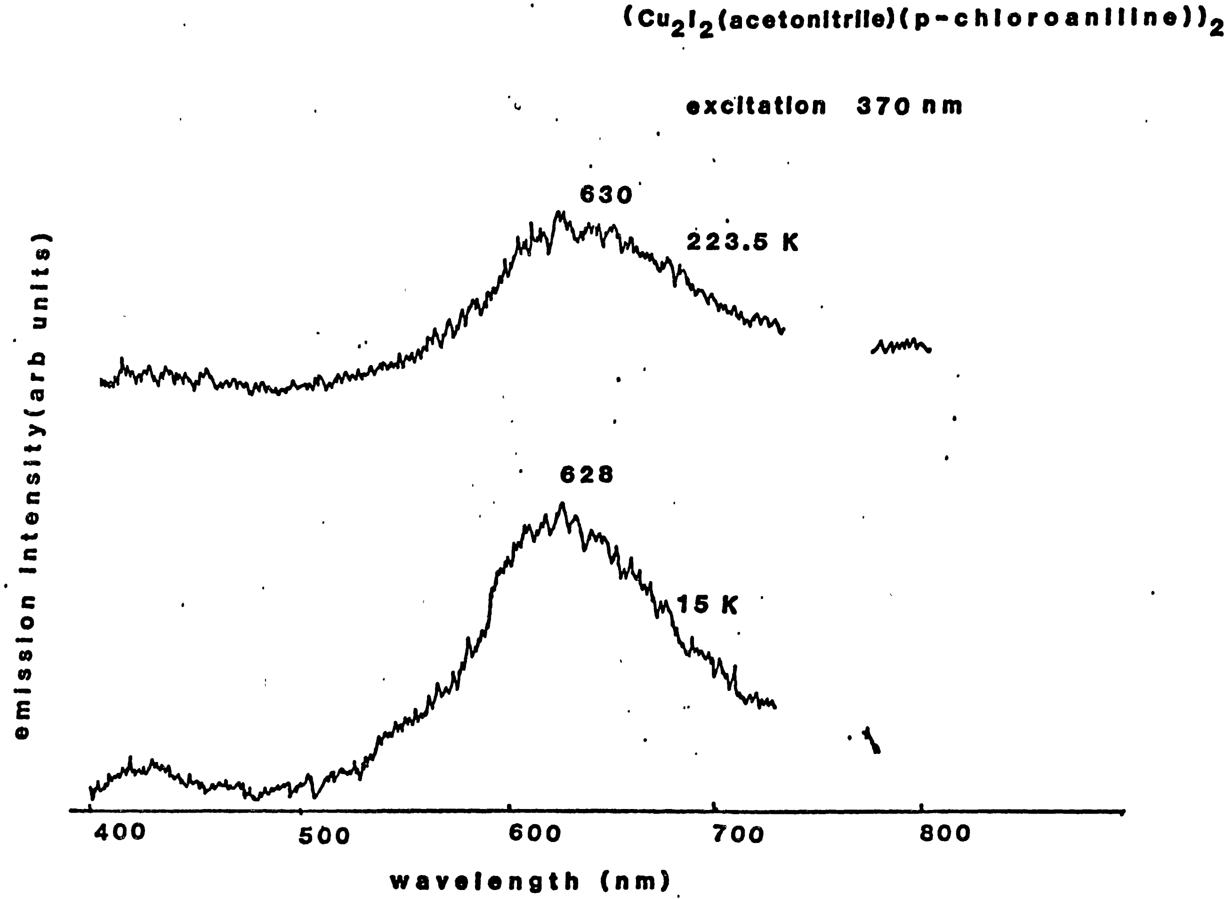

Figure 4. Emission Spectra of II

Stokes shifted from the absorption maximum. Only trivial shifts of the emission maxima with temperature were observed. From these results, it can be concluded that the presence or absence of a crystallographic symmetry element in the cubic cluster, $(CuIL)_4$, is not the deciding factor in the thermochromicity of the systems.

As discussed, the solid state emission spectra for Cu(I) systems can be assigned to ligand centered, MLCT, or metal centered transitions. For ligand centered emission, the fine structure of the uncoordinated ligand appears, shifted by less than 1000 cm^{-1} from that of the uncoordinated ligand. Therefore, neither the acetonitrile nor the substituted aniline moieties can be responsible for the emission observed. The spectra must then be interpreted in terms of the MLCT or d $\rightarrow$ pi^* transitions, in both cases only acetonitrile offers suitably situated pi^* levels for MLCT. These pi^* orbitals are of considerably higher energy than those of pyridine. These two systems display further excitation possibilities due to the presence of metal atoms in close proximity of each other. The Cu-Cu distances in I and II which are slightly longer than the Cu-Cu metallic distance of 2.47 Å, therefore, there is some involvement of interacting metal centers. Cu-Cu distances of 2.8 Å or less can be considered as indicative of interactive metal-metal atoms. $(CuIL)_4$ systems having a Cu-Cu separation of 2.8 Å or less show emission in the 550-628 nm range. Therefore, assignment of emission in this range to metal-metal interaction seems reasonable. Because the CuI distances seen in I and II, are comparable to those in the CuI crystal, for which emission has been assigned to electron movement in Cu-I bonds, the DAP phenomenon arises. Thus while molecules I and II have the capability of emitting from excited states due to the ligand alone, to MLCT interactions between metal and acetonitrile, to transition on isolated metal centers, to coupled metal centers or to Cu-I DAP phenomenon(67), the emission is to be regarded as derived from MLCT and metal metal interactions, the population of the excited states changing with temperature. The presence or absence of symmetry element in the thermochromism of CuI systems does not seem to be of relevance.

The literature report that the inclusion of a crown ether in the cell influences (18) fluorescence, was investigated. $(CuICH_3CN)_x$ (III), was prepared, which has been purported to luminesce yellow at 298 K but green at 77 K. This compound exhibits a polymeric pleated sheet structure as can be seen from the projection view of the molecule (Figure 5). III crystallizes in the orthorhombic space group $Pbn2_1$ (Table IX). The pleated double chain structure shown by III is similar to that of $(CuX(CH_3CN))_x$, $(CuX\ benzonitrile)_x$ and $(CuX\ trans\text{-}acrylonitrile)_x$; where X= Br or Cl(31-33,68). In the pleated double chain structure, parallelograms of alternating copper and iodide atoms share opposite sides in infinite

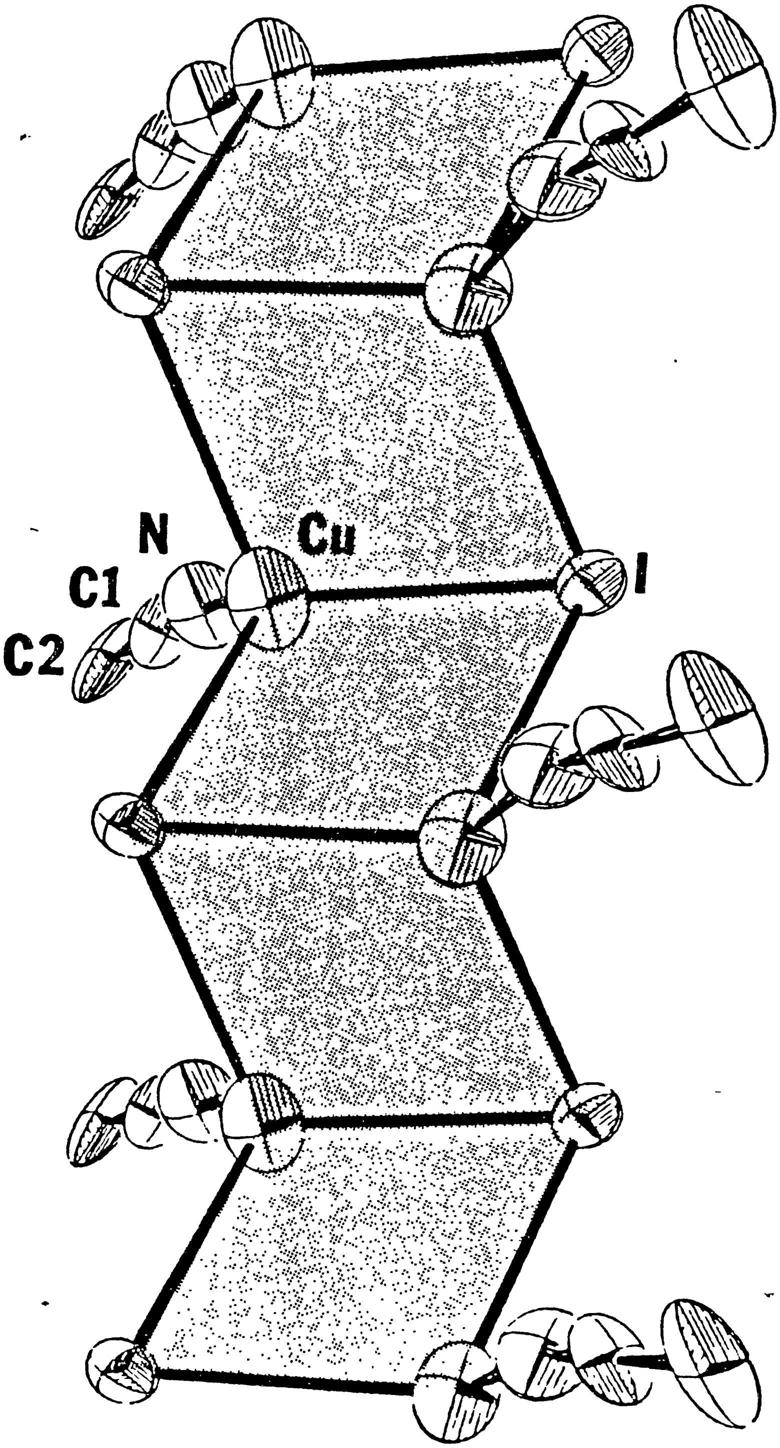

Figure 5. Projection View of III

TABLE IX

CRYSTAL DATA FOR $(CuI(CH_3CN))_x$ (III)

Formula	$CuIC_2H_3N$
M.Wt.	231.503 g mole^{-1}
a	13.618(8) Å
b	8.742(2)
c	4.298(2)
α	90.0(0)°
β	90.0(0)
γ	90.0(0)
V	511.6(5) Å^3
F(000)	416
μ MoK_α	100.869 cm^{-1}
λ MoK_α	0.71069 Å
D_{cal}	3.00 g cm^{-3}
Z	4
Measur. Refl.	1228
Obs. Refl.	759
R	8.1%
Rw	11.4%
Space Group	$Pbn2_1$ (Orthorhombic)
Octants Measur.	+h,+k,+l

series. Each copper atom is tetrahedrally bonded to three iodide atoms and a nitrogen donor acetonitrile molecule. The Cu-I distances average 2.658(8) Å. The Cu-Cu distance across the parallelogram is 3.022(10) Å, whereas the Cu-Cu distance across the fold of the chain is longer, 4.358(4) Å. The larger Cu-Cu distance across the folds is manifested in a I-I distance of 4.298(2) Å, shorter than the I-I distances across the four sided figure, 4.358(4) Å. Like the Cu-I distance, the Cu-N distance does not change markedly (1.97(2) Å). (Complete list of bond distances and angles; Table X. Positional parameters and anistropic thermal parameters; Tables XI and XII respectively)

Contradictory to what has been reported, the dry crystals of III do not show a change in emission wave length upon cooling, although the compound is strongly luminescent. The literature observation probably stems from measurement of luminescence of a crystal stabilized in its own mother liquor, a tactic used to stabilize air sensitive, unstable materials. So the crystal luminesces only one color at room temperature and at low temperature; however, the lowered temperature causes the mother liquor to freeze and the frozen glass emits at a different wave length, which is blue shifted. The luminescence of the frozen mother liquor obscures the emission of the crystal. Thawing the solution reverses the phenomenon.

CuI and acetonitrile form a different compound

TABLE X

BOND DISTANCES(Å) AND BOND ANGLES(°) FOR $(CuICH_3CN)_x$ (III)

I1 - Cu1(1)	2.630(5)	Cu1(1)-I1-Cu1(2)	69.0(2)
I1 - Cu1(2)	2.704(10)	Cu1(1)-I1-Cu1(3)	69.9(2)
I1 - Cu1(3)	2.641(10)	Cu1(2)-I1-Cu1(3)	107.0(4)
I1 - I1(4)	4.358(4)	I1-Cu1(1)-I1(4)	111.5(3)
I1 - I1(6)	4.298(2)	I1-Cu1(1)-I1(5)	109.5(3)
Cu1(1)-Cu1(3)	3.022(10)	I1(4)-Cu1-I1(5)	107.0(3)
Cu1(1)-Cu1(7)	4.298(13)	I1-Cu1(1)-N1(1)	113.7(8)
Cu1 - N1	1.97(2)	I1(4)-Cu1(1)-N1(1)	111.4(6)
N1 - C1	1.12(3)	I1(5)-Cu1(1)-N1(1)	103.2(6)
C1 - C2	1.50(3)	Cu1-N1-C1	175.2(9)
		N1-C1-C2	175.2(9)

Symmetry operations :

1 = 1.0+x, y, z

2 = 1.0-x, 1.0-y, -0.5-z

3 = 1.0-x, 1.0-y, 0.5+z

4 = 2.0-x, 1.0-y, -0.5+z

5 = 2.0-x, 1.0-y, 0.5+z

6 = x, y, 1.0+z

7 = 1.0+x, y, 1.0+z

TABLE XI

POSITIONAL PARAMETERS FOR $(CuICH_3CN)_x$ (III)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.8623(1)	0.4682(2)	0.3509( )
Cu1	0.0516(2)	0.4089(3)	0.3418(21)
N1	0.0826(17)	0.1896(21)	0.379(10)
C1	0.1027(16)	0.0648(21)	0.379(11)
C2	0.1350(18)	0.9025(26)	0.340(11)

TABLE XII

ANISOTROPIC THERMAL PARAMETERS FOR $(CuICH_3CN)_x$ (III)

ATOM	U11	U22	U33	U12	U13	U23
I1	36(1)	43(1)	28(0)	7(0)	-4(1)	4(1)
Cu1	50(2)	32(1)	66(2)	4(1)	8(4)	23(2)
N1	54(11)	34(8)	47(16)	3(8)	10(14)	24(15)
C1	37(10)	21(7)	44(18)	0(6)	-11(14)	19(12)
C2	47(13)	33(10)	69(19)	2(8)	-36(19)	-22(16)

Anisotropic thermal parameters in the form :

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

in the presence of dibenzo-18-crown-6 (db-18-C-6), which has been reported to exhibit thermochromic fluorescence. Structural elucidation of this compound, $((Cu_4I_4(CH_3CN)_4)$- db-18-c-6)(69), shows the compound to display the expected Cu_4I_4 pseudo-cubic structure with one acetonitrile molecule per copper atom (Figure 6). The average Cu-Cu distance, 2.770(5) Å is longer than that of other cubic clusters; e.g, 2.690(5) Å average for $(CuIpy)_4$. This distance is the largest observed for CuI complexes with nitrogen donor ligands. The atoms of this cluster are not related to each other by any crystallographic symmetry element. The crown ether has only second sphere interaction with the hydrogens of the coordinated acetonitrile and has no direct interaction with the copper atoms, contrary to what had been thought. Deformation of the cubic faces brings the copper atoms at opposite faces into closer proximity, which in turn pushes the iodides farther away from each other. Cu-I and Cu-N bonds are rather constant and are comparable with those of other structures. This compound has been reported to be thermochromic. The difference in luminescence behavior between the two compounds of CuI and acetonitrile, with and without the presence of crown ether, may stem from alteration of donicity of the nitrile nitrogen atom due to a second sphere interaction of the crown ether with the methyl hydrogens of the acetonitrile group.

Attempts were made to synthesize other compounds

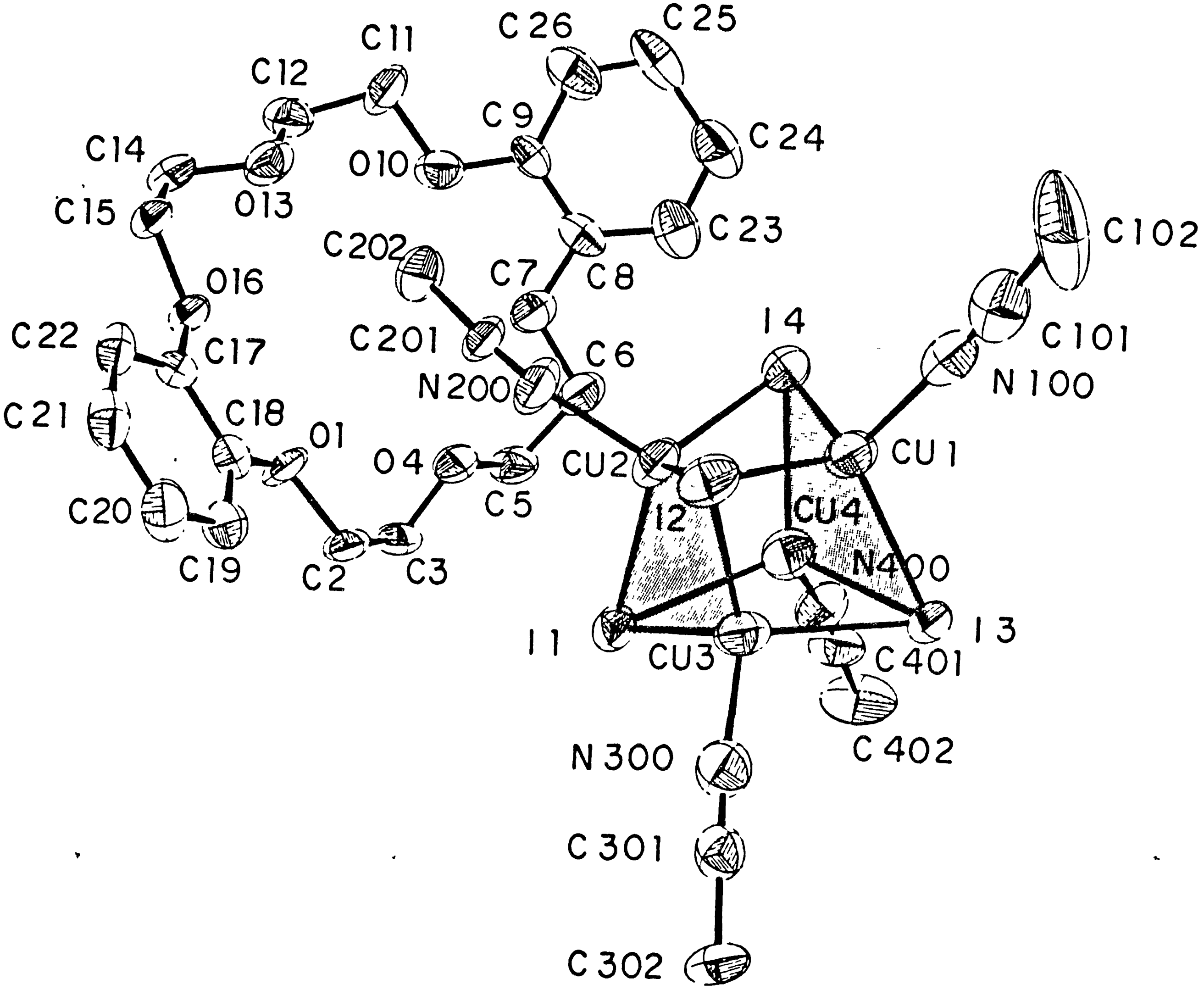

Figure 6. Projection View of XVII

of CuI and acetonitrile in presence of other 18-crown-6 polyethers. The two other crown ethers used in this series were dicyclohexano-18-crown-6 (dch-18-C-6) and unsubstituted 18-crown-6 (18-C-6). Surprisingly enough, even though the same synthetic conditions were employed, the compounds obtained were inclusion compounds, (18-crwn-6 $(CH_3CN)_2$) (IV) and (dicyclohexano-18-crown-6 $(CH_3CN)_2$) (V), with crown ether acting as host and the acetonitrile molecules as guests. Both the compounds are unstable and give off the trapped solvent molecules from the host lattice on exposure to air. Acetonitrile inclusion compounds of the crown ethers have been used by synthetic organic chemists to form the crystalline product for the purpose of purifying the synthesized crown ether(70). However, structural studies on both of these compounds have not been previously carried out.

The compound (18-C-6$(CH_3CN)_2$) (IV) crystallizes in the monoclinic space group $P2_1/n$ (Table XIII). A projection view of the molecule is shown in Figure 7. The solid state compound shows less disorder than the uncoordinated 18-C-6 because of less flexibilty. The insertion of the two acetonitrile molecules into the crystal lattice makes the host molecule more rigid and therefore, less disordered. The acetonitrile molecules are held inside the the crown ether cavity in a "needle-thread" arrangement (Figure 7) by dipole-dipole interaction. The nitrogen atoms of the acetonitrile molecules are more than 4.0 Å

TABLE XIII

CRYSTAL DATA FOR (18-crown-6(acetonitrile)$_2$) (IV)

Formula	$C_{16}H_{30}O_6N_2$
M.W.	346.423 g mole^{-1}
a	9.123(2) Å
b	8.522(2)
c	13.693(3)
$\alpha = \gamma$	90.0°
β	104.61(2)
V	1030.18(44) Å^3
F(000)	376
μ MoK$_\alpha$	0.794 cm^{-1}
λ MoK$_\alpha$	0.71069 Å
D_{cal}	1.117g cm^{-3}
Z	2
Meas refl	2902
Obs refl	625
R	10%
R_w	12.3%
Space group	$P2_1/n$ (Monoclinic)
Octants meas	±h, +k, +l

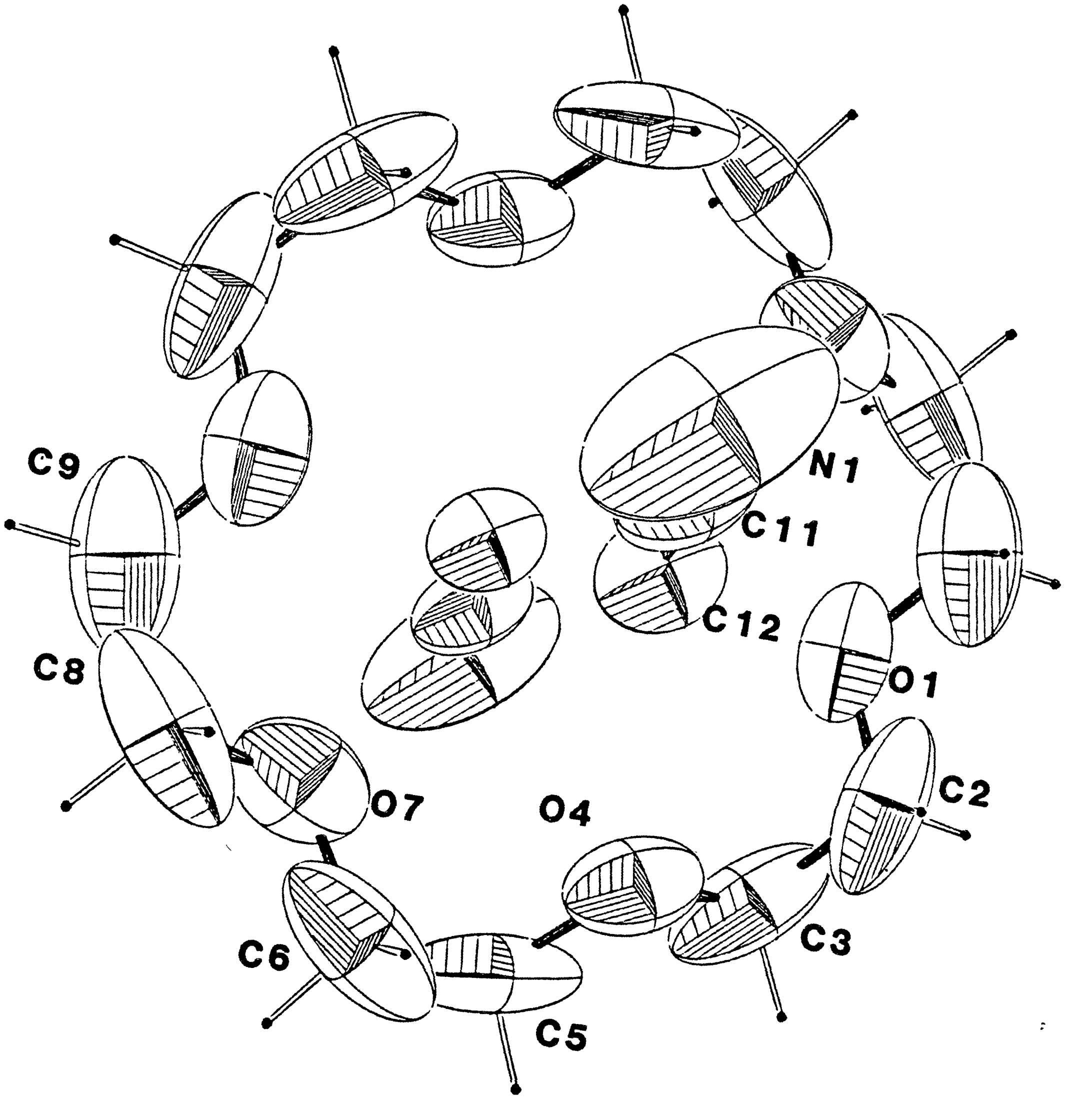

Figure 7. Projection View of IV

from any atom of the crown ether ring. The complete listing of bond distances and angles are presented in Table XIV and the positional parameters and anisotropic thermal parameters are listed in Tables XV and XVI.

(Dicyclohexano-18-crown-6 $(CH_3CN)_2$) (V) crystallizes in the triclinic space group $P\bar{1}$ (Table XVII). Like the other compound of this series (IV), the molecule has a center of symmetry relating one half of the molecule to the other half. As can be seen from the projection view of the molecule (Figure 8), the crown ether ring is more rigid and therefore more ordered compared to that of IV due to the presence of the cyclohexano bridges. This manifests itself in the thermal parameters of the atoms (Table XVIII). The cyclohexane rings have chair confirmation. Unlike the other inclusion compound, IV, the acetonitrile molecules do not thread the crown ether cavity, rather they lie on a plane oblique to the plane of the oxygen atoms of the host molecule. The separation between the acetonitrile nitrogen and the atoms of the crown ether being greater than 4.0 Å, thus in this case also, dipole-dipole interactions may be presumed to be the binding force between the host crown ether and the guest, acetonitrile molecules. (Bond distances and angles as well as atomic parametrs; Tables XIX and XX respectively)

The difference in behavior of the CuI with acetonitrile in presence of different crown ethers, resulting in the second sphere interaction compound

TABLE XIV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR (18-Crown-6 (Acetonitrile)$_2$) (IV)

O1-C2	1.39(3)	C2-O1-C9'	111(1)
O1-C9'	1.37(2)	C3-O4-C5	116(1)
O4-C3	1.41(2)	C6-O7-C8	114(1)
O4-C5	1.42(2)	N1-C11-C12	179(2)
O7-C6	1.40(2)	O1-C2-C3	110(1)
O7-C8	1.43(2)	O4-C3-C2	110(1)
N1-C11	1.12(2)	O4-C5-C6	110(1)
C11-C12	1.41(2)	O7-C8-C9	108(1)
C2-C3	1.44(2)	O1'-C9-C8	109(1)
C5-C6	1.49(3)		
C8-C9	1.42(3)		

Symmetry operation :

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

TABLE XV

POSITIONAL PARAMETERS FOR (18-Crown-6 (Acetonitrile)$_2$) (IV)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
O1	0.2867(9)	0.4229(9)	0.4669(9)
O4	0.0214(12)	0.4476(9)	0.3013(6)
O7	-0.2417(11)	0.6079(9)	0.3394(7)
N1	-0.1825(22)	0.0727(17)	0.5766(13)
C11	-0.1294(15)	0.1684(16)	0.5415(9)
C12	-0.0630(12)	0.2881(11)	0.4956(8)
C2	0.2664(17)	0.3531(15)	0.3729(18)
C3	0.1734(25)	0.4518(17)	0.2957(11)
C5	-0.0815(30)	0.54442(16)	0.2322(10)
C6	-0.2363(22)	0.5330(169	0.2495(17)
C8	-0.3854(19)	0.5962(20)	0.3633(16)
C9	-0.3720(19)	0.6707(20)	0.4584(20)
H21	0.3664	0.3369	0.3597
H22	0.2190	0.2492	0.3756
H31	0.2072	0.5591	0.3003
H32	0.1732	0.4099	0.2270
H51	-0.0466	0.6525	0.2408
H52	-0.0851	0.5084	0.1637
H61	-0.3086	0.5840	0.1931
H62	-0.2638	0.4226	0.2529
H81	-0.4625	0.6466	0.3094

TABLE XV (Continued)

H82	-0.4108	0.4856	0.3682
H91	-0.3158	0.7744	0.4567
H92	-0.4701	0.6953	0.4672

TABLE XVI

ANISOTROPIC THERMAL PARAMETERS FOR (18-Crown-6 $(\text{Acetonitrile})_2$) (IV)

ATOM	U11	U22	U33	U12	U13	U23
O1	92(6)	79(5)	158(8)	11(4)	46(6)	-2(6)
O4	150(7)	93(5)	74(5)	-24(5)	53(5)	2(4)
O7	115(7)	89(5)	106(6)	-22(5)	-4(6)	-3(5)
N1	385(24)	126(11)	247(16)	-91(13)	222(17)	-20(10)
C11	146(10)	81(9)	91(9)	-12(8)	50(8)	-28(7)
C12	113(8)	59(6)	92(7)	-25(6)	45(6)	4(5)
C2	115(10)	70(9)	256(21)	0(8)	131(13)	0(13)
C3	226(18)	87(10)	136(12)	-50(11)	140(13)	-27(8)
C5	268(219	93(10)	46(7)	-47(13)	-25(11)	-6(7)
C6	145(14)	72(9)	152(15)	-23(10)	-60(13)	45(10)
C8	72(9)	108(12)	217(19)	-19(9)	-30(12)	77(12)
C9	64(9)	108(12)	260(23)	0(9)	50(13)	21(14)

Anisotropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^*+2U13hla^*c^*+2U23klb^*c^*)) \times 10^3$$

TABLE XVII

CRYSTAL DATA FOR (dicyclohexano-18-crown-6 (acetonitrile)$_2$) (V)

Formula	$C_{24}H_{42}O_6N_2$
M.W.	454.606 g mole^{-1}
a	9.928(5) Å
b	7.074(2)
c	9.557(7)
α	81.31(4)^{o}
β	81.07(5)
γ	81.57(4)
V	650.28(64) Å^3
F(000)	248
μMoK_α	0.772 cm^{-1}
λMoK_α	0.71069 Å
D_{cal}	1.161 g mole^{-3}
Z	1
Meas refl	3723
Obs refl	1382
R	6.4%
R_w	7.8%
Space group	$P\bar{1}$ (Triclinic)
Octants meas	$\pm h$, $\pm k$, $+l$

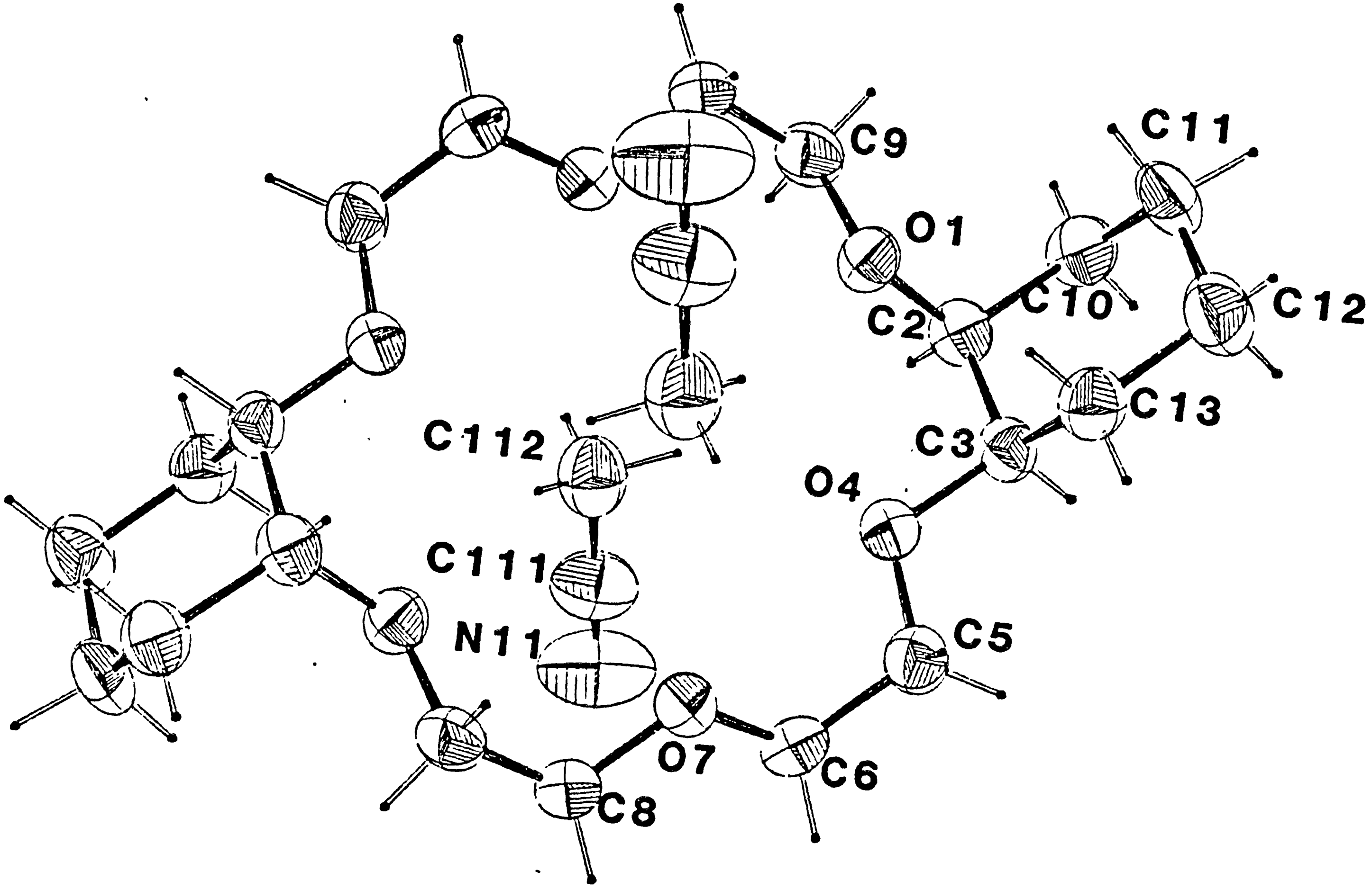

Figure 8. Projection View of V

TABLE XVIII

ANISOTROPIC THERMAL PARAMETERS FOR

(Dicyclohexano-18-Crown-6 (Acetonitrile)$_2$) (V)

ATOM	U11	U22	U33	U12	U13	U23
O1	37(1)	43(1)	53(1)	-6(1)	-7(1)	-12(1)
O4	45(1)	46(1)	44(1)	3(1)	-14(1)	-11(1)
O7	43(1)	57(2)	40(1)	-1(1)	-8(1)	-8(1)
N11	152(5)	93(4)	84(4)	-45(3)	16(3)	-23(3)
C111	94(4)	50(3)	65(3)	-23(3)	-5(3)	-11(2)
C112	61(3)	56(3)	77(4)	-8(2)	-18(3)	-5(3)
C2	39(2)	44(2)	46(2)	-13(2)	-8(2)	-2(2)
C3	28(2)	54(2)	40(2)	-6(2)	-5(1)	-3(2)
C5	51(39	42(2)	52(3)	1(2)	-15(29	-7(2)
C6	45(2)	42(2)	47(2)	0(2)	0(2)	-13(2)
C8	53(3)	52(3)	46(2)	5(2)	-11(2)	-18(2)
C9	56(3)	48(3)	51(39	-3(2)	-18(2)	-18(2)
C10	39(2)	65(3)	64(3)	-13(2)	-10(2)	-19(2)
C11	60(3)	83(3)	45(3)	-3(2)	-27(2)	-5(2)
C12	72(3)	58(3)	53(3)	-1(29	-23(3)	5(2)
C13	48(2)	43(2)	51(2)	-4(29	-8(2)	-3(2)

Anisotropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^*$$

$$+2U13hla^*c^*+2U23klb^*c^*))\ X10^3$$

TABLE XIX

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR (Dicyclohexano-18-Crown-6 (Acetonitrile)$_2$) (V)

O1-C2	1.435(5)	C2-O1-C9	114.6(4)
O1-C9	1.418(6)	C3-O4-C5	115.1(3)
O4-C3	1.418(6)	C6-O7-C8	112.7(3)
O4-C5	1.410(6)	N11-C111-C112	179.3(9)
O7-C6	1.411(6)	O1-C2-C3	106.8(4)
O7-C8	1.417(6)	O1-C2-C10	112.9(4)
N11-C111	1.120(8)	C3-C2-C10	109.6(4)
C111-C112	1.432(8)	O4-C3-C2	107.7(3)
C2-C3	1.514(6)	O4-C3-C13	114.2(4)
C2-C10	1.522(8)	C2-C3-C13	110.9(4)
C3-C13	1.520(6)	O4-C5-C6	110.2(4)
C5-C6	1.480(7)	O7-C6-C5	110.3(4)
C8-C9'	1.494(7)	O7-C8-C9'	109.8(4)
C10-C11	1.521(7)	O1-C9-C8'	109.2(4)
C11-C12	1.523(8)	C2-C10-C11	110.6(5)
C12-C13	1.514(8)	C10-C11-C12	111.8(4)
		C11-C12-C13	110.9(4)
		C3-C13-C12	111.3(4)

Symmetry operation :

' = -x, -y, -z.

TABLE XX

POSITIONAL PARAMETERS FOR (Dicyclohexano-18-Crown-6 (Acetonitrile)$_2$) (V)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
O1	-0.1750(3)	-0.0242(4)	-0.2254(3)
O4	-0.2669(3)	0.1740(4)	0.0035(3)
O7	-0.0921(3)	0.2573(4)	0.1916(3)
N11	0.2104(7)	0.2728(8)	-0.3763(6)
C111	0.1482(7)	0.2530(8)	-0.2680(7)
C112	0.0690(6)	0.2252(9)	-0.1296(7)
C2	-0.3181(4)	-0.0035(6)	-0.1684(5)
C3	-0.3486(4)	0.1861(6)	-0.1075(4)
C5	-0.2991(5)	0.3256(7)	0.0882(5)
C6	-0.2368(5)	0.2721(7)	0.2218(5)
C8	-0.0271(5)	0.2156(8)	0.3166(5)
C9	-0.1252(5)	-0.2028(7)	-0.2768(5)
C10	-0.4118(5)	-0.0032(8)	-0.2804(6)
C11	-0.3929(6)	0.1644(8)	-0.3986(8)
C12	-0.4167(6)	0.3570(8)	-0.3402(6)
C13	-0.3277(5)	0.3544(7)	-0.2246(5)
H1121	0.122(4)	0.148(6)	-0.062(4)
H1122	0.050(4)	0.339(6)	-0.105(4)
H1123	-0.001(4)	0.191(6)	-0.143(4)
H21	-0.334(4)	-0.115(5)	-0.090(4)
H31	-0.448(4)	0.203(5)	-0.068(4)

TABLE XX (Continued)

H51	-0.398(4)	0.366(5)	0.101(4)
H52	-0.267(4)	0.428(6)	0.036(4)
H61	-0.266(4)	0.369(6)	0.283(4)
H62	-0.259(4)	0.157(6)	0.266(4)
H81	-0.064(4)	0.304(6)	0.377(4)
H82	-0.053(4)	0.088(6)	0.373(4)
H91	-0.164(4)	-0.211(5)	-0.355(4)
H92	-0.147(4)	-0.297(6)	-0.195(4)
H101	-0.501(4)	0.018(5)	-0.236(4)
H102	-0.391(4)	-0.113(6)	-0.318(4)
H111	-0.295(4)	0.143(5)	-0.454(4)
H112	-0.462(4)	0.166(5)	-0.465(4)
H121	-0.515(4)	0.373(5)	-0.293(4)
H122	-0.400(4)	0.452(6)	-0.414(4)
H131	-0.231(4)	0.341(5)	-0.264(4)
H132	-0.349(4)	0.471(6)	-0.187(4)

($Cu_4I_4(CH_3CN)_4$ (db-18-C-6)), and in two other cases with a crown ether of similar cavity size but differing rigidity, resulting only in inclusion compounds of the solvent is not well understood. Of course our analysis is based on the identification of solid state materials and does not exhaustively identify all species present in solution.

Our attention turned to families of complexes with a single ligand, some of which display temperature dependent luminescence while others emit at a constant wavelength at all temperatures. Complexes with L= pyridine derivative were chosen because of their extreme flexibility in stoichiometry and structure. Two complexes of quinoline were isolated and their single crystal X-ray structures as well as their luminescence spectra were measured.

($CuI(quinoline)_2)_2$ (VI), synthesized at room temperature with stoichiometric ratio 1:1:2, exists in the solid state as an isolated rhombohedron. The compound crystallizes in monoclinic space group A2/a (Table XXI). The structure of VI shows (Figure 9) the standard Cu_2I_2 rhomb with alternating Cu and I atoms (average Cu-I distance 2.686(4) Å). The rhombs are distorted such that the Cu atoms are at a distance of 3.364(5) Å which in turn forces the I atoms further apart to a distance of 4.188(2) Å, greater than the diagonal distance of 3.779 Å calculated for a square of sides 2.686(4) Å. The Cu_2I_2 rhombohedron is planar and centered about a $\bar{1}$ symmetry

TABLE XXI

CRYSTAL DATA FOR (CuI(Quinoline)$_2$) (VI)

Formula	$CuIC_{18}H_{14}N_2$
M.W	448.772 $gmole^{-1}$
a	25.620(5) Å
b	7.495(2)
c	20.314(4)
$\alpha=\gamma$	90.0°
β	111.60(2)
V	3626.7(15) $Å^3$
F(000)	1744
μMoK_α	28.890 cm^{-1}
λMoK_α	0.71069 Å
D_{cal}	1.643 g cm^{-1}
Z	8
Meas refl	4440
Obs refl	1828
R	8.2%
R_w	10.2%
Space group	A2/a (Monoclinic)
Octants measr	±h, +k, +l

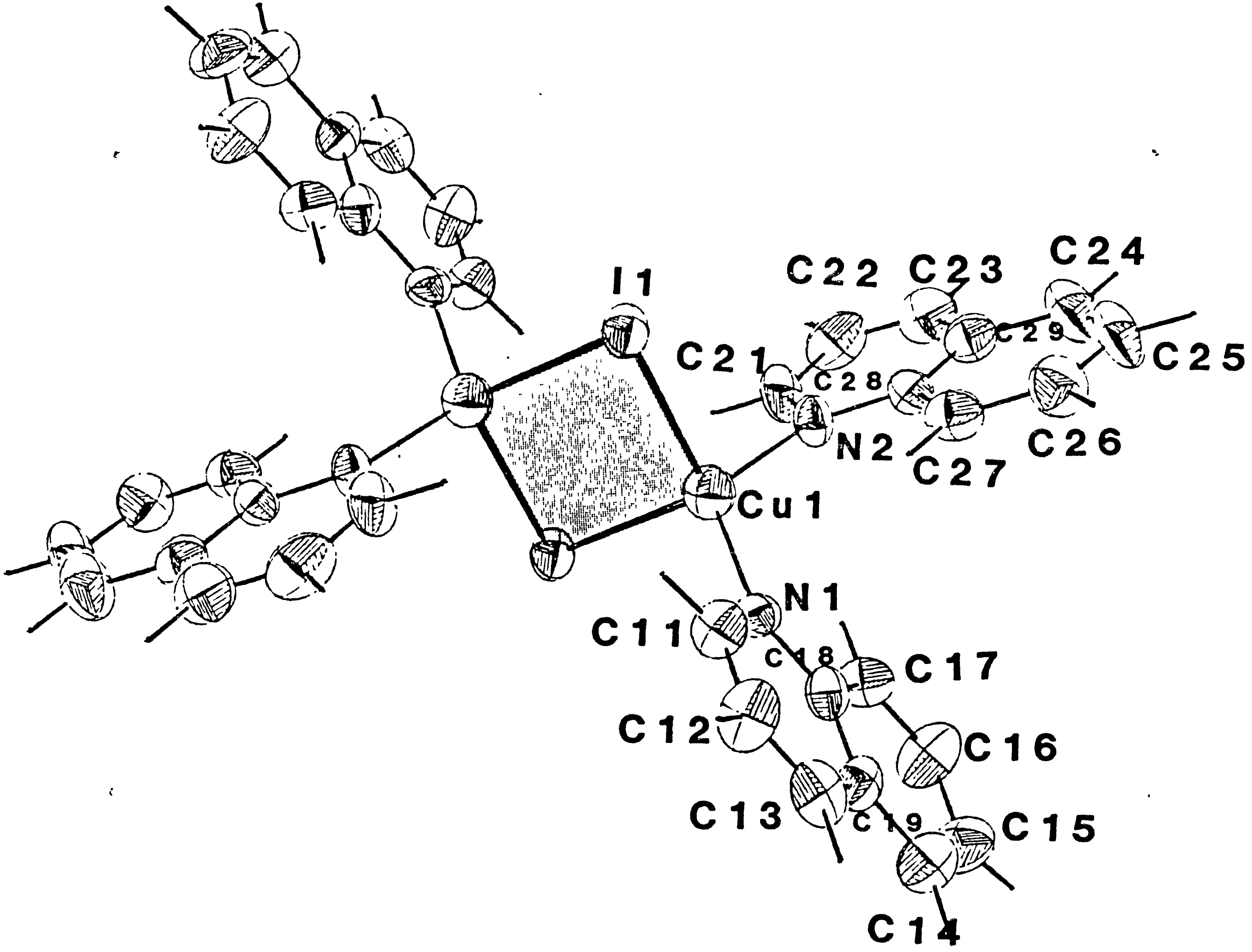

Figure 9. Projection View of VI

element. The tetracoordination of Cu atoms is completed by two ligand molecules ligated through nitrogen atoms (Cu-N average distance 2.065(2) Å). (Bond distances and angles, positional and thermal parameters are listed in Table XXII, XXIII, XXIV respectively.)

The Cu-Cu separation in VI is rather larger than those seen in other known structures with planar Cu_2X_2 rhombohedron : $(CuI(Ph_3As)(MeCN))_2$, 2.779(1) Å (71); $(CuBr(2\text{-picoline})_2)_2$, 3.349(6) Å (72). The bulky quinoline ligand, probably, opens the N-Cu-N angle causing the closing of the I-Cu-I angle and hence the greater separation of the Cu atoms across the rhomb.

The packing diagram of VI shows no significant interaction between quinoline rings (Figure 10), the planes of the rings lying perpendicular to the plane of Cu_2I_2 rhombohedron and packed such that the planes of adjecent rings are well separated.

The other complex formed by CuI and quinoline, synthesized and crystallized at a higher temperature, has stoichiometry 1:1:1 with the molecular formula; Cu_4I_4-(quinoline)$_4$ (VII). This compound displays a structure (Figure 11), previously unknown for CuI N-ligand cluster systems (73). The compound VII crystallizes in triclinic space group $P\bar{1}$ (Table XXV) and displays a parallelogram of Cu atoms with two short sides, (Cu1-Cu2 2.582(10) Å, Cu3-Cu4 2.535(15) Å). and two long sides (Cu2-Cu3 3.279(10) Å, Cu1-Cu4 3.325(12) Å) which is bridged by four iodide

TABLE XXII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR (CuI(Quinoline)$_2$)$_2$ (VI)

Cu1-I1	2.685(3)	I1-Cu1-I1'	102.4(1)
Cu1-I1'	2.687(4)	Cu1-I1-Cu1'	77.6(1)
Cu1-Cu1'	3.364(5)	I1-Cu1-N1	108.2(4)
I1-I1'	4.188(2)	I1-Cu1-N2	109.4(5)
Cu1-N1	2.06(2)	I1'-Cu1-N1	111.9(6)
Cu1-N2	2.07(2)	I1'-Cu1-N2	102.8(6)
N1-C11	1.33(3)	N1-Cu1-N2	120.6(8)
N1-C18	1.40(3)	Cu1-N1-C11	122(2)
C11-C12	1.38(4)	Cu1-N1-C18	123(1)
C12-C13	1.31(4)	C11-N1-C18	115(2)
C13-C19	1.42(3)	N1-C11-C12	124(3)
C19-C18	1.37(3)	C11-C12-C13	120(2)
C19-C14	1.41(4)	C12-C13-C19	119(2)
C14-C15	1.31(5)	C13-C19-C18	118(2)
C15-C16	1.39(7)	C13-C19-C14	122(2)
C16-C17	1.29(4)	C14-C19-C18	121(2)
C17-C18	1.46(3)	C19-C14-C15	114(4)
N2-C21	1.35(3)	C14-C15-C16	129(6)
N2-C28	1.34(3)	C15-C16-C17	117(3)
C21-C22	1.38(4)	C16-C17-C18	120(2)
C22-C23	1.33(4)	C17-C18-C19	119(2)
C23-C29	1.38(4)	C17-C18-N1	118(2)
C29-C28	1.41(3)	C19-C18-N1	123(2)

TABLE XXII (Continued)

C29-C24	1.42(4)	Cu1-N2-C21	119(1)
C24-C25	1.32(5)	Cu1-N2-C28	125(1)
C25-C26	1.38(4)	C21-N2-C28	116(2)
C26-C27	1.38(4)	N2-C21-C22	126(2)
C27-C28	1.39(3)	C21-C22-C23	117(2)
		C22-C23-C29	121(2)
		C23-C29-C28	118(2)
		C23-C29-C24	124(2)
		C24-C29-C28	118(2)
		C29-C24-C25	122(2)
		C24-C25-C26	121(2)
		C25-C26-C27	120(2)
		C26-C27-C28	120(2)
		C27-C28-C29	119(2)
		C27-C28-N2	119(2)
		C29-C28-N2	122(2)

Symmetry operations :

' = 2.0-x, 0.5-y, 0.5-z.

TABLE XXIII

POSITIONAL PARAMETERS FOR ((CuI(Quinoline)$_2$)$_2$ (VI)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIGZ))
I1	0.9594(1)	0.0692(2)	0.1696(1)
Cu1	1.0540(1)	0.2625(4)	0.2218(2)
N1	1.0561(7)	0.4384(26)	0.1450(9)
N2	1.1210(7)	0.0944(25)	0.2711(9)
C11	1.0356(10)	0.6030(30)	0.1406(13)
C12	1.0356(11)	0.7270(32)	0.0902(15)
C13	1.0548(10)	0.6846(31)	0.0408(13)
C14	1.0958(11)	0.4561(31)	-0.0136(13)
C15	1.1149(17)	0.2917(62)	-0.0068(34)
C16	1.1186(12)	0.1672(34)	0.0456(15)
C17	1.0987(10)	0.2147(31)	0.0928(12)
C18	1.0770(9)	0.3944(28)	0.0924(12)
C19	1.0763(9)	0.5100(31)	0.0398(12)
C21	1.1108(9)	-0.0728(36)	0.2878(13)
C22	1.1505(13)	-0.1971(36)	0.3245(15)
C23	1.2041(12)	-0.1461(38)	0.3460(14)
C24	1.2747(11)	0.0871(44)	0.3546(15)
C25	1.2866(10)	0.2506(42)	0.3399(15)
C26	1.2445(11)	0.3688(35)	0.3043(14)
C27	1.1892(11)	0.3152(32)	0.2814(13)
C28	1.1753(9)	0.1433(29)	0.2952(11)
C29	1.2186(11)	0.0238(35)	0.3322

TABLE XXIII (Continued)

H11	1.0180	0.6382	0.1744
H12	1.0223	0.8528	0.0943
H13	1.0542	0.7770	0.0040
H14	1.0966	0.4994	-0.0547
H15	1.1500	0.3091	0.0168
H16	1.1350	0.0586	0.0319
H17	1.0982	0.1284	0.1296
H21	1.0710	-0.1113	0.2715
H22	1.1412	-0.3192	0.3375
H23	1.2358	-0.2289	0.3762
H24	1.3073	0.0023	0.3831
H25	1.3244	0.3021	0.3582
H26	1.2496	0.4862	0.2894
H27	1.1588	0.4069	0.2553

TABLE XXIV

ANISOTROPIC THERMAL PARAMETERS FOR (CuI(Quinoline)$_2$)$_2$ (VI)

ATOM	U11	U22	U33	U12	U13	U23
I1	391(8)	519(9)	516(9)	-86(9)	182(6)	-188(9)
Cu1	51(1)	46(1)	56(1)	4(1)	20(1)	1(1)
N1	40(10)	46(11)	35(9)	-13(10)	12(8)	-3(9)
N2	28(10)	40(12)	52(11)	6(8)	15(8)	8(9)
C11	51(15)	33(15)	66(16)	4(11)	25(13)	-2(12)
C12	68(17)	29(14)	83(19)	6(12)	36(15)	-3(13)
C13	46(14)	31(13)	64(16)	-20(11)	17(12)	-12(11)
C14	74(17)	39(16)	58(15)	-10(13)	30(13)	-1(12)
C15	91(31)	78(32)	34(71)	-16(25)	-12(36)	-35(39)
C16	100(20)	30(15)	76(18)	8(14)	59(17)	-3(13)
C17	63(16)	39(13)	44(13)	5(11)	23(12)	4(11)
C18	36(12)	33(13)	50(13)	0(9)	17(10)	-4(10)
C19	40(13)	46(13)	46(14)	-18(10)	22(11)	-13(11)
C21	38(13)	45(14)	65(15)	-18(13)	13(11)	-10(14)
C22	85(20)	45(16)	74(18)	0(15)	42(16)	13(14)
C23	74(19)	55(18)	57(16)	23(15)	28(14)	10(13)
C24	46(16)	73(22)	71(17)	-1(17)	5(13)	-25(18)
C25	32(14)	74(20)	75(19)	-16(14)	5(13)	-26(16)
C26	57(17)	54(16)	62(16)	-7(13)	20(13)	1(13)
C27	61(17)	41(14)	46(159	8(12)	17(13)	4(11)

TABLE XXIV (Continued)

C28	39(13)	33(12)	36(12)	4(10)	11(10)	4(9)
C29	54(16)	57(18)	45(15)	0(13)	23(13)	-10(12)

Anisotropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^*+ +2U13hla^*c^*+2U23klb^*c^*))\ X10^4 \text{ for I,}$$

$$X10^3 \text{ for Cu,N,C.}$$

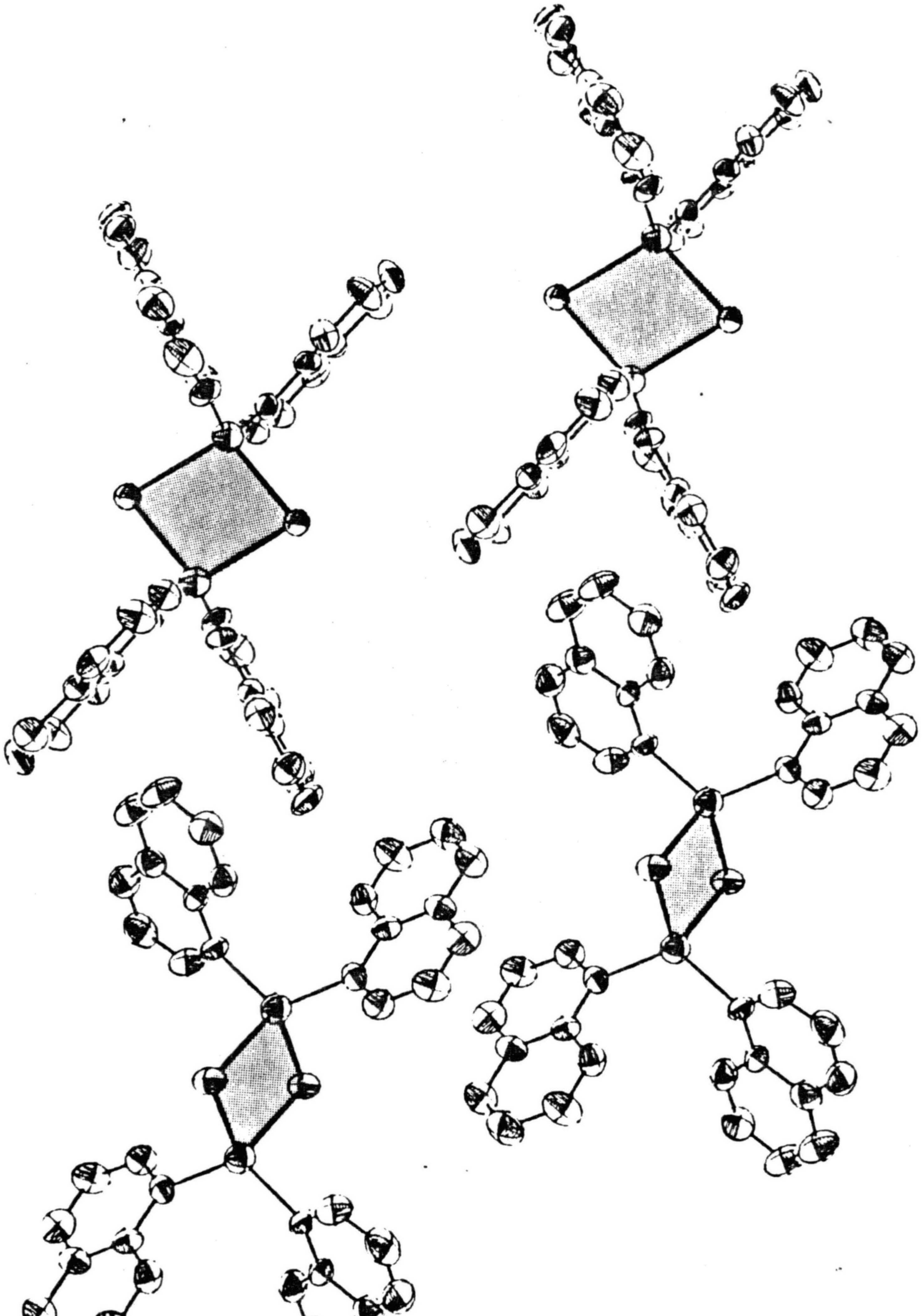

Figure 10. Packing Diagram of VI

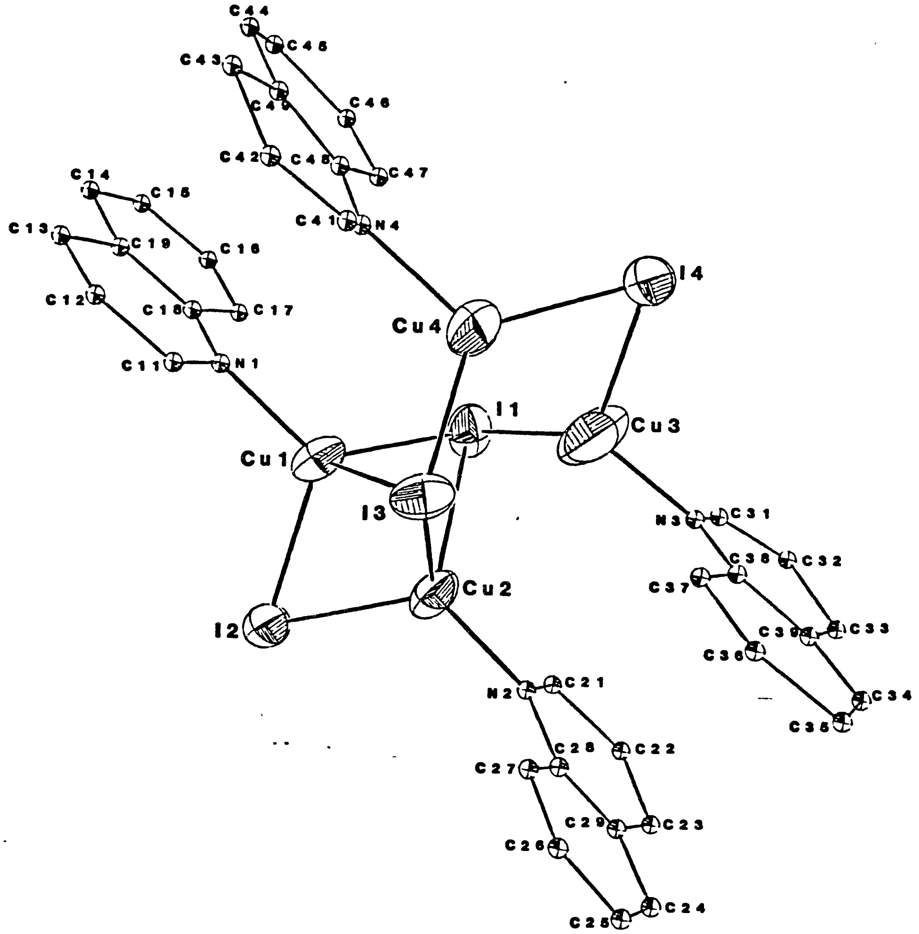

Figure 11. Projection View of VII

TABLE XXV

CRYSTAL DATA FOR (Cu_4I_4(quinoline)$_4$) (VII)

Formula	$Cu_4I_4C_{36}H_{28}N_4$
M.W.	1278.445 g mole^{-1}
<u>a</u>	12.161(8) Å
<u>b</u>	15.142(8)
<u>c</u>	12.162(6)
α	103.75(4)°
β	109.54(5)
γ	107.18(5)
V	1870.2(19) Å^3
F(000)	1200
μMoK_α	55.517 cm^{-1}
λMoK_α	0.71069 Å
D_{cal}	2.270 g cm^{-3}
Z	2
Meas refl	12663
Obs refl	2802
R	9.5%
R_w	12.7%
Space group	P$\bar{1}$ (Triclinic)
Octants measr	±h, ±k, +l

atoms. The short sides of the parallelogram display μ2-bridging(Figure 12) iodide atoms with I2 bridging Cu1-Cu2 and I4 bridging Cu3-Cu4; whereas the faces of the parallelogram are bridged by μ3-iodide atoms. There is similarity of this structure to that of $(CuI_2(Ph_2PCH_2)_2)$ (74), which displays a parallelogram of four Cu atoms of short sides bridged by two iodide atoms, with faces bridged by three iodide atoms and long sides by bidentate $(Ph_3P)_2C$ groups. Each Cu atom of VII is bound to the electron pair donor nitrogen atom of a quinoline ring. The angles about Cu3 and Cu4 show them to be of trigonal planar coordination (105.0(8), 120.8(4)°, Table XXVI) whereas Cu1 and Cu2 are of distorted tetrahedral geometry with an average angle of 109.6°.

The quinoline rings lie in planes parallel to each other projecting outward from the Cu_4I_4 framework. The planes of the rings have a separation of approximately the long Cu-Cu distances of 3.325(12) Å. The close stacking of quinoline rings continues through out the crystal as seen in packing diagram (Figure 13). Positional parameters Table: XXVII. Anistropic thermal parameters Table: XXVIII)

Previous reference to complexes of CuI with quinoline leaves some confusion about their structural identity. Hardt et al (5) reported sythesis of a light yellow compound fluorescing orange at 20 °C and yellow orange at -120 °C. The second compound reported was yellow

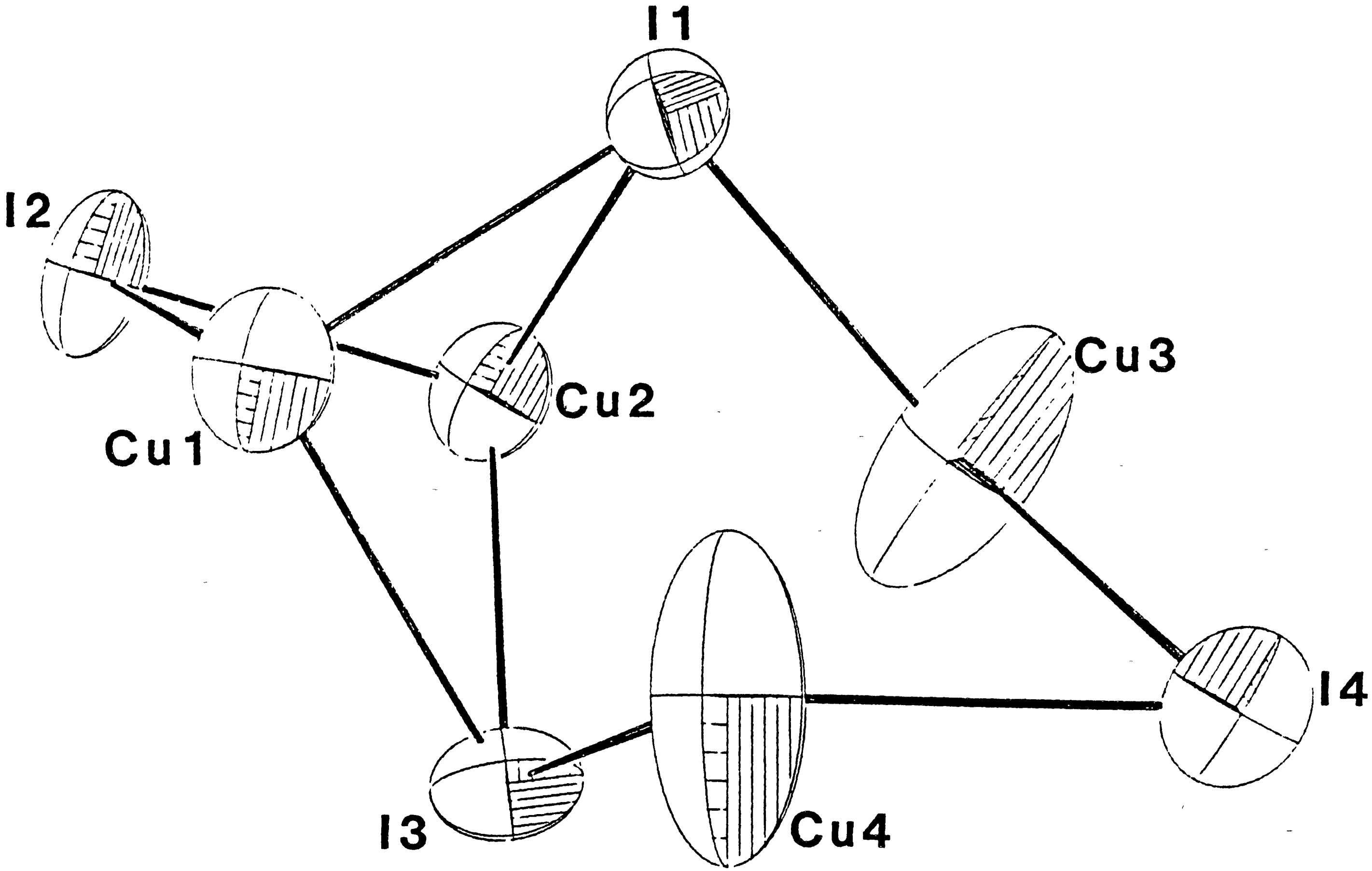

Figure 12. Arrangement of Cu and I atoms in VII

TABLE XXVI

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

($Cu_4I_4(Quinoline)_4$) (VII)

I1-Cu1	2.680(6)	Cu1-I1-Cu2	54.2(2)
I1-Cu2	2.961(6)	Cu1-I1-Cu3	98.6(3)
I1-Cu3	2.634(14)	Cu2-I1-Cu3	71.5(2)
I1-Cu4	3.394(12)	Cu1-I2-Cu2	59.0(2)
I1-I2	4.263(5)	Cu1-I3-Cu2	54.4(2)
I1-I3	4.092(5)	Cu1-I3-Cu4	73.5(3)
I2-I3	4.245(6)	Cu2-I3-Cu4	101.7(3)
I2-I1	4.263(5)	Cu3-I4-Cu4	49.9(3)
I2-Cu1	2.624(6)	I1-Cu1-I2	106.9(3)
I2-Cu2	2.619(8)	I1-Cu1-I3	93.1(2)
I3-Cu1	2.951(8)	I2-Cu1-I3	99.0(2)
I3-Cu2	2.670(7)	I1-Cu1-N1	124.5(6)
I3-Cu3	3.268(10)	I2-Cu1-N1	117.7(8)
I3-Cu4	2.582(7)	I3-Cu1-N1	109.6(10)
I4-Cu3	2.531(11)	I1-Cu2-I2	99.4(2)
I4-Cu4	2.551(9)	I1-Cu2-I3	93.0(2)
Cu1-Cu2	2.582(10)	I2-Cu2-I3	106.7(2)
Cu1-Cu4	3.325(12)	I1-Cu2-N2	111.4(6)
Cu1-N1	1.99(4)	I2-Cu2-N2	117.3(9)
Cu2-Cu3	3.279(10)	I3-Cu2-N2	123.6(10)
Cu2-N2	1.96(4)	I1-Cu3-I4	119.9(4)
Cu3-Cu4	2.545(15)	I1-Cu3-N3	105.0(16)
Cu3-N3	2.05(5)	I4-Cu3-N3	116.4(13)

TABLE XXVI (Continued)

Cu4-N4	2.21(5)	I3-Cu4-I4	120.8(4)
N1-C11	1.36(4)	I3-Cu4-N4	105.0(8)
N1-C18	1.40(5)	I4-Cu4-N4	120.4(11)
N2-C21	1.33(9)	Cu1-N1-C11	115(2)
N2-C28	1.44(5)	Cu1-N1-C18	122(2)
N3-C31	1.42(5)	C11-N1-C18	122(3)
N3-C38	1.13(7)	Cu2-N2-C21	113(4)
N4-C41	1.03(8)	Cu2-N2-C28	128(3)
N4-C48	1.38(6)	C21-N2-C28	119(5)
C11-C12	1.44(7)	Cu3-N3-C31	124(5)
C12-C13	1.47(7)	Cu3-N3-C38	125(4)
C13-C19	1.58(6)	C31-N3-C38	110(5)
C14-C15	1.55(6)	Cu4-N4-C41	116(6)
C14-C19	1.27(6)	Cu4-N4-C48	109(3)
C15-C16	1.36(8)	C41-N4-C48	133(7)
C16-C17	1.41(6)	N1-C11-C12	124(3)
C17-C18	1.35(5)	C11-C12-C13	118(3)
C18-C19	1.41(6)	C12-C13-C19	114(4)
C21-C22	1.49(9)	C15-C14-C19	110(4)
C22-C23	1.43(6)	C14-C15-C16	122(4)
C23-C29	1.33(6)	C15-C16-C17	121(4)
C24-C25	1.11(6)	C16-C17-C18	117(4)
C24-C29	1.56(5)	N1-C18-C17	121(4)
C25-C26	1.38(8)	N1-C18-C19	118(3)
C26-C27	1.40(6)	C13-C19-C14	109(4)

TABLE XXVI (Continued)

C27-C28	1.36(6)	C13-C19-C18	122(3)
C28-C29	1.28(7)	C14-C19-C18	129(4)
C31-C32	1.38(7)	C17-C18-C19	120(4)
C32-C33	1.54(7)	N2-C21-C22	116(6)
C33-C39	1.34(7)	C21-C22-C23	120(4)
C34-C35	1.63(7)	C22-C23-C29	116(4)
C34-C39	1.39(7)	C25-C24-C29	125(4)
C35-C36	1.50(12)	C24-C25-C26	121(5)
C36-C37	1.36(13)	C25-C26-C27	118(4)
C37-C38	1.51(9)	C26-C27-C28	120(4)
C38-C39	1.42(7)	N2-C28-C27	115(4)
C41-C42	1.42(12)	N2-C28-C29	122(3)
C42-C43	1.55(12)	C27-C28-C29	122(4)
C43-C49	1.60(8)	C23-C29-C24	122(4)
C44-C45	1.10(7)	C23-C29-C28	125(4)
C44-C49	1.48(7)	C24-C29-C28	113(3)
C45-C46	1.56(8)	N3-C31-C32	129(4)
C46-C47	1.37(8)	C31-C32-C33	112(3)
C47-C48	1.41(8)	C32-C33-C39	115(5)
C48-C49	1.36(7)	C35-C34-C39	122(5)
		C34-C35-C36	95(5)
		C35-C36-C37	152(7)
		C36-C37-C38	103(6)
		N3-C38-C37	106(5)
		N3-C38-C39	134(5)

TABLE XXVI (Continued)

	C37-C38-C39	120(5)
	C33-C39-C34	114(5)
	C33-C39-C38	119(5)
	C34-C39-C38	126(5)
	N4-C41-C42	124(9)
	C41-C42-C43	119(7)
	C42-C43-C49	104(6)
	C45-C44-C49	118(6)
	C44-C45-C46	127(6)
	C45-C46-C47	116(4)
	C46-C47-C48	115(5)
	N4-C48-C47	124(5)
	N4-C48-C49	112(5)
	C47-C48-C49	123(5)
	C43-C49-C44	116(5)
	C43-C49-C48	125(5)
	C44-C49-C48	118(4)

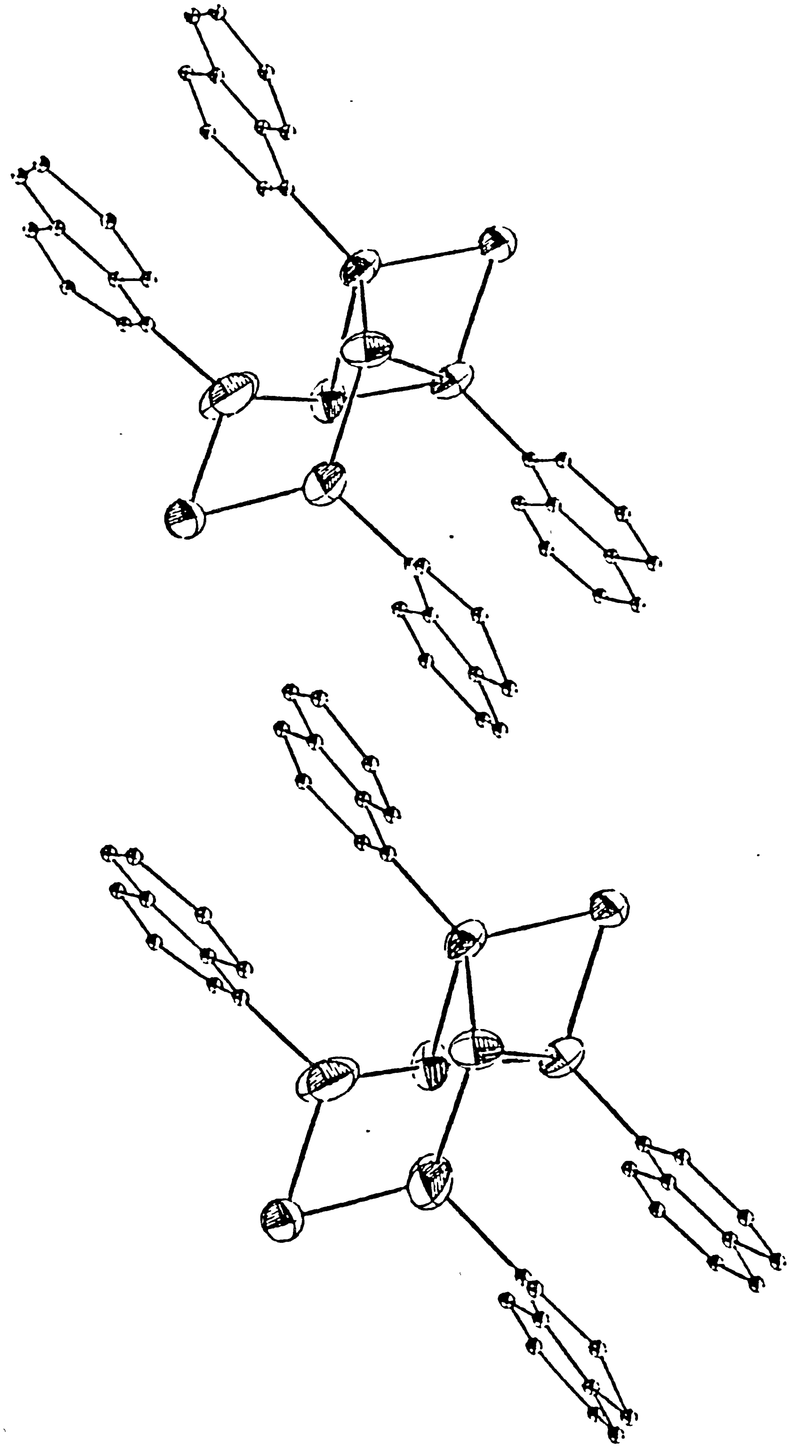

Figure 13. Packing Diagram of VII

TABLE XXVII

POSITIONAL PARAMETRS FOR ($Cu_4I_4(Quinoline)_4$) (VII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.3965(3)	0.4019(2)	0.1108(3)
I2	0.0365(3)	0.2495(3)	-0.2130(3)
I3	0.2099(3)	0.0997(2)	-0.0041(2)
I4	0.5860(3)	0.2502(2)	0.3361(3)
Cu1	0.1516(5)	0.2774(4)	0.0253(5)
Cu2	0.2477(5)	0.2232(4)	-0.1251(5)
Cu3	0.5006(10)	0.2731(8)	0.1292(8)
Cu4	0.3510(7)	0.2187(8)	0.2279(7)
N1	0.0505(26)	0.2783(20)	0.1248(27)
N2	0.3405(28)	0.2177(22)	-0.2294(24)
N3	0.6236(32)	0.3004(34)	0.0475(35)
N4	0.2261(43)	0.1877(24)	0.3230(35)
C11	-0.0312(26)	0.1871(20)	0.1069(27)
C12	-0.1131(40)	0.1702(30)	0.1695(41)
C13	-0.1216(38)	0.2571(27)	0.2454(36)
C14	-0.0325(34)	0.4305(25)	0.3355(25)
C15	0.0575(47)	0.5334(32)	0.3485(36)
C16	0.1358(45)	0.5421(28)	0.2906(46)
C17	0.1377(38)	0.4568(23)	0.2146(33)
C18	0.0533(32)	0.3669(24)	0.1963(21)
C19	-0.0257(36)	0.3606(29)	0.2596(31)
C21	0.4115(63)	0.3075(71)	-0.2192(52)

TABLE XXVII (Continued)

C22	0.4889(38)	0.3110(24)	-0.2923(32)
C23	0.4722(33)	0.2209(34)	-0.3808(33)
C24	0.3732(29)	0.0324(21)	-0.4693(27)
C25	0.3041(49)	-0.0405(33)	-0.4817(47)
C26	0.2424(40)	-0.0466(28)	-0.4052(34)
C27	0.2579(37)	0.0422(35)	-0.3215(33)
C28	0.3307(41)	0.1309(26)	-0.3187(33)
C29	0.3914(34)	0.1367(26)	-0.3866(30)
C31	0.7022(30)	0.3973(22)	0.0620(30)
C32	0.7975(38)	0.4243(24)	0.0240(46)
C33	0.8012(45)	0.3339(33)	-0.0625(36)
C34	0.7272(38)	0.1638(25)	-0.1518(39)
C35	0.6380(44)	0.0488(45)	-0.1808(54)
C36	0.5621(71)	0.0758(64)	-0.1137(69)
C37	0.5435(51)	0.1430(71)	-0.0331(62)
C38	0.6375(42)	0.2416(35)	-0.0167(37)
C39	0.7178(39)	0.2452(41)	-0.0797(32)
C41	0.1844(71)	0.1147(49)	0.3127(53)
C42	0.0986(52)	0.0809(72)	0.3639(81)
C43	0.0981(61)	0.1569(57)	0.4739(67)
C44	0.1897(56)	0.3516(37)	0.5699(37)
C45	0.2408(44)	0.4250(27)	0.5719(43)
C46	0.3241(44)	0.4505(31)	0.5009(39)
C47	0.3237(45)	0.3708(43)	0.4183(38)

TABLE XXVII (Continued)

C48	0.2437(38)	0.2764(42)	0.4051(37)
C49	0.1818(35)	0.2626(239	0.4785(32)

TABLE XXVIII

ANISOTROPIC THERMAL PARAMETERS FOR (Cu_4I_4(Quinoline)$_4$) (VII)

ATOM	U11	U22	U33	U12	U13	U23
I1	51(1)	43(1)	67(1)	23(1)	23(1)	2(1)
I2	68(2)	115(2)	45(1)	59(2)	26(1)	26(1)
I3	84(2)	42(1)	45(1)	26(1)	31(1)	13(1)
I4	64(1)	71(2)	51(1)	36(1)	27(1)	24(1)
Cu1	77(3)	84(4)	53(3)	42(3)	42(3)	16(3)
Cu2	72(3)	76(3)	60(3)	44(3)	43(3)	21(3)
Cu3	212(9)	281(11)	107(5)	203(9)	121(6)	123(7)
Cu4	87(5)	262(10)	64(4)	91(6)	33(4)	-4(5)
N1	38(17)	37(18)	58(20)	20(15)	18(15)	20(15)
N2	59(20)	64(20)	26(15)	38(17)	28(15)	22(14)
N3	49(22)	175(42)	86(27)	61(26)	54(21)	88(29)
N4	158(41)	37(21)	82(27)	61(25)	45(28)	24(19)
C11	16(14)	12(16)	31(17)	-4(13)	10(13)	13(13)
C12	59(28)	59(27)	81(32)	33(23)	39(25)	8(24)
C13	51(26)	31(22)	44(23)	-2(19)	-19(20)	-32(18)
C14	46(23)	26(20)	63(25)	-17(17)	34(21)	14(18)
C15	124(39)	95(33)	52(24)	99(32)	58(27)	50(24)
C16	81(34)	31(23)	92(35)	23(23)	28(29)	20(23)
C17	69(27)	7(16)	46(22)	13(18)	1(20)	-13(15)
C18	42(21)	39(20)	41(20)	37(18)	15(17)	16(16)
C19	71(26)	84(28)	34(20)	66(24)	40(19)	41(19)

TABLE XXVIII (Continued)

C21	137(54)	435(20)	83(39)	205(72)	52(39)	167(61)
C22	71(28)	20(19)	28(19)	13(19)	-3(19)	-3(15)
C23	25(20)	108(34)	43(21)	38(23)	29(17)	49(23)
C24	28(18)	3(15)	27(17)	4(14)	10(14)	-4(13)
C25	79(36)	33(27)	83(37)	14(26)	-8(29)	-51(25)
C26	62(28)	47(25)	27(20)	10(21)	7(19)	-30(17)
C27	57(25)	117(38)	38(21)	59(27)	33(19)	63(25)
C28	88(31)	38(23)	35(21)	33(22)	36(22)	19(18)
C29	34(21)	35(21)	18(17)	1(18)	-10(16)	-22(15)
C31	33(19)	24(17)	44(20)	17(15)	18(16)	25(15)
C32	46(25)	5(18)	116(39)	6(17)	-36(25)	-23(20)
C33	77(32)	56(28)	39(23)	26(25)	25(23)	-4(20)
C34	62(27)	17(18)	71(28)	2(19)	11(23)	31(19)
C35	47(29)	143(51)	129(47)	-1(31)	56(33)	92(41)
C36	117(60)	230(90)	102(55)	106(62)	-7(48)	109(62)
C37	41(31)	272(95)	91(46)	-11(47)	10(33)	128(56)
C38	65(30)	90(34)	45(25)	43(28)	19(23)	-8(23)
C39	48(26)	132(44)	20(20)	55(29)	8(18)	34(25)
C41	191(66)	146(54)	102(43)	163(56)	38(45)	56(41)
C42	35(30)	268(7)	158(67)	-27(47)	-43(41)	193(78)
C43	74(46)	173(72)	105(50)	13(46)	-38(42)	110(35)
C44	179(52)	104(38)	39(24)	131(41)	-14(28)	-3(24)
C45	91(34)	31(22)	93(33)	35(23)	28(28)	49(23)
C46	81(33)	52(27)	47(24)	23(25)	23(24)	12(21)
C47	60(30)	123(45)	31(23)	48(32)	16(22)	26(27)

TABLE XXVIII (Continued)

C48	29(23)	156(48)	42(25)	50(29)	15(20)	42(28)
C49	65(269	22(17)	47(21)	37(18)	22(19)	10(16)

Anistropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^* +2U13hla^*c^*+2U23klb^*c^*))\ X10^3.$$

in color and emitted orange at both temperatures. The emission spectra reported for the first compound shows a broad band of emission (at room temperature λ_{max} = 590 nm, shoulder at 500 nm) which sharpens and shifts slightly to λ_{max} of 580 nm on cooling. A later published spectrum of a (CuI(quinoline) complexes (75), shows broad band room temperature emission (λ_{max} = 625 nm) which develops considerable fine structure between 490-620 nm similar to that seen in the solution emission spectrum of quinoline alone at 77 °C but red shifted by 1200 cm^{-1}. Because the structures of these componds are unknown it is not possible to correlate these results with ours.

The two new complexes of quinoline, VI and VII, are of different stoichiometries and of markedly different structural format. The interpretation of the solid state emission spectra of these two then must be based on specific differences in the two structures. VI displays long Cu-Cu distances greater than those (2.8 Å) (53) considered representative of possible interaction whereas VII shows two short Cu-Cu distances nearly as short as the Cu-Cu metal distance (2.54 Å). The aromatic quinoline ligands are packed perpendicular to each other in VI whereas they are stacked parallel to each other and in close proximity in VII.

The solid state emission spectra measured for both complexes show very similar room temperature behavior, while the low temperature spectrum of VI differ markedly (Figures 14 and 15) from that of VII. At room temperature VI and VII both show broad band emission at λ_{max} = 620 and 625 nm respectively. For VI the spectrum is relatively unchanged on cooling to 15.4 K. The spectrum of VI (1:1:2 stoichiometry) is similar in lack of fine structure or temperature dependence to that published for CuI(quinoline) (5) but different in λ_{max} and in the lack of a shoulder at lower wavelength. The powder pattern of VI based on the single crystal cell parameters, determined from diffractometer data, was calculated and was found incompatible with the the d-spacing reported from film data by these workers for CuI(quinoline) or CuI(quinoline)$_2$. This suggests that VI was previously unknown. However, the calculation of the powder pattern of VII is roughly comparable with that previously reported for CuI(quinoline) (5), but the work did not report the emission spectra of this specific preparation. The low temperature spectrum of VII shows the appearance of large amounts of fine structure on the high energy side of the broad band emission evident at room temperature. This spectrum is consistant with that published for CuI-quinoline prepared by an unidentified synthetic route by another group of workers(75). The relative intensity of the 610 nm band appears lesser in their work. Both spectra display great similarity to the emission spectrum of quinoline in ethanol(75) and to the low energy segment of the total emission spectrum of quinoline reported

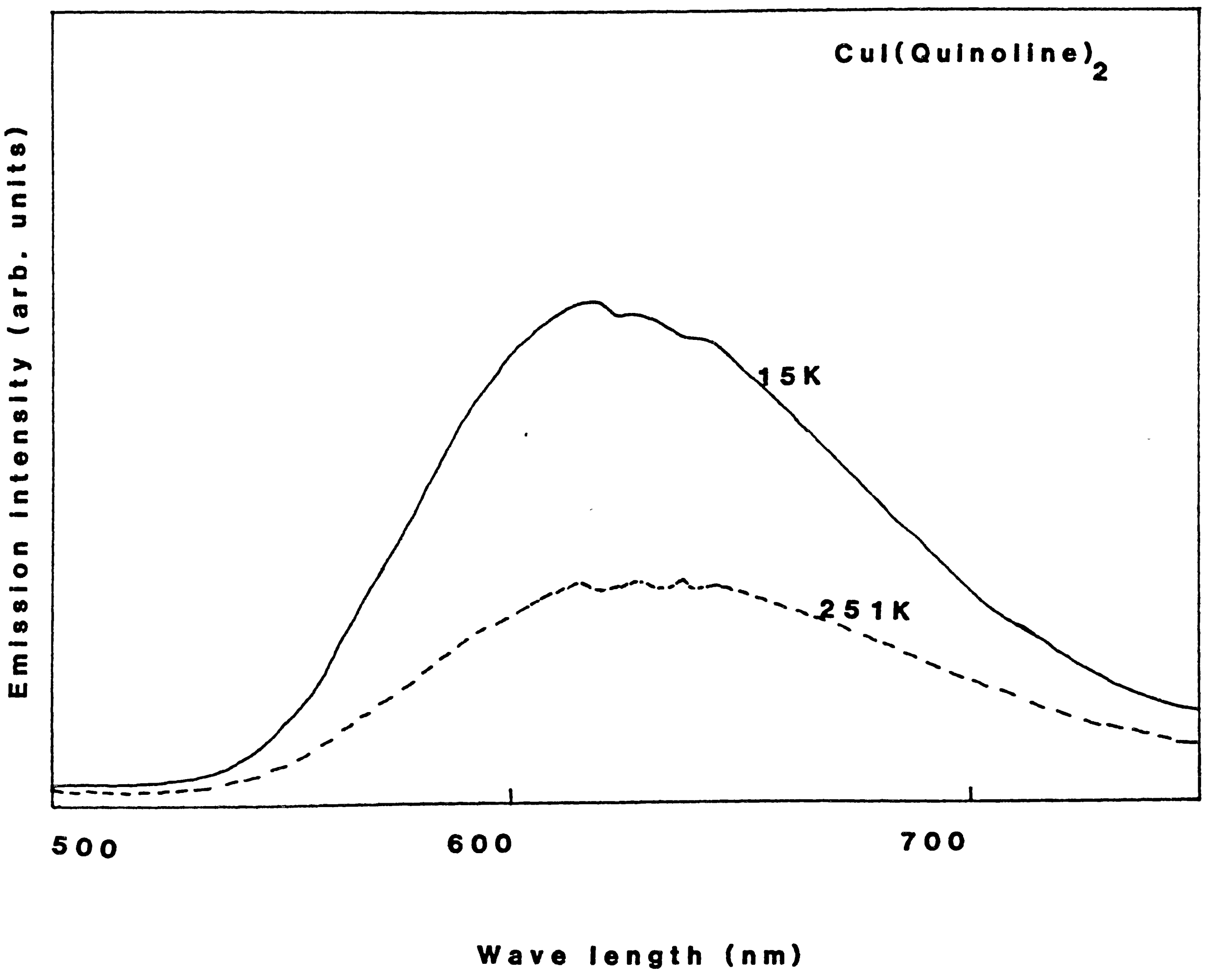

Figure 14. Emission Spectra of VI

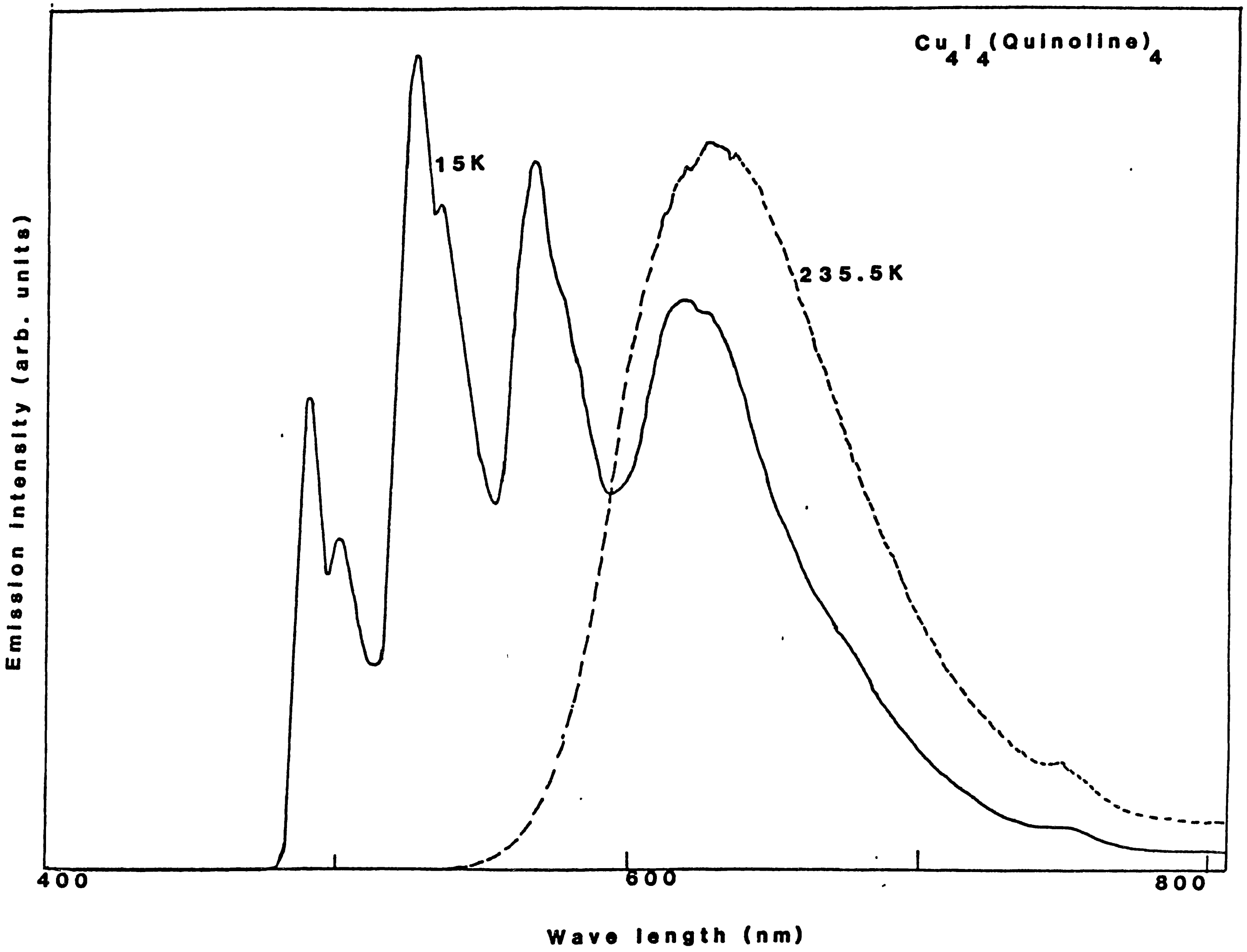

Figure 15. Emission Spectra of VII

elsewhere (76). The fine structure of the 15 K emission spectrum of VII can thus be recognized as arising from ligand alone processes in accord with the expectation that the ligand alone emission from coordinated ligands should display the same fine structure as the emission of the uncoordinated ligand but slightly shifted in wavelength. The appearance of this fine structure in the emission spectra of crystalline VII but not VI leads to the conclusion that its appearance involves pi-pi* transitions between molecules of quinoline situated in parallel planes, close packed. The 625 nm room temperature emission (610 nm, 15 K) for VII, which is missing in the quinoline alone spectrum (76) and which is of considerably less intensity in the solution spectrum(75) but which constitutes the spectrum of VI, may be suspected to arise from metal to ligand charge transfer (MLCT) interactions as observed in the solid state emission of $Cu_4I_4Py_4$ (λ_{max} 370 nm, assigned to $d^{10}\rightarrow d^9pi^*$) (4) but shifted to lower energy due to the lower energy of the quinoline extended aromatic system. Consistant with the observation of emission (550-628 nm) from systems which display close Cu-Cu interactions, VII but not VI should have emission in this range(67). The presence or absence of this component of the emission spectrum can not be verified for VI or VII due to the MLCT component in this area.

Thus the broad band emission spectrum of VI appears to exhibit major contribution from MLCT interactions between Cu(I) and quinoline. The room temperature spectrum of VII displays contribution from the same transitions and may also exhibit emission due to a mechanism involving a metal centered interaction consistant with the close proximity Cu(I) centers in the solid state structure. Emission from VII at 15 K displays an additional set of emission bands arising from ligand alone interactions and suspected of arising from intermolecular quinoline interactions made possible in VII because of the close proximity of the packed aromatic rings. The temperature dependence of the emission of VII thus arises from a change of relative populations of the collection of emitting states between room temperature and 15 K.

2-Methyl pyridine or 2-picoline has been used by earlier works in the synthesis of CuIL complexes of various stoichiometry and structure. Healy et al (24,36) have reported three different types of CuI adducts with 2-picoline : a (CuI(2-picoline))$_4$ has a cubic structure whereas b Cu$_4$I$_4$(2-picoline)$_6$ has a chair type structure. c The third modification of this series reported by them, (CuI(2-picoline)$_2$)$_2$ has an isolated rhomb structure. A new compound in this series was synthesized with stoichiometry 1:1:1, (CuI(2-picoline))$_x$ (VIII). Unlike the 1:1:1 structure of Healy, this compound exhibits a polymeric pleated sheet structure (Figure 16). It crystallizes in the space group P2$_1$/a (Table XXIX). Like polymeric

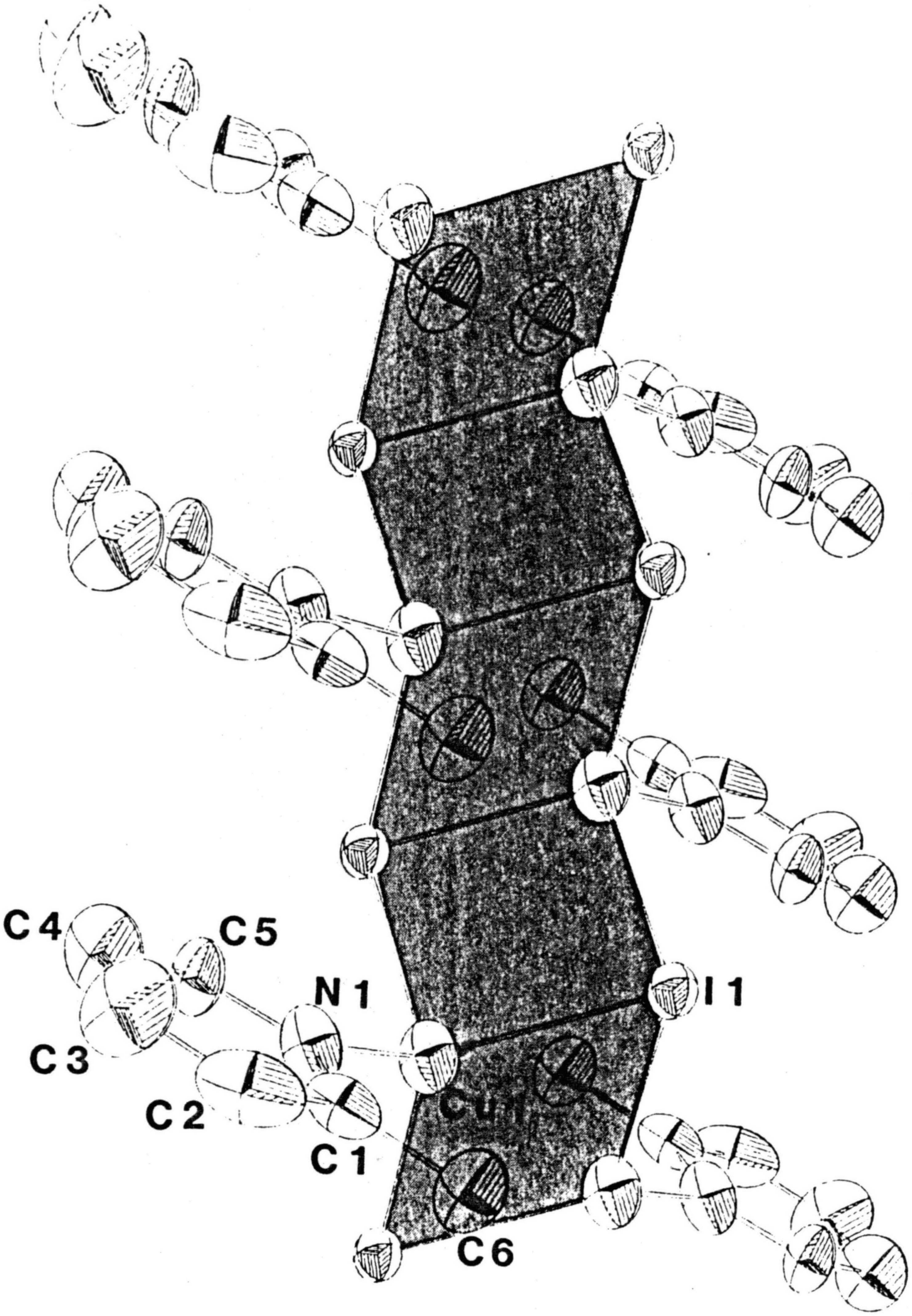

Figure 16. Projection View of VIII

TABLE XXIX

CRYSTAL DATA FOR $(\mathrm{CuI(2\text{-}picoline)})_x$ (VIII)

Formula	$CuIC_6H_7N$
M.W.	283.578 g $mole^{-1}$
a	11.834(5) Å
b	14.914(6)
c	4.381(2)
$\alpha = \gamma$	90.0°
β	93.80(4)
V	771.4(6) $Å^3$
F(000)	528
μ MoK_{α}	67.131 cm^{-1}
λ MoK_{α}	0.71069 Å
D_{cal}	2.441 g cm^{-3}
Z	4
Meas refl	3060
Obs refl	1082
R	7.8%
R_w	9.9%
Space group	$P2_1/a$ (Monoclinic)
Octants meas	±h, +k, +l

structure III, this compound shows edge sharing Cu_2I_2 rhombs extending infinitely along one of the crystal axes.

In this compound the Cu-Cu separation across the rhomb is 2.708(5) Å whereas the Cu-Cu distance between two adjecent rhombs (across the folds) is 3.706(5) Å. Both of these Cu-Cu separations are short compared to those in the $(CuI(MeCN))_x$ structure. The Cu-Cu separation of 2.708(5) Å indicates the possiblity of metal-metal interaction, being shorter than the informal cutoff distance of 2.8 Å. Cu-I distances are 2.681(4) Å and 2.806(4) Å respectively for the iodide atom of the same rhomb and the iodide of the rhomb adjacent to it (across the parallelogram). The Cu-N distance is 2.07(2) Å. Cu-I and Cu-N distances are reasonably constant as expected (Bonded distances and angles, Table XXX). As seen from the projection view of the molecule the planes of the aromatic ligands are parallel to each other projecting away from the rhomb with the planes of the pi systems separated by 3.706 Å. (Positional parameters and anistropic thermal parameters Tables: XXXI and XXXII)

This compound exhibits temperature dependent luminescence (blue-white at room temperature and blue at liq. nitrogen temperature). The thermochromicity can be attributed to the appearance at low temperatures of inter-ligand pi to pi^* interactions joining emission due to MLCT and metal-metal interactions present in both room temperature and low temperature spectra. Detailed measurment of

TABLE XXX

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR (CuI (2-Picoline))$_x$ (VIII)

Cu1-Cu1''	2.708(5)	I1-Cu1-I1'	106.9(1)
Cu1-Cu1''''	3.706(5)	I1-Cu1-I1''	118.9(1)
Cu1-I1	2.646(4)	I1'-Cu1-I1''	95.1(1)
Cu1-I1'	2.806(4)	I1-Cu1-N1	111.3(7)
Cu1-I1''	2.681(4)	I1'-Cu1-N1	105.8(7)
Cu1-N1	2.07(2)	I1''-Cu1-N1	116.1(6)
N1-C1	1.34(4)	Cu1-I1-Cu1''	61.1(1)
C1-C2	1.44(4)	Cu1-I1-Cu1'''	106.1(1)
C1-C6	1.48(4)	Cu1''-I1-Cu1'''	84.9(1)
C2-C3	1.38(6)	Cu1-N1-C1	122(2)
C3-C4	1.36(6)	Cu1-N1-C5	117(2)
C4-C5	1.39(4)	N1-C1-C2	119(3)
C5-N1	1.33(4)	N1-C1-C6	121(2)
		C2-C1-C6	120(3)
		C1-C2-C3	119(3)
		C2-C3-C4	121(3)
		C3-C4-C5	118(3)
		C4-C5-N1	123(3)
		C5-N1-C1	121(2)

TABLE XXX (Continued)

Symmetry operations :

' = x, y, -1.0+z.

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

''' = x, y, 1.0+z

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

TABLE XXXI

POSITIONAL PARAMETERS FOR (CuI(2-Picoline))$_x$ (VIII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.6521(1)	0.0287(1)	0.8378(4)
Cu1	0.5270(3)	0.0734(2)	0.3382(9)
N1	0.502(2)	0.210(1)	0.313(6)
C1	0.416(2)	0.251(2)	0.441(6)
C2	0.402(3)	0.346(2)	0.400(8)
C3	0.478(4)	0.392(2)	0.235(9)
C4	0.566(3)	0.349(2)	0.112(8)
C5	0.577(2)	0.258(2)	0.163(7)
C6	0.337(3)	0.199(2)	0.620(8)
H2	0.339	0.376	0.488
H3	0.462	0.456	0.210
H4	0.622	0.382	-0.008
H5	0.644	0.226	0.087

TABLE XXXII

ANISOTROPIC THERMAL PARAMETERS FOR $(CuI(2\text{-Picoline}))_x$ (VIII)

ATOM	U11	U22	U33	U12	U13	U23
I1	401(8)	285(8)	385(7)	-42(8)	49(5)	2(9)
Cu1	58(2)	20(1)	65(2)	0(1)	0(1)	3(1)
N1	45(13)	20(11)	71(16)	7(9)	-8(11)	0(10)
C1	58(16)	25(13)	42(13)	15(11)	-13(11)	-4(10)
C2	103(28)	44(20)	56(19)	39(18)	-10(18)	-13(14)
C3	121(34)	30(18)	92(28)	16(19)	29(24)	5(17)
C4	89(26)	25(17)	86(25)	7(16)	19(19)	-13(15)
C5	54(17)	19(13)	66(17)	-3(12)	22(14)	-6(11)
C6	66(20)	42(16)	71(21)	2(15)	23(16)	-1(15)

Anisotropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^* +2U13hla^*c^*+2U23klb^*c^*)) \times 10^4 \text{ for I,}$$

$$\times 10^3 \text{ for Cu,N,C.}$$

the luminescence of this compound is necessary for exact assignment of the thermochromism.

A complex of CuI with L=3-picoline (1:1:1), has been reported by Schramm _et al_ which is of cubic structure (77). Two new members of the CuI(3-picoline) family were synthesized and their structures determined. The structure of the adduct with the stoichiometry 1:1:3 was underway when Dyason _et al_ (38) independently reported this structure. Further refinement of the structure was abandoned because the reported cell parameters and atom positions were identical within experimental error. This compound crystallizes in rhombohedral space group R3m and has isolated tetrahedrally bound $CuI(3\text{-picoline})_3$ molecules. A three fold axis passes through the Cu-I bond and each copper atom is bonded to three more ligand molecules related by the symmetry axis.

$Cu_2I_2(3\text{-picoline})_4)$ (IX), with stoichiometry 1:1:2, crystallizes in monoclinic space group, $P2_1$, (Table XXXIII) as an isolated rhombohedron (Figure 17). Each copper is bonded to two iodide atoms and two ligand molecules thus making it tetracoordinated. Cu-I distances vary from 2.638(3) to 2.688(3) Å. The Cu-Cu separation is 2.782(3) Å which shorter than that observed for the quinoline rhomb, VI, 3,364(5) Å. The Cu-Cu separation is just within the range of interactive metal-metal distance. The ligands lie perpendicular to the plane of the rhomb and to each other (packing diagram of the molecule; Figure

TABLE XXXIII

CRYSATL DATA FOR (Cu_2I_2(3-picoline)$_4$) (IX)

Formula	$Cu_2I_2C_{24}H_{28}N_4$
M.W.	763.41 g $mole^{-1}$
<u>a</u>	7.912(2) Å
<u>b</u>	19.390(6)
<u>c</u>	8.774(2)
$\alpha=\gamma$	90.0°
β	102.22(2)
V	1315.4(6) $Å^3$
F(000)	728
μMoK_α	39.63 cm^{-1}
λMoK_α	0.71069 Å
D_{cal}	1.902 g cm^{-3}
Z	2
Meas refl	3229
Obs refl	2072
R	4.6%
R_w	5.2%
Space group	$P2_1$ (Monoclinic)
Octants meas	±h, +k, +l

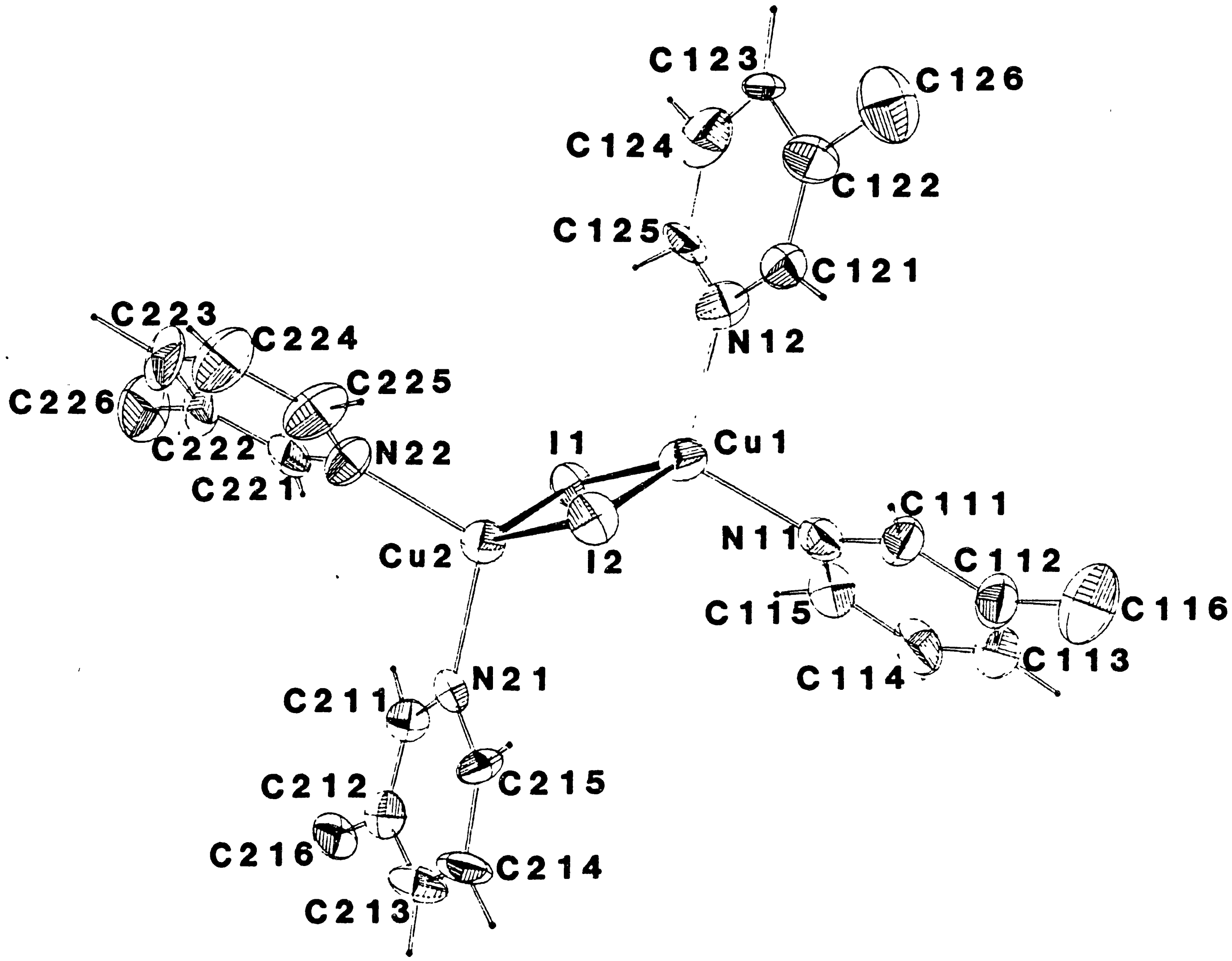

Figure 17. Projection View of IX

18). Because of the perpendicular arrangement of the pi orbitals of the aromatic rings no interligand interaction is possible. This compound is luminescent under UV light, but very little change in emission was observed upon cooling. The temperature independent luminescence is probably due to metal-metal interaction made possible by the close proximity of metal centers, i.e., copper atoms held at a distance of 2.782 Å and to MLCT interactions. No contribution to the luminescence is possible from the aromatic ligands because their positioning in crystal lattice prohibits interligand interactions. Complete structural parameters are listed in tables XXXIV and XXXV. Bond distances and angles for IX are presented in Table XXXVI.

Dyason _et_ _al_ had synthesized and elucidated the structure of $CuI(2,4\text{-lutidine})_2$ which has a rhombohedral structure (37). With the same ligand, we have been able to isolate an adduct with stoichiometry 1:1:1, $(CuI(2,4\text{-lutidine}))_x$ (X), which has a polymeric pleated sheet structure (Figure 19). The compound crystallizes in triclinic space group of $P\bar{1}$ (Table XXXVII). Like the other two polymeric structures, X displays edge sharing rhombs with each copper atom bonded to three iodides. The lutidine molecules project outward from the pleated sheet, the pleated sheet structure continuing indefinitely along a crystallographic axes. Cu-Cu separation across the parallelogram is 2.734(4) Å which can be considered to be a

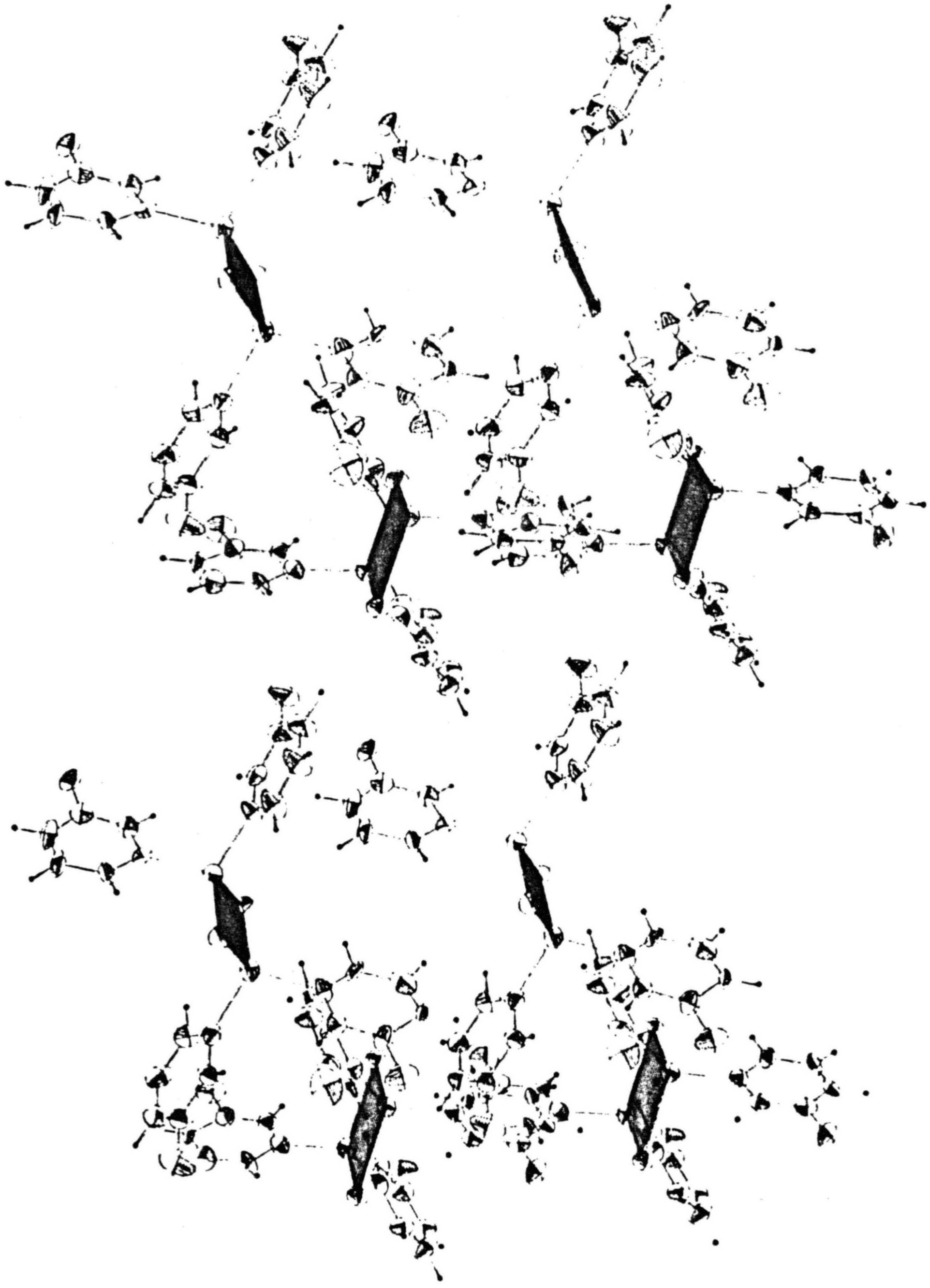

Figure 18. Packing Diagram of IX

TABLE XXXIV

POSITIONAL PARAMETERS FOR (Cu_2I_2(3-Picoline)$_4$) (IX)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.4440(1)	0.3287(1)	0.2944(1)
I2	0.9448(2)	0.2382(1)	0.2134(1)
Cu1	0.7802(3)	0.3443	0.3156(3)
Cu2	0.6089(3)	0.2249(1)	0.1931(3)
N11	0.8211(20)	0.4333(9)	0.1932(18)
N12	0.8960(20)	0.3594(9)	0.5482(18)
N21	0.4887(18)	0.2128(8)	-0.0372(17)
N22	0.5678(21)	0.1375(9)	0.3171(18)
C111	0.982(3)	0.453(1)	0.184(3)
C112	1.013(3)	0.512(1)	0.094(3)
C113	0.872(3)	0.546(1)	0.018(3)
C114	0.709(3)	0.528(1)	0.028(3)
C115	0.680(3)	0.472(1)	0.118(3)
C116	1.197(4)	0.529(2)	0.086(4)
C121	1.068(2)	0.367(1)	0.589(2)
C122	1.157(2)	0.374(1)	0.738(2)
C123	1.059(3)	0.369(1)	0.865(2)
C124	0.885(3)	0.364(1)	0.813(3)
C125	0.809(2)	0.358(1)	0.656(2)
C126	1.355(3)	0.382(2)	0.786(3)
C211	0.315(2)	0.209(1)	-0.085(2)

TABLE XXXIV (Continued)

C212	0.229(3)	0.200(1)	-0.238(2)
C213	0.328(3)	0.203(1)	-0.342(2)
C214	0.501(3)	0.208(1)	-0.308(2)
C215	0.583(3)	0.211(1)	-0.151(2)
C216	0.031(3)	0.192(1)	-0.280(3)
C221	0.407(3)	0.121(1)	0.337(2)
C222	0.370(3)	0.063(1)	0.412(3)
C223	0.510(5)	0.020(1)	0.475(4)
C224	0.674(4)	0.037(2)	0.458(3)
C225	0.694(3)	0.097(1)	0.383(3)
C226	0.184(4)	0.047(2)	0.425(4)
H111	1.0850	0.4214	0.2302
H113	0.8856	0.5870	-0.0476
H114	0.6083	0.5555	-0.0218
H115	0.5687	0.4549	0.1155
H121	1.1611	0.3704	0.5317
H123	1.1147	0.3700	0.9745
H124	0.8113	0.3579	0.8864
H125	0.6838	0.3454	0.6315
H211	0.2484	0.2123	-0.0022
H213	0.2676	0.2021	-0.4546
H214	0.5684	0.2125	-0.3908
H215	0.7135	0.2098	-0.1157
H221	0.3064	0.1447	0.2812
H223	0.4782	-0.0234	0.5401

TABLE XXXIV (Continued)

H224	0.7753	0.0005	0.4922
H225	0.8141	0.1088	0.3888

TABLE XXXV

ANISITROPIC THERMAL PARAMETERS FOR (Cu_2I_2(3-Picoline)$_4$) (IX)

ATOM	U11	U22	U33	U12	U13	U23
I1	324(6)	361(7)	431(7)	1(6)	67(5)	-56(6)
I2	311(6)	412(8)	454(7)	23(6)	85(5)	-28(6)
Cu1	41(1)	41(1)	34(1)	0(1)	5(1)	4(1)
Cu2	38(1)	39(1)	35(1)	-2(1)	4(1)	1(1)
N11	44(8)	33(9)	34(8)	-1(7)	4(6)	-8(6)
N12	36(8)	49(10)	38(8)	3(7)	17(6)	2(7)
N21	30(7)	24(8)	35(8)	-4(5)	4(6)	-8(6)
N22	38(8)	44(9)	42(9)	-2(7)	19(7)	10(7)
C111	42(11)	35(14)	42(12)	-5(9)	6(9)	9(10)
C112	56(14)	32(13)	52(13)	-9(10)	16(11)	1(10)
C113	79(17)	21(13)	51(14)	0(11)	6(12)	8(9)
C114	65(15)	28(13)	63(15)	0(11)	-21(12)	5(11)
C115	32(11)	36(13)	59(14)	3(9)	4(9)	0(10)
C116	67(17)	39(16)	106(22)	13(13)	35(15)	20(15)
C121	31(10)	36(11)	35(10)	1(7)	6(7)	1(8)
C122	30(9)	49(12)	38(10)	5(7)	2(7)	-4(8)
C123	59(12)	28(10)	13(8)	-5(8)	-8(7)	0(6)
C124	66(15)	48(15)	58(14)	0(11)	29(12)	8(11)
C125	36(9)	40(11)	27(9)	-11(7)	6(7)	-22(8)
C126	32(13)	67(17)	92(19)	-5(11)	6(12)	-7(14)
C211	34(10)	37(11)	37(11)	2(8)	14(8)	-2(8)
C212	33(10)	31(10)	47(10)	5(7)	10(8)	0(7)

TABLE XXXV (Continued)

C213	48(11)	52(13)	28(9)	21(9)	5(8)	-15(8)
C214	68(13)	48(13)	19(10)	5(10)	7(9)	-12(8)
C215	48(11)	38(12)	21(9)	1(8)	6(8)	8(8)
C216	29(10)	51(13)	44(12)	-10(8)	-14(8)	-2(9)
C221	55(12)	30(11)	34(10)	-1(9)	14(8)	-17(8)
C222	64(14)	19(12)	57(14)	1(10)	26(11)	-4(10)
C223	111(23)	15(13)	72(17)	9(13)	25(16)	10(11)
C224	60(15)	55(18)	74(17)	21(13)	12(13)	27(14)
C225	48(13)	63(18)	57(15)	23(12)	6(10)	28(12)
C226	75(19)	79(22)	89(22)	-38(16)	39(16)	3(17)

Anisotropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^*$$
$$+2U13hla^*c^*+2U23klb^*c^*)) \times 10^4 \text{ for I},$$
$$\times 10^3 \text{ for Cu,N,C.}$$

TABLE XXXVI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR (Cu_2I_2 (3-Picoline)$_4$) (IX)

I1-Cu1	2.644(3)	Cu1-I1-Cu2	63.3(1)
I1-Cu2	2.652(4)	Cu1-I2-Cu2	62.9(1)
I2-Cu1	2.688(3)	I1-Cu1-I2	116.1(1)
I2-Cu2	2.638(3)	I1-Cu1-N11	108.7(4)
Cu1-N11	2.09(2)	I1-Cu1-N12	108.3(5)
Cu1-N12	2.07(2)	I2-Cu1-N11	108.7(5)
N11-C111	1.35(3)	I2-Cu1-N12	107.0(5)
N11-C115	1.39(3)	N11-Cu1-N12	107.8(6)
C111-C112	1.43(3)	Cu1-N11-C111	121(1)
C112-C113	1.35(3)	Cu1-N11-C115	120(1)
C112-C116	1.51(4)	C111-N11-C115	119(2)
C113-C114	1.35(4)	N11-C111-C112	122(2)
C114-C115	1.38(4)	C111-C112-C113	116(2)
N12-C121	1.34(2)	C111-C112-C116	119(2)
N12-C125	1.28(3)	C113-C112-C116	125(2)
C121-C122	1.35(2)	C112-C113-C114	122(2)
C122-C123	1.49(3)	C113-C114-C115	121(2)
C122-C126	1.54(3)	C114-C115-N11	119(2)
C123-C124	1.36(3)	Cu1-N12-C121	119(1)
C124-C125	1.39(3)	Cu1-N12-C125	122(1)
Cu2-N21	2.06(1)	C121-N12-C125	119(2)
Cu2-N22	2.08(2)	N12-C121-C122	124(2)
N21-C211	1.35(2)	C121-C122-C123	118(2)

TABLE XXXVI (Continued)

N21-C215	1.37(3)	C121-C122-C126	124(2)
C211-C212	1.39(3)	C123-C122-C126	118(2)
C212-C213	1.33(3)	C122-C123-C124	114(2)
C212-C216	1.54(3)	C123-C124-C125	122(2)
C213-C214	1.34(3)	C124-C125-N12	123(2)
C214-C215	1.39(3)	Cu2-N21-C211	123(1)
N22-C221	1.36(3)	Cu2-N21-C215	121(1)
N22-C225	1.31(3)	C211-N21-C215	117(2)
C221-C222	1.36(3)	N21-C211-C212	125(2)
C222-C223	1.40(4)	C211-C212-C213	115(2)
C222-C226	1.54(4)	C211-C212-C16	121(2)
C223-C224	1.38(5)	C213-C212-C216	125(2)
C224-C225	1.36(4)	C212-C213-C214	125(2)
Cu1-Cu2	2.782(3)	C213-C214-C215	118(2)
		C214-C215-N21	121(2)
		Cu2-N22-C221	121(1)
		Cu2-N22-C225	122(2)
		C221-N22=c225	116(2)
		N22-C221-C222	124(2)
		C221-C222-C223	117(2)
		C221-C222-C226	121(2)
		C223-C222-C226	123(2)
		C222-C223-C224	120(3)
		C223-C224-C225	117(2)
		C224-C225-N22	125(2)

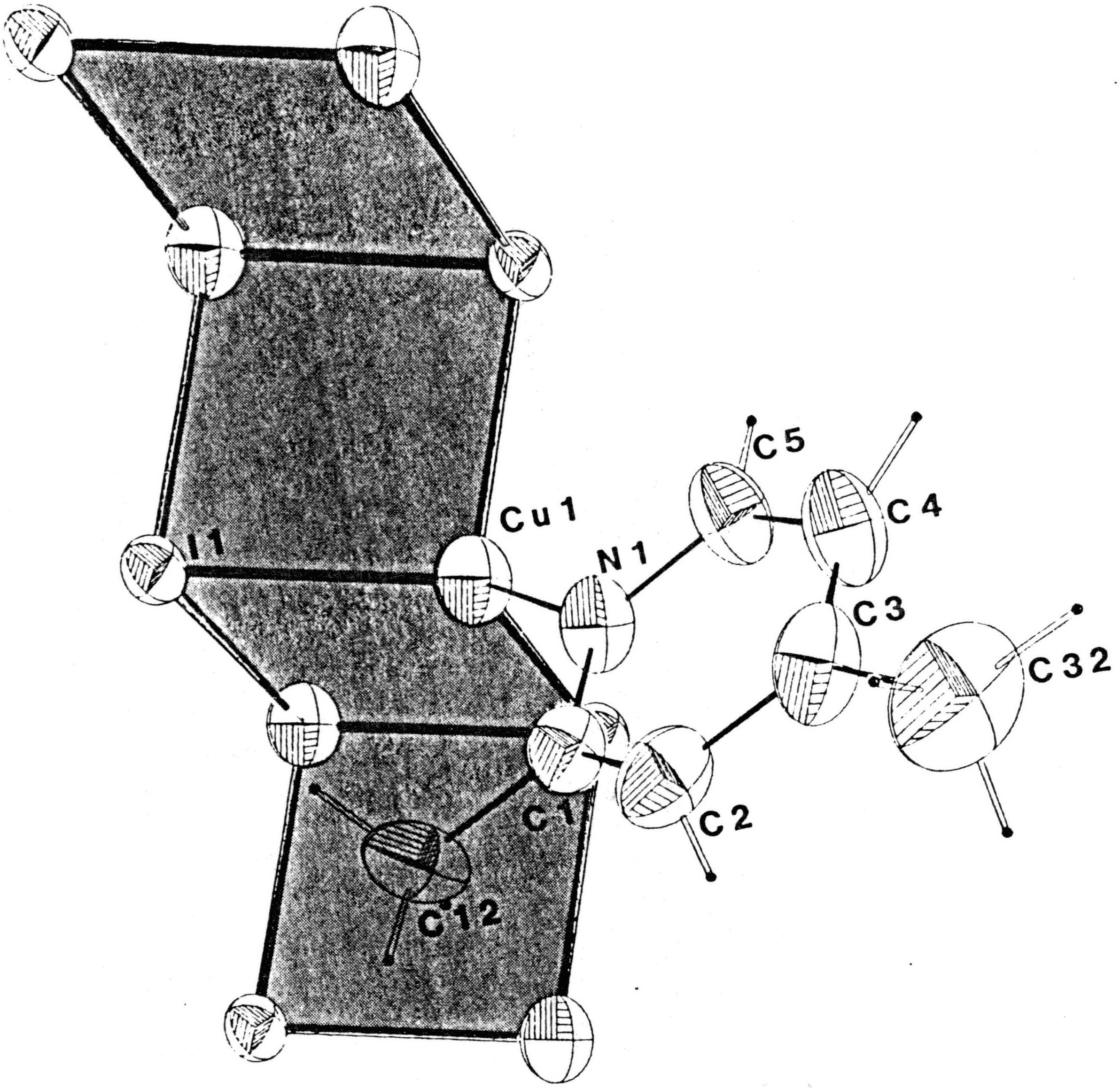

Figure 19. Projection View of X

TABLE XXXVII

CRYSTAL DATA FOR (CuI(2,4-lutidine))x (X)

Formula	$CuIC_7H_9N$
M.W.	297.605 g mole^{-1}
a	11.648(8) Å
b	4.328(3)
c	10.198(4)
α	77.64(5)^{o}
β	68.45(4)
γ	104.25(5)
V	436.21(46) Å^3
F(000)	280
μMoK_{α}	59.413 cm^{-1}
λMoK_{α}	0.71069 A
D_{cal}	2.265 g cm^{-3}
Z	2
Meas refl	4229
Obs refl	1731
R	6.3%
R_w	7.3%
Space group	$P\bar{1}$ (Triclinic)
Octants measr	±h, ±k, +l

metal-metal interactive distance, being less than 2.8 Å. The relatively short Cu-Cu distance pushes the iodides further apart (I-I distance 4.328(3) Å). Cu-I and Cu-N bond distances (Table XXXVIII) are comparable with those of other structures. The packing diagram of the compound (Figure 20) shows that the planes of the aromatic rings are parallel to each other. Complete listing of positional and anistropic thermal parameters are listed in Tables XXXIX and XL respectively.

This compound exhibits thermochromic luminescence, emitting white-blue at room temperature and changing to blue at liquid nitrogen temperature. The thermochromicity can be explained in terms of the low temperature contribution of ligand-ligand interactions. Emission due to the short Cu-Cu distances and to MLCT is probable at room temperature.

One of the general methods used to stabilize Cu(I) in solution and thus permit syntheses of Cu(I) complexes is the use of excess halide ion in aqueous solution as the medium of reaction. CuI is soluble in aqueous solution of KI and the Cu(I)$\rightleftharpoons$Cu(II) equilibrium is shifted to the left. Use of the CuI-KI water systems in the presence of various crown ethers has led to a very interesting series of luminescent materials whose structures differ markedly from each other depending on the size of the cavity of the crown ether involved. Some of these compounds display temperature dependent

TABLE XXXVIII

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

$(\mathrm{CuI(2,4 - Lutidine)})_x$ (X)

I1 - I1'	4.328(3)	C2 - H2	0.79(2)
I1 - I1''	4.096(3)	C3 - C4	1.34(3)
I1 - Cu1	2.675(2)	C3 - C32	1.52(3)
I1 - Cu1'''	2.644(3)	C4 - C5	1.37(3)
I1 - Cu1''	2.782(3)	C4 - H4	0.96(2)
Cu1 - Cu1'''	2.734(4)	C5 - H5	0.99(2)
Cu1 - N1	2.05(2)	C12 - H121	1.02(2)
N1 - C1	1.32(2)	C12 - H122	0.97(2)
N1 - C5	1.38(2)	C12 - H123	0.94(2)
C1 - C2	1.38(3)	C32 - H321	0.98(2)
C1 - C12	1.50(2)	C32 - H322	1.00(2)
C2 - C3	1.39(3)	C32 - H323	0.98(2)
Cu1-I1-Cu1'''	61.85(8)	C4-C3-C32	122(1)
I1-Cu1-I1'''	118.15(10)	C3-C4-C5	120(1)
I1-Cu1-I1''	97.27(9)	C3-C4-H4	128(2)
I1''-Cu1-I1'''	112.75(10)	C5-C4-H4	110(1)
N1-Cu1-I1	116.4(4)	N1-C5-C4	122(2)
N1-Cu1-I1'''	110.0(3)	N1-C5-H5	119(2)
N1-Cu1-I1''	107.3(4)	C4-C5-H5	119(2)
N1-Cu1-Cu1'''	139.9(4)	C1-C12-H121	106(1)
C1-N1-C5	116(1)	C1-C12-H122	109(1)
C1-N1-Cu1	126(1)	C1-C12-H123	118(2)
C5-N1-Cu1	117.1(1)	H121-C12-H122	106(1)
N1-C1-C2	123.1(1)	H121-C12-H123	106(1)

TABLE XXXVIII (Continued)

N1-C1-C12	116(1)	H122-C12-H123	111(2)
C2-C1-C12	121(1)	C3-C32-H321	109(2)
C1-C2-C3	120(1)	C3-C32-H322	108(2)
C1-C2-H2	114(1)	C3-C32-H323	122(2)
C3-C2-H2	101(1)	H321-C32-H322	106(2)
C2-C3-C4	118(1)	H321-C32-H323	106(2)
C2-C3-C32	120(1)	H322-C32-H323	104(2)

Symmetry Operations :

' = x, 1.0+y, z

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

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

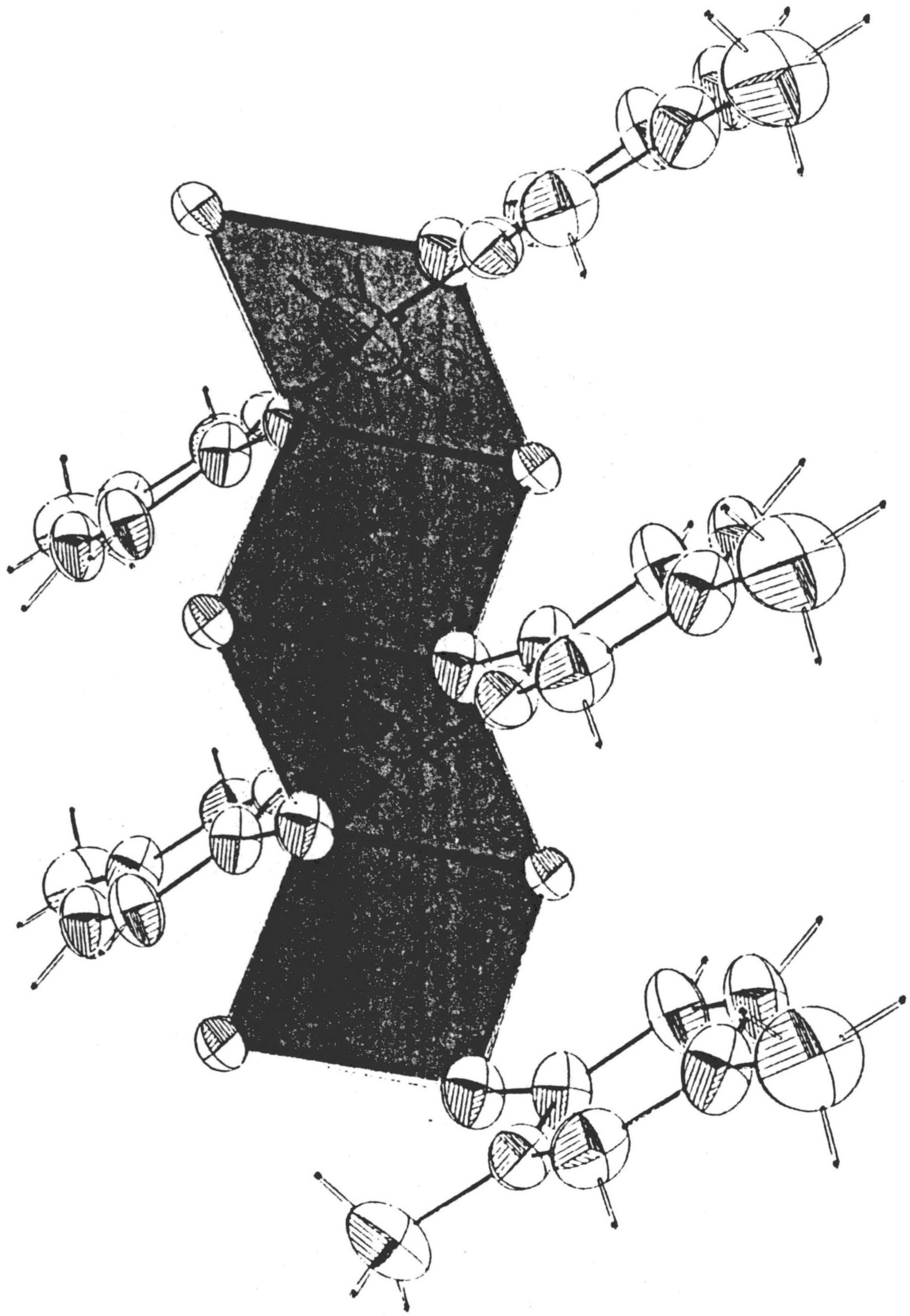

Figure 20. Packing Diagram of X

TABLE XXXIX

POSITIONAL PARAMETERS FOR $(CuI(2,4\text{-Lutidine}))_x$ (X)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.8687(1)	0.0095(2)	0.1973(1)
Cu1	0.9710(2)	0.3528(5)	-0.0954(2)
N1	0.8418(11)	0.3062(30)	-0.1897(12)
C1	0.7255(14)	0.3395(33)	-0.1374(15)
C2	0.6427(16)	0.2925(39)	-0.2056(18)
C3	0.6842(15)	0.2263(39)	-0.3393(16)
C4	0.8017(16)	0.1896(43)	-0.3931(17)
C5	0.8790(15)	0.2246(44)	-0.3189(16)
C12	0.6861(16)	0.4279(44)	0.0035(19)
C32	0.5943(21)	0.1812(53)	-0.4161(22)
H2	0.6222	0.4500	-0.2271
H4	0.8325	0.0781	-0.4643
H5	0.9644	0.1887	-0.3593
H121	0.6869	0.2387	0.0823
H122	0.7542	0.6308	-0.0115
H123	0.6021	0.4439	0.0452
H321	0.5102	-0.0035	-0.3467
H322	0.5729	0.3907	-0.4365
H323	0.6209	0.1380	-0.5110

TABLE XL

ANISOTROPIC THERMAL PARAMETERS FOR $(CuI(2,4\text{-Lutidine}))_x$ (X)

ATOM	U11	U22	U33	U12	U13	U23
I1	435(5)	363(4)	309(4)	136(3)	-180(3)	-155(3)
Cu1	498(11)	574(11)	461(10)	138(9)	-325(9)	-207(8)
N1	30(5)	53(6)	37(5)	6(5)	-20(4)	-12(5)
C1	45(8)	36(6)	40(7)	8(5)	-26(6)	-13(5)
C2	54(9)	52(8)	58(9)	19(7)	-40(8)	-15(7)
C3	44(8)	56(8)	46(8)	1(6)	-34(7)	-10(6)
C4	54(9)	68(10)	38(7)	7(7)	-26(7)	-21(7)
C5	43(8)	76(10)	41(7)	19(7)	-23(6)	-28(7)
C12	48(9)	74(10)	66(10)	29(8)	-39(8)	-43(8)
C32	82(14)	90(14)	71(12)	15(11)	-61(11)	-25(10)

Anisotropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^*$$
$$+2U13hla^*c^*+2U23klb^*c^*)) \times 10^4 \text{ for I and Cu,}$$
$$\times 10^3 \text{ for N and C.}$$

flurescence. These structures have in common their lack of copper-organic ligand bonds; all Cu binding sites being occupied by iodide atoms. All of the compounds of this series have structures which are previously unobserved for CuI compounds.

CuI and KI in the presence of 12-crown-4 (12-C-4), the crown ether with smallest cavity of those used, forms the compound $Cu_{12}I_{19}K_7$(12-crown-4) (XI); which crystallizes in tetragonal space group $P\bar{4}$ (Table XLI) and has two different clusters in the assymetric unit (Figure 21). The two different clusters are $Cu_4I_6^{2-}$ and $Cu_8I_{13}^{5-}$, their combined charges being balanced by seven K^+ ions, six of which are coordinated to crown ether rings and all of which display ionic interactive distances to iodide neighbors. The smaller of the two clusters, $Cu_4I_6^{2-}$ shows a tetrahedral arrangement of the copper atoms with Cu-Cu average distance of 2.76(1) Å (Table XLII). Each pair of copper atoms is bridged by an iodide. The cluster of greater nuclearity, $Cu_8I_{13}^{5-}$, exhibits a cubic arrangement of eight copper atoms (Cu-Cu average distance 3.35(1) Å) centered by an iodide atom and bridged on all twelve edges by further iodide atoms. The larger clusters pack parallel to the <u>c</u>-axis (packing diagram, Figure 22); two succesive units being separated by K atoms having ionic interactions with iodide atoms (K-I average distance 3.76(1) Å). The remaining six K atoms are centered at the other faces(Figure 23) of the $Cu_8I_{13}^{5-}$ cluster and in the voids

TABLE XLI

CRYSTAL DATA FOR $((Cu_4I_6)(Cu_8I_{13})K_7(12\text{-crown-}4)_6)$ (XI)

Formula	$Cu_{12}I_{19}K_7C_{48}H_{96}O_{24}$
M.W.	4504.695 g $mole^{-1}$
a	17.702(5) Å
b	17.715(5)
c	10.581(4)
$\alpha = \beta = \gamma$	90.0°
V	3318.1(18) $Å^3$
F(000)	2064
μMoK_α	65.27 cm^{-1}
λMoK_α	0.71069 Å
D_{cal}	2.254 g cm^{-3}
Z	1
Meas refl	7535
Obs refl	3290
R	8.7%
R_w	13.8%
Space group	$P\bar{4}$ (Tetragonal)
Octants meas	+h, +k, +l

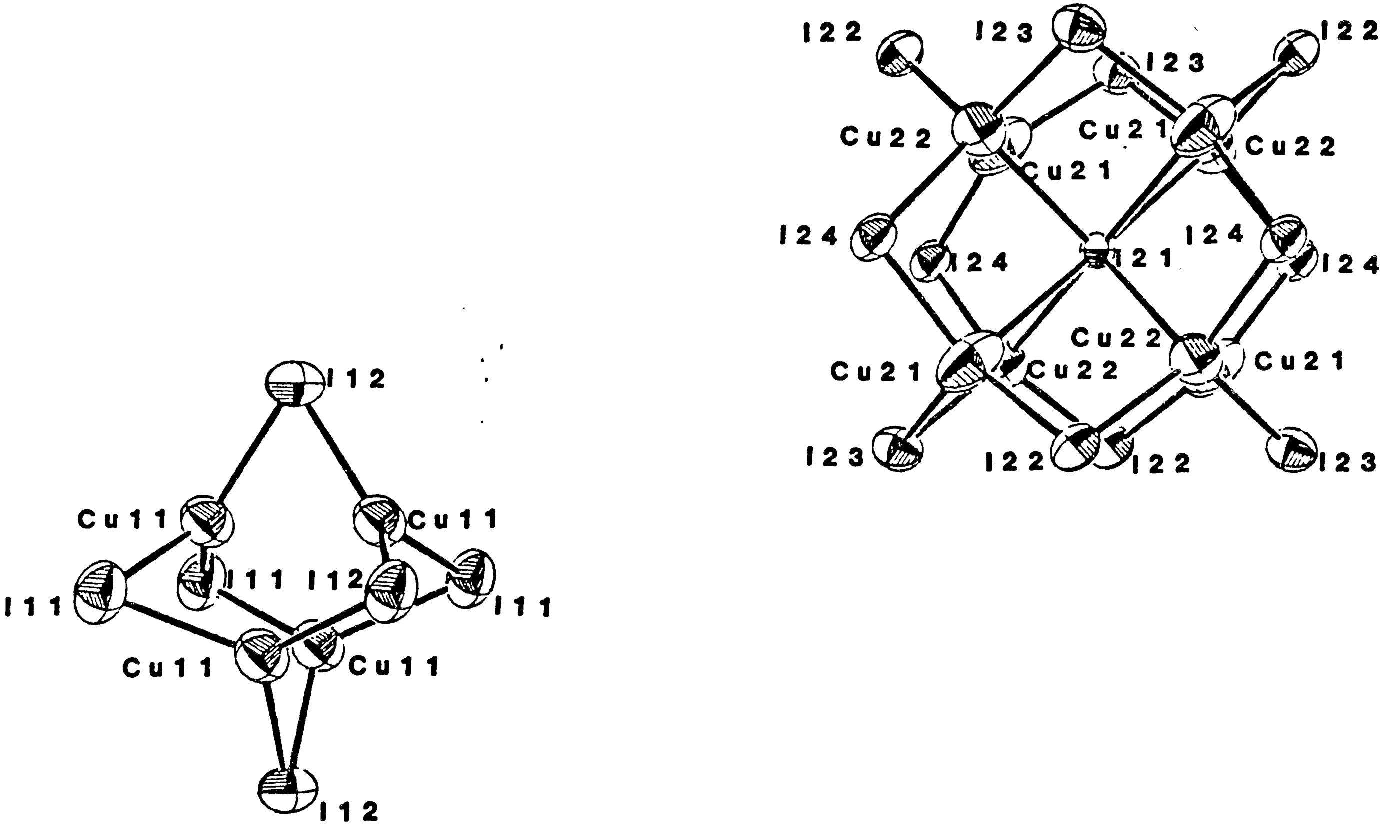

Figure 21. Arrangement of Cu and I atoms in XI

TABLE XLII

BOND DISTANCES (Å) AND ANGLES (°) FOR ((Cu_4I_6) (Cu_8I_{13}) K_7(12-Crown-4) (XI)

I11-I11(6)	4.388(4)	Cu11-I11-Cu11(6)	66.3(2)
I12-I12(5)	4.191(5)	Cu11-I12-Cu11(3)	64.0(2)
I21-I23	4.369(5)	Cu21-I21-Cu22	73.5(3)
I21-I24	4.251(2)	Cu21-I21-Cu21(4)	105.9(3)
I21-I22(1)	4.391(5)	Cu21-I21-Cu22(4)	179.2(3)
I22-I23	4.348(8)	Cu21-I21-Cu21(7)	111.2(3)
I22-I24(2)	4.293(7)	Cu21-I21-Cu22(7)	68.6(2)
I23-I24(10)	4.313(7)	Cu21(11)-I22-Cu22(2)	81.1(4)
Cu11-I11	2.561(8)	Cu21-I23-Cu22(10)	82.1(4)
Cu11-I12	2.571(7)	Cu21-I24-Cu22	86.6(4)
Cu11-I11(9)	2.551(8)	I11-Cu11-I12	120.1(3)
Cu11-Cu11(10)	2.797(9)	I11-Cu11-I11(9)	118.3(3)
Cu21-I21	2.989(14)	I21-Cu21-I23	103.5(4)
Cu21-I23	2.564(12)	I22(8)-Cu21-I23	117.1(5)
Cu21-I24	2.610(14)	I22(8)-Cu21-I24	114.7(5)
Cu21-I22(8)	2.554(12)	I23-Cu21-I24	115.2(5)
Cu21-Cu22(7)	3.332(15)	I21-Cu21-I24	98.5(4)
Cu21-Cu22(10)	3.373(15)	I21-Cu21-I22(8)	104.5(4)
Cu22-I21	2.928(9)	I21-Cu22-I24	101.4(3)
Cu22-I24	2.556(10)	I21-Cu22-I22(1)	105.8(3)
Cu22-I22(1)	2.572(9)	I21-Cu22-I23(7)	104.9(3)
Cu22-I23(7)	2.574(9)	I24-Cu22-I22(1)	113.7(3)
K1-I22	3.801(5)	I24-Cu22-I23(7)	114.4(4)

TABLE XLII (Continued)

K1-I23	3.733(5)	I22(1)-Cu22-I23(7)	114.8(4)
K2-I23	3.751(18)	I22-K1-I23	70.5(1)
K2-I24	3.690(19)	I22-K1-I22(4)	109.7(1)
K2-I22(1)	3.720(18)	I22-K1-I23(4)	179.6(11)
		I23-K1-I23(4)	109.4(1)
		I23-K2-I24	71.9(2)
		I23-K2-I22(1)	113.1(2)
		I24-K2-I24(10)	109.3(2)

Symmetry operations :

1 = x, y, 1.0+z

2 = x, y, -1.0+z

3 = 1.0-x, 1.0-y, z

4 = -x, -y, z

5 = 1.0-y, x, 1.0-z

6 = 1.0-y, x, -z

7 = -y, -x, 1.0-z

8 = -y, x, -z

9 = y, -x, -z

10 = y, -x, 1.0-z

11 = y, -x, -z

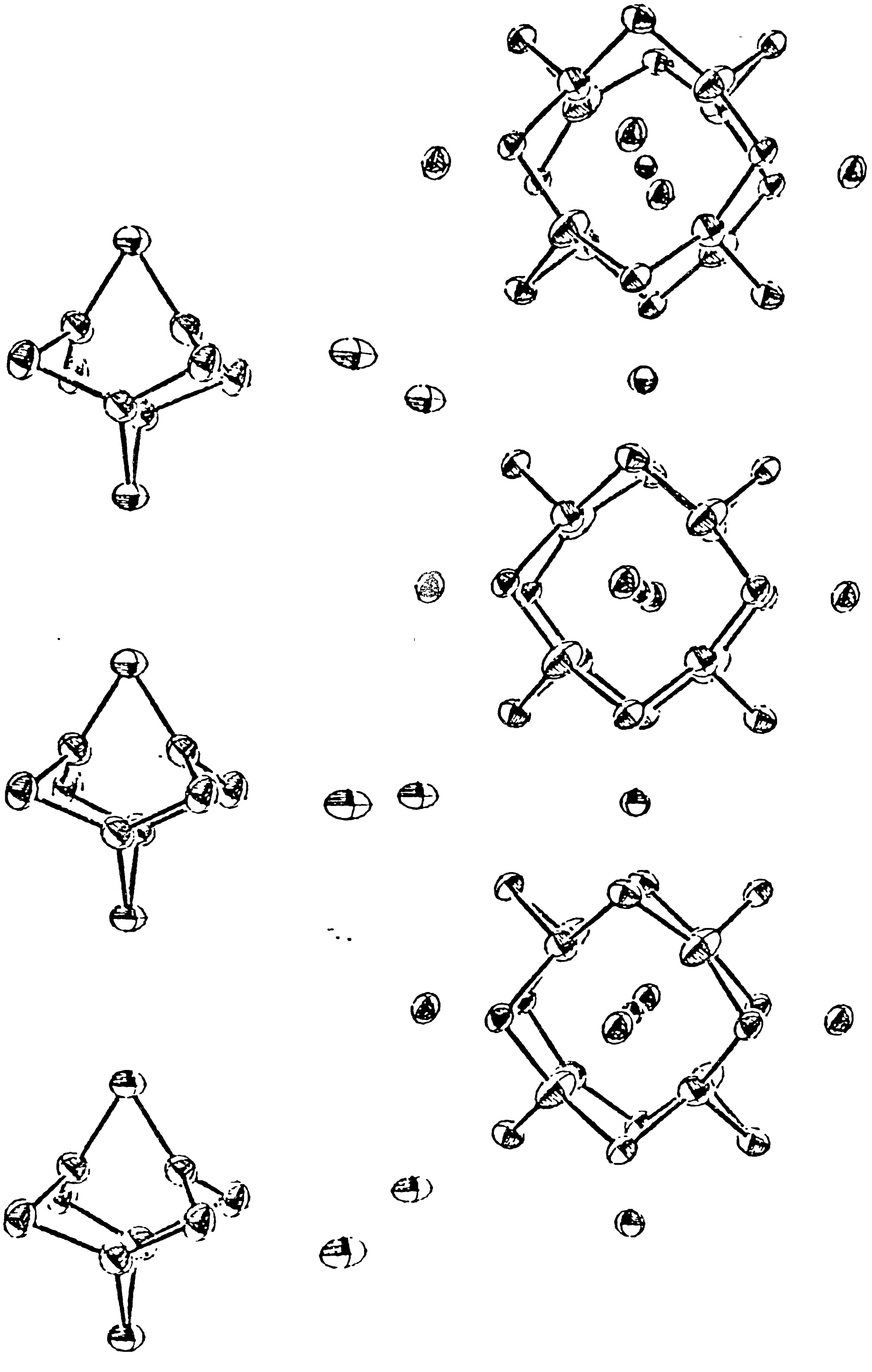

Figure 22. Packing Diagram of XI

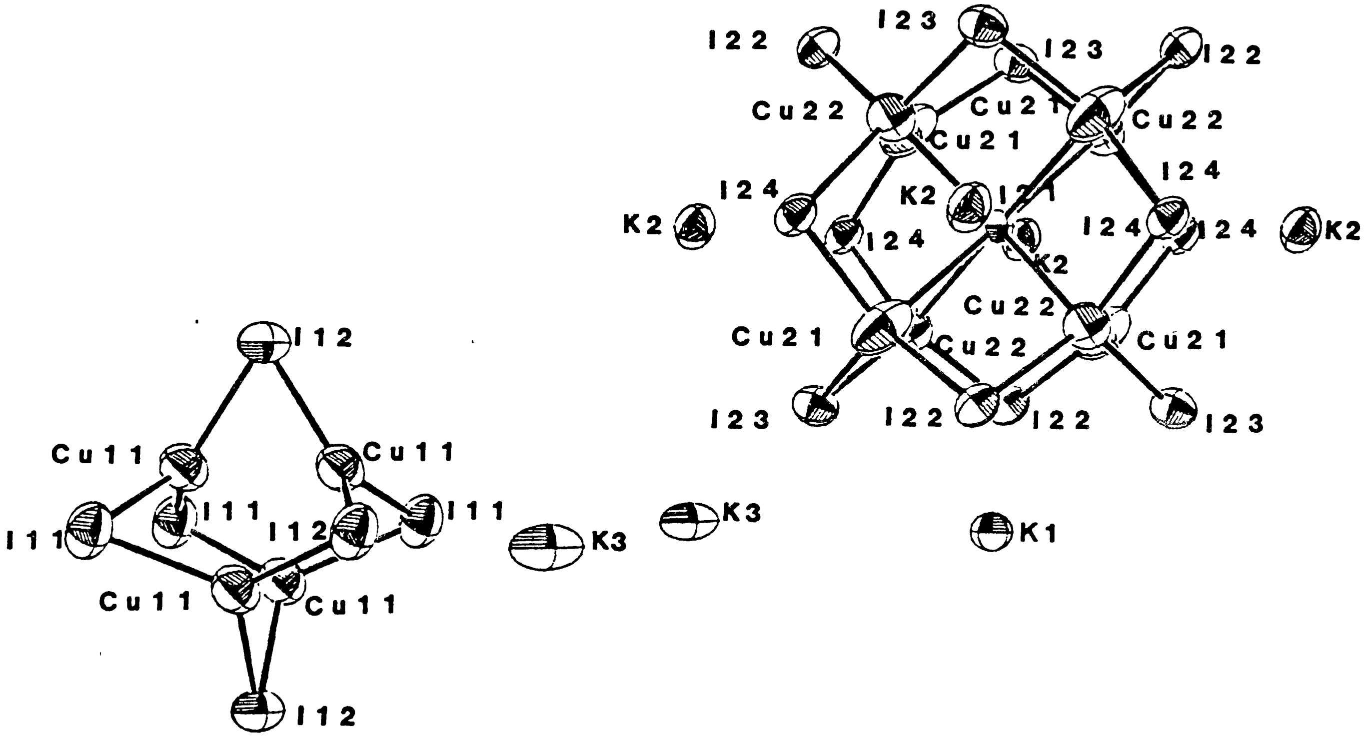

Figure 23. Projection View of XI

of the cell between the large and small clusters. The larger cluster is reminescent of the Cu(I) frame work seen in $Cu^{(II)}{}_6Cu^{(I)}{}_6S_{12}N_{12}Cl$ (Cu(I)-Cu(I) average distance 3.30(2) Å) (78) but the smaller one is of unknown precedence (79). Positional and anisotropic thermal parameters for the atoms are listed in Tables XLIII and XLIV respectively.

Compound XI exhibits thermochromic luminescence, changing emission from yellow to green on going from room temperature to 15 K. The emission (Figure 24) at room temperature shows a broad featureless spectrum (λ_{max} = 540 nm) which is resolved into three distinct maxima (λ_{max} = 420, 535, 650 nm) at 15 K. Assignment of the 420 nm emission to Cu-Cu interaction is consistant with observations for other CuI systems with Cu-Cu distance of less than 2.8 Å. Assignment of the lower energy emission maxima must wait until further emission measurments in this series are completed.

The use of 15-crown-5 (15-C-5) with CuI-KI in aqueous medium, the crown ether having a bigger cavity than that of 12-C-4, results in an unexpectedly different polymeric cluster with molecular formula ($Cu_4I_6K_2$(15-crown-5)$_2$) (XII). It crystallizes in triclinic space group $P\bar{1}$ (Table XLV). The polymeric structure is reminescent of the $(CuI(MeCN))_x$, $(CuI(2\text{-picoline}))_x$, and $(CuI(2,4\text{-lutidine}))_x$ pleated sheets with the addition of a bridging iodide across alternate Cu_2I_2 faces of the polymeric chain

TABLE XLIII

POSITIONAL PARAMETERS FOR $((Cu_4I_6)(Cu_8I_{13})$ $K_7(12\text{-Crown-}4)_6)$ (XI)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I11	0.5002(2)	0.3248(1)	0.0009(8)
I12	0.5000	0.5000	0.3019(3)
I21	0.0000	0.0000	0.5000
I22	0.1237(3)	0.1246(3)	-0.2068(5)
I23	0.1221(3)	0.1212(3)	0.2040(5)
I24	-0.0001(1)	0.2400(1)	0.5026(6)
Cu11	0.4452(4)	0.4460(4)	0.0958(6)
Cu21	-0.0010(6)	0.1348(8)	0.3299(12)
Cu22	0.0007(5)	0.1330(5)	0.6646(9)
K1	0.0000	0.0000	0.0000
K2	0.2054(5)	0.2049(5)	0.4984(19)
K3	0.5000	0.0000	-0.0020(31)
O21	0.3537(34)	0.1858(34)	0.3694(59)
O22	0.2907(51)	0.3331(51)	0.3195(91)
O23	0.1859(38)	0.3561(37)	0.3711(64)
O24	0.3323(48)	0.2848(49)	0.6652(87)
O31	0.6401(49)	0.1038(50)	0.0282(96)
O32	0.3894(55)	0.0945(57)	0.2008(105)
O33	0.6330(92)	0.0923(89)	-0.1398(159)

TABLE XLIV

ANISOTROPIC THERMAL PARAMETERS FOR $((Cu_4I_6)(Cu_8I_{13})K_7(12\text{-Crown-}4)_6)$ (XI)

ATOM	U11	U22	U33	U12	U13	U23
I11	870(19)	540(15)	967(22)	5(13)	-265(44)	-52(40)
I12	1315(17)	702(57)	490(21)	-173(59)		
I21	307(11)		327(19)			
I22	456(269)	540(29)	541(31)	83(23)	-113(24)	-62(24)
I23	684(33)	562(31)	492(32)	48(26)	26(27)	73(24)
I24	600(13)	411(11)	510(14)	-8(9)	-62(32)	3(31)
Cu11	69(3)	73(4)	74(4)	-9(3)	8(3)	4(3)
Cu22	46(5)	85(6)	66(7)	-4(4)	-16(4)	27(5)
K1	54(5)		56(9)			
K2	64(5)	65(5)	70(6)	-20(4)	-29(9)	35(9)
K3	20(4)	149(12)	54(6)	-1(5)		

Anisotropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^* +2U13hla^*c^*+2U23klb^*c^*)) \times 10^3 \text{ for Cu and K}$$

$$\times 10^4 \text{ for I.}$$

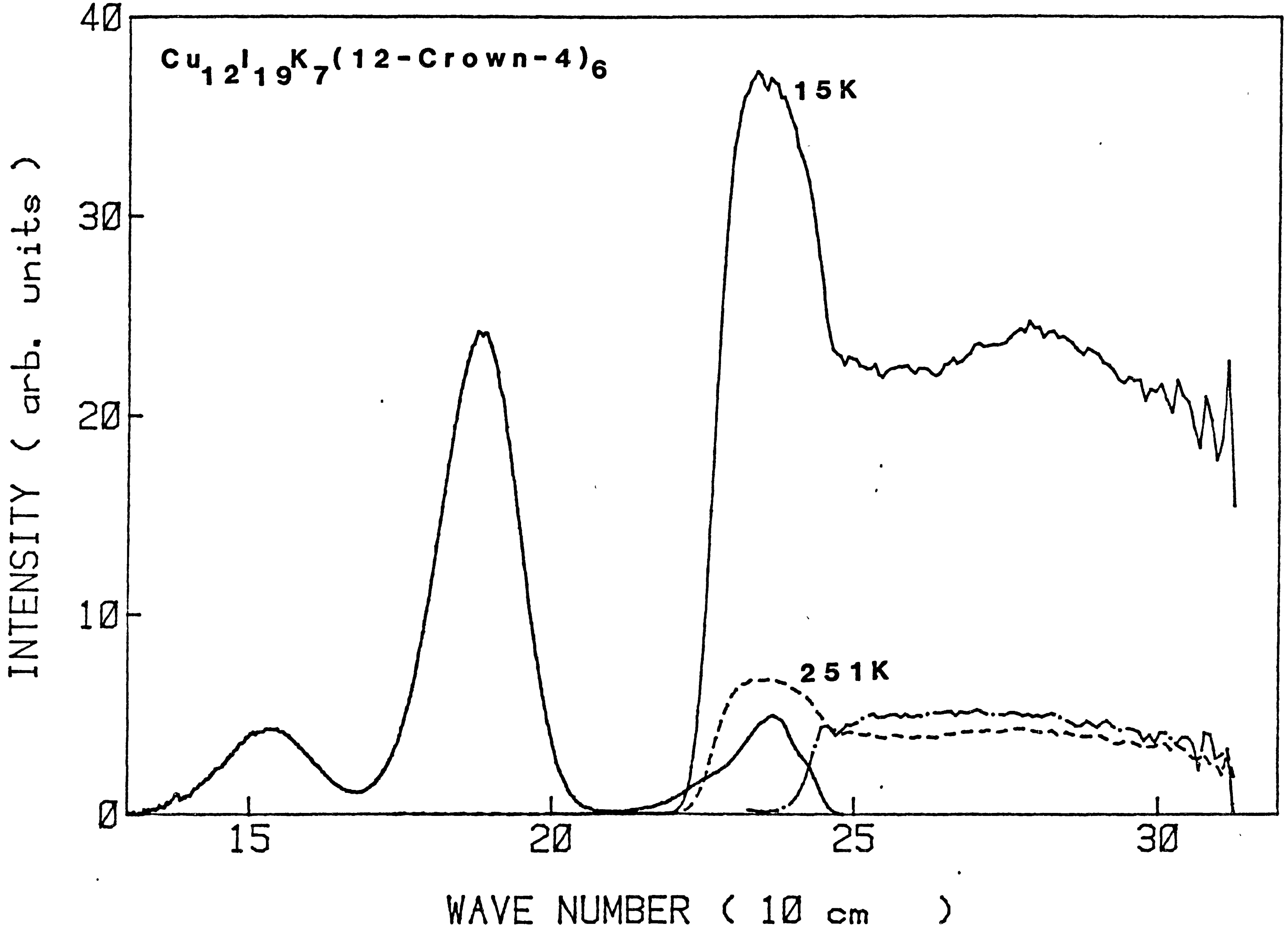

Figure 24. Emission Spectra of XI

TABLE XLV

CRYSTAL DATA FOR ($Cu_4I_6K_2$(15-crown-5)$_2$) (XII)

Formula	$Cu_4I_6K_2C_{20}H_{40}O_{10}$
M.W.	1534.337 g $mole^{-1}$
a	11.131(7) Å
b	13.313(6)
c	16.396(8)
α	92.89°
β	70.20
γ	65.34
V	2024.71 $Å^3$
F(000)	1424
μMoK_α	68.546 cm^{-1}
λMoK_α	0.71069 Å
D_{cal}	2.516 g cm^{-3}
Z	2
Meas refl	10057
Obs refl	4016
R	9.5%
R_w	12.3%
Space group	$P\bar{1}$ (Triclinic)
Octants meas	±h, ±k, +l

of edge sharing Cu_2I_2 rhombs (Figure 25). Due to this bridging, every other rhomb is distorted bringing the copper atoms of these rhombohedra into close proximity (2.466(8) Å), a distance which is shorter than the Cu-Cu metallic distance. The non bridged copper atoms are 2.716(8) Å (average) apart. The bridging iodide atoms are directed towards potassium (Figure 26) ions which are in turn bound to a molecule of 15-C-5 through the electron pair donor oxygen atoms. The K atoms show ionic interaction with the I atoms (K-I distance 3.852(10) Å). The Cu atoms display a nearly linear arrangement in the polymeric back bone. The polymeric chains pack (Figure 27) such that crown ether molecules bound to K^+ ions separate them from each other. A complete list of bond distances and angles are presented in Table XLVI and the positional parameters and anisotropic thermal parameters are listed in Tables XLVII and XLVIII respectively.

Compound XII, like XI, also exhibits thermochromic luminescence, luminescing bright yellow at room temperature and changing to green upon cooling to liq. nitrogen temperature. It is very likely that the very short Cu-Cu distance of 2.466(8) Å (Table XLVI) and the linear arrangement of copper atoms along the pleated sheet, contribute to thermochromicity. The involvement of multiple Cu-I bonding can not be assessed at this time. Because of the linear arrangement of copper atoms at a separation shorter than the Cu-Cu metallic distance, the

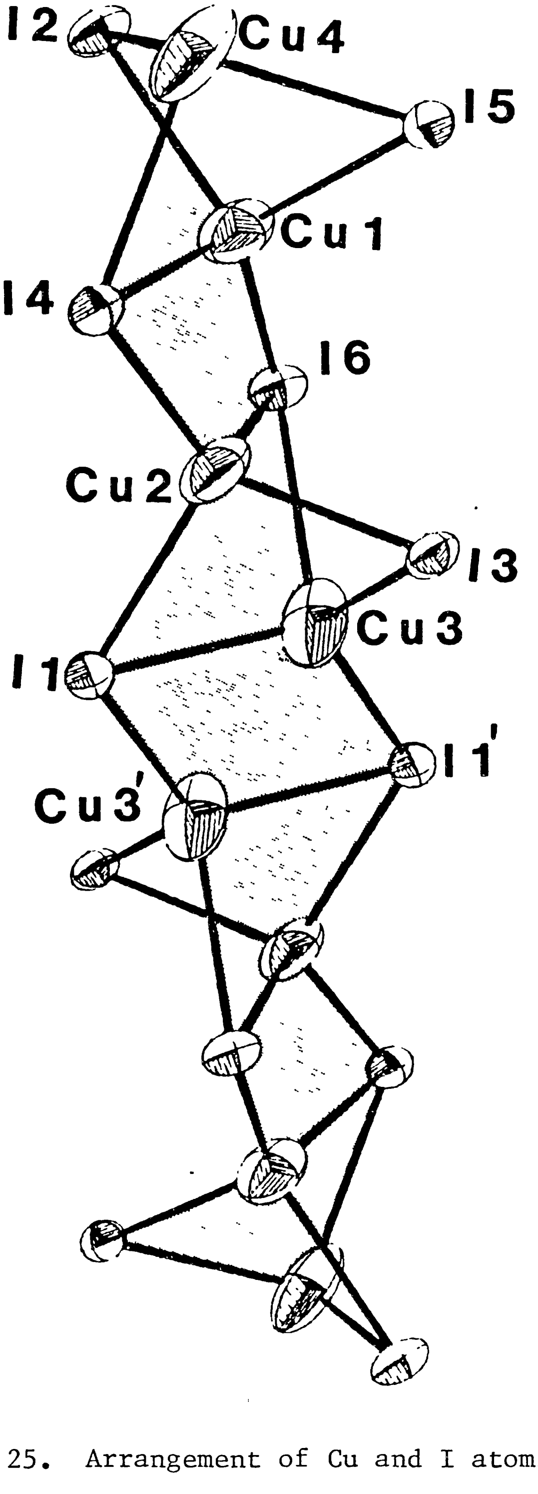

Figure 25. Arrangement of Cu and I atoms in XII

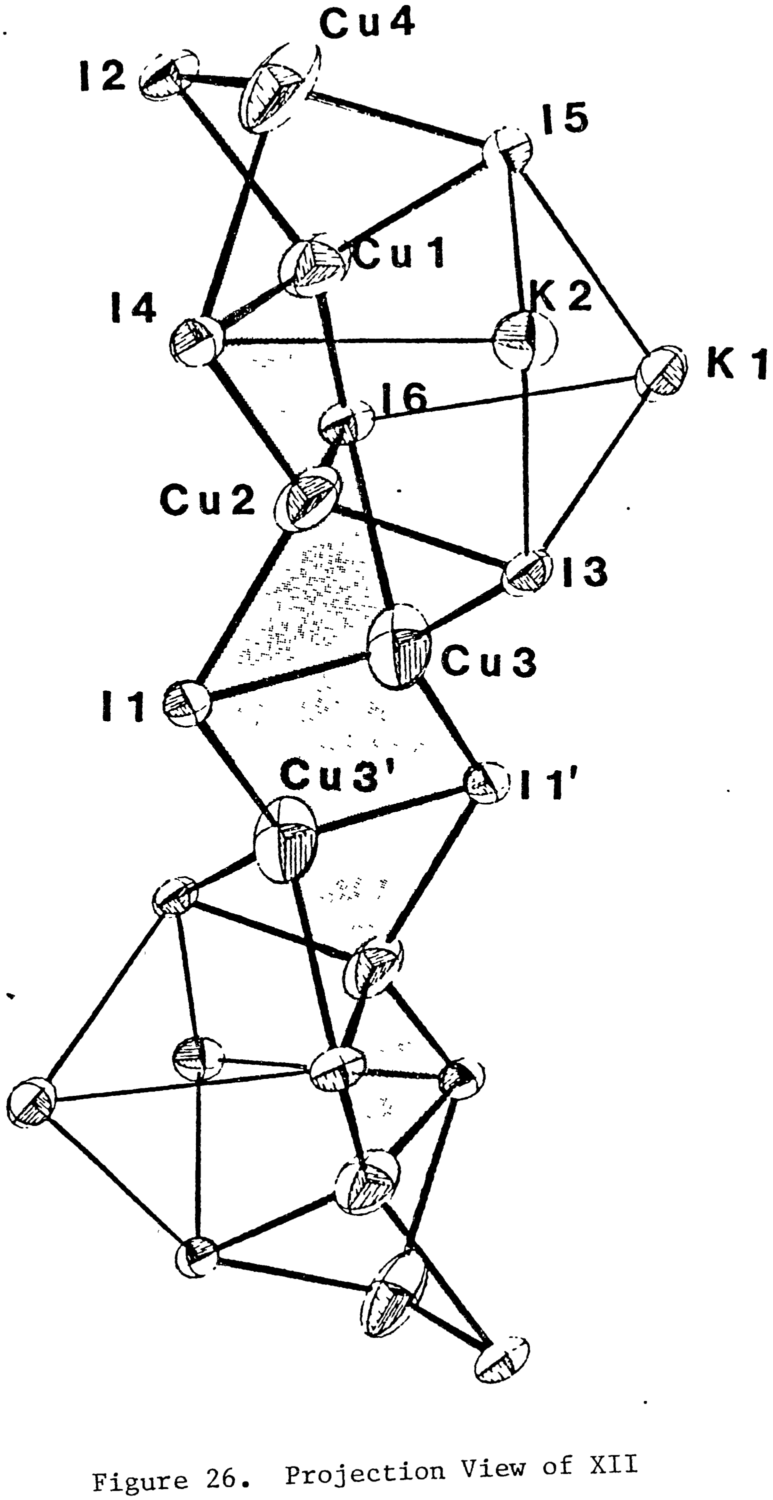

Figure 26. Projection View of XII

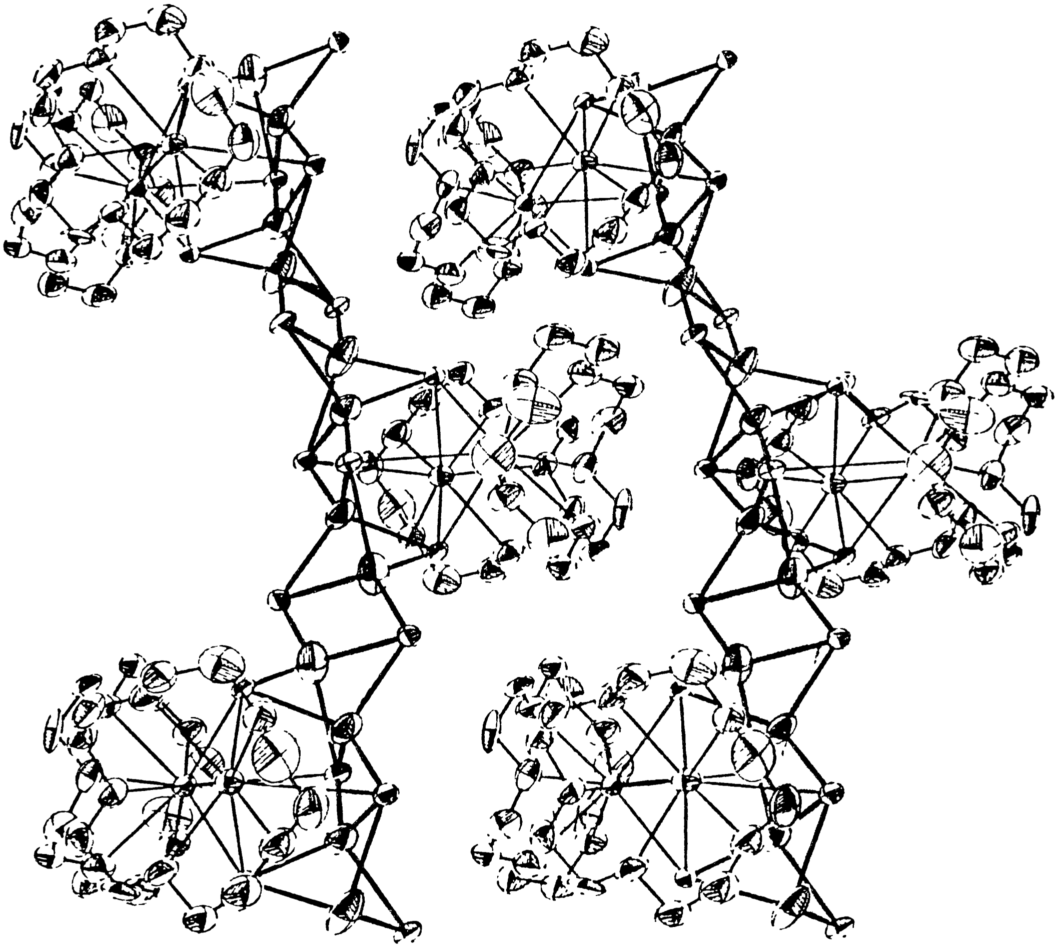

Figure 27. Packing Diagram of XII

TABLE XLVI

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

$(Cu_4I_6K_2(15\text{-crown-}5)_2)$ (XII)

I1-I3	4.288(4)	Cu2-I1-Cu3	53.6(2)
I1-I6	4.335(8)	Cu2-I1-Cu3'	116.0(2)
I2-I4	4.336(4)	Cu3-I1-Cu3'	62.5(3)
I2-I5	4.290(4)	Cu1-I2-Cu4	53.6(2)
I3-I6	4.221(4)	Cu1-I2-Cu4''	115.9(2)
I4-I5	4.214(4)	Cu4-I4-Cu4''	62.4(2)
Cu1-I2	2.747(6)	Cu2-I3-Cu3	55.3(2)
Cu1-I4	2.882(7)	Cu2-I3-K2	85.7(2)
Cu1-I5	2.659(8)	Cu2-I3-K1''''	95.4(2)
Cu1-I6	2.546(7)	Cu3-I3-K1''''	87.6(2)
Cu1-Cu2	2.699(8)	Cu3-I3-K2	140.9(2)
Cu1-Cu4	2.464(9)	Cu1-I4-Cu2	59.2(2)
Cu2-I1	2.737(8)	Cu2-I4-Cu4	107.0(2)
Cu2-I3	2.670(6)	Cu2-I4-K2	81.5(2)
Cu2-I4	2.553(5)	Cu4-I4-K2	80.0(2)
Cu2-I6	2.873(7)	Cu1-I4-Cu4	50.1(1)
Cu2-Cu3	2.467(7)	Cu1-I5-Cu4	55.4(2)
Cu3-I1	2.736(8)	Cu1-I5-K2	95.5(2)
Cu3-I3	2.649(9)	Cu1-I5-K1''''	85.8(2)
Cu3-I6	2.931(8)	K1''''-I5-K2	94.3(2)
Cu3-I1'	2.545(6)	Cu1-I6-Cu2	59.4(2)
Cu3-Cu3'	2.746(13)	Cu1-I6-Cu3	107.3(2)
Cu4-I2	2.721(8)	Cu2-I6-Cu3	50.4(2)

TABLE XLVI (Continued)

Cu4-I4	2.932(9)	Cu1-I6-K1''''	89.2(2)
Cu4-I5	2.646(6)	Cu2-I6-K1''''	87.7(2)
Cu4-I2''	2.550(7)	Cu3-I6-K1''''	79.8(2)
Cu4-Cu4''	2.733(8)	I2-Cu1-I4	100.8(2)
K1-I3'''	3.639(9)	I2-Cu1-I5	105.0(2)
K1-I5'''	3.555(7)	I2-Cu1-I6	113.9(3)
K1-I6'''	3.852(9)	I4-Cu1-I5	99.0(2)
K1-O11	2.75(3)	I4-Cu1-I6	117.4(2)
K1-O12	2.86(2)	I5-Cu1-I6	118.3(2)
K1-O13	2.76(3)	I1-Cu2-I3	105.0(2)
K1-O14	2.77(3)	I1-Cu2-I4	113.9(2)
K1-O15	2.88(4)	I1-Cu2-I6	101.2(2)
K2-I3	3.555(8)	I3-Cu2-I4	117.9(3)
K2-I4	3.839(10)	I3-Cu2-I6	99.0(2)
K2-I5	3.634(9)	14-Cu2-I6	117.4(2)
K2-O21	2.76(3)	I1-Cu3-I3	105.6(2)
K2-O22	2.92(3)	I1-Cu3-I6	99.9(2)
K2-O23	2.75(3)	I1-Cu3-I1'	117.5(3)
K2-O24	2.75(3)	I3-Cu3-I6	98.2(3)
K2-O25	2.88(4)	I3-Cu3-I1'	110.1(3)
O11-C11	1.40(6)	I6-Cu3-I1'	114.5(3)
O11-C12	1.42(4)	I2-Cu4-I4	100.1(3)
O12-C13	1.50(6)	I2-Cu4-I5	106.1(2)
O12-C14	1.37(7)	I2-Cu4-I2''	117.6(2)
O13-C15	1.44(5)	I4-Cu4-I5	98.0(2)
O13-C16	1.43(8)	I4-Cu4-I2''	113.9(3)

TABLE XLVI (Continued)

O14-C17	1.39(6)	I5-Cu4-I2''	118.0(3)
O14-C18	1.48(7)	I3'''-K1-I5'''	78.2(2)
O15-C19	1.46(7)	I3'''-K1-I6'''	68.5(2)
O15-C110	1.42(7)	I5'''-K1-I6'''	74.2(1)
O21-C21	1.45(4)	O11-K1-O12	60.0(9)
O21-C210	1.42(6)	O11-K1-O13	117.9(9)
O22-C22	1.40(6)	O11-K1-O14	116.0(10)
O22-C23	1.41(6)	O11-K1-O15	60.6(10)
O23-C24	1.49(6)	O12-K1-O13	58.6(10)
O23-C25	1.46(6)	O12-K1-O14	94.8(8)
O24-C26	1.41(7)	O12-K1-O15	87.2(8)
O24-C27	1.44(8)	O13-K1-O14	61.3(9)
O25-C28	1.39(4)	O13-K1-O15	107.2(10)
O25-C29	1.40(5)	O14-K1-O15	60.5(10)
C11-C110	1.51(7)	I3-K2-I4	74.4(2)
C12-C13	1.45(7)	I3-K2-I5	78.0(2)
C14-C15	1.57(9)	I4-K2-I5	68.6(2)
C16-C17	1.50(12)	O21-K2-O22	60.3(9)
C18-C19	1.41(9)	O21-K2-O23	115.5(10)
C21-C22	1.46(7)	O21-K2-O24	117.2(11)
C23-C24	1.40(10)	O21-K2-O25	59.1(8)
C25-C26	1.36(9)	O22-K2-O23	60.5(8)
C27-C28	1.46(9)	O22-K2-O24	106.7(10)
C29-C210	1.52(5)	O22-K2-O25	87.0(9)
		O23-K2-O24	60.8(9)
		O23-K2-O25	95.1(10)

TABLE XLVI (Continued)

O24-K2-O25	59.1(10)
C11-O11-C12	114(4)
C13-O12-C14	109(4)
C15-O13-C16	118(4)
C17-O14-C18	113(5)
C19-O15-C110	109(4)
C21-O21-C210	112(4)
C22-O22-C23	112(4)
C24-O23-C25	117(5)
C26-O24-C27	115(4)
C28-O25-C29	115(3)
O11-C11-C110	114(4)
O11-C12-C13	110(4)
O12-C13-C12	104(3)
O12-C14-C15	103(4)
O13-C15-C14	107(3)
O13-C16-C17	113(7)
O14-C17-C16	103(5)
O14-C18-C19	115(4)
O15-C19-C18	106(5)
O15-C110-C11	106(4)
O21-C12-C22	111(3)
O22-C22-C21	110(4)
O22-C23-C24	110(6)
O23-C24-C23	115(5)
O23-C25-C26	112(6)

TABLE XLVI (Continued)

O24-C26-C25	112(5)
O24-C27-C28	110(5)
O25-C28-C27	109(4)
O25-C29-C210	110(3)
O21-C210-C29	107(4)

Symmetry operations :

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

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

''' = x, 1.0+y, z

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

TABLE XLVII

POSITIONAL PARAMETERS FOR $((Cu_4I_6)K_2(15\text{-Crown-}5)_2)$ (XII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.3045(2)	0.1618(2)	0.0156(1)
I2	-0.0182(2)	0.3382(2)	0.4843(1)
I3	0.6212(2)	0.1791(2)	0.1008(1)
I4	0.1597(2)	0.4397(2)	0.2429(1)
I5	0.4010(2)	0.3210(2)	0.3991(1)
I6	0.3421(2)	0.0605(2)	0.2570(1)
Cu1	0.2380(6)	0.2644(5)	0.3396(4)
Cu2	0.3415(5)	0.2349(5)	0.1604(4)
Cu3	0.5173(7)	0.0408(5)	0.0716(5)
Cu4	0.1295(6)	0.4583(5)	0.4290(5)
K1	0.6818(7)	0.0447(6)	0.2808(5)
K2	0.5059(8)	0.4560(6)	0.2193(5)
O11	0.888(3)	0.117(2)	0.254(2)
O12	0.973(3)	-0.101(2)	0.162(2)
O13	0.772(3)	-0.182(3)	0.214(2)
O14	0.675(3)	-0.098(2)	0.398(2)
O15	0.790(3)	0.053(2)	0.416(2)
O21	0.758(3)	0.385(2)	0.247(2)
O22	0.761(3)	0.449(2)	0.083(2)
O23	0.474(3)	0.599(3)	0.104(2)
O24	0.307(3)	0.681(2)	0.286(2)
O25	0.534(3)	0.600(2)	0.341(2)

TABLE XLVII (Continued)

C11	0.885(5)	0.161(4)	0.334(3)
C12	1.029(4)	0.043(4)	0.189(3)
C13	1.019(4)	-0.020(4)	0.118(2)
C14	0.972(4)	-0.172(5)	0.099(2)
C15	0.920(6)	-0.251(4)	0.154(4)
C16	0.710(7)	-0.225(5)	0.285(5)
C17	0.748(8)	-0.213(4)	0.363(5)
C18	0.699(5)	-0.066(5)	0.476(3)
C19	0.820(6)	-0.047(5)	0.455(3)
C110	0.908(4)	0.078(4)	0.394(3)
C21	0.883(4)	0.341(3)	0.164(3)
C22	0.875(4)	0.425(4)	0.110(3)
C23	0.731(5)	0.545(5)	0.045(3)
C24	0.610(7)	0.570(6)	0.026(4)
C25	0.383(9)	0.718(4)	0.147(5)
C26	0.268(6)	0.735(5)	0.221(4)
C27	0.323(6)	0.750(4)	0.349(4)
C28	0.396(5)	0.679(6)	0.399(3)
C29	0.616(5)	0.525(4)	0.381(2)
C210	0.768(5)	0.452(4)	0.312(3)
H111	0.7973	0.2283	0.3638
H112	0.9684	0.1787	0.3175
H121	1.0737	0.0944	0.1623
H122	1.0920	-0.0054	0.2150
H131	0.9423	0.0281	0.0976

TABLE XLVII (Continued)

H141	0.9082	-0.1337	0.0717
H142	1.0702	-0.2218	0.0541
H151	0.9240	-0.3085	0.1107
H152	0.9797	-0.2852	0.1842
H161	0.6046	-0.1842	0.2994
H162	0.7441	-0.3054	0.2578
H171	0.7077	-0.2523	0.4068
H172	0.8481	-0.2430	0.3465
H181	0.6129	0.0035	0.5142
H182	0.7132	-0.1272	0.5075
H191	0.8357	-0.0302	0.5080
H192	0.9069	-0.1108	0.4113
H1101	0.9069	0.1136	0.4459
H1102	0.9967	0.0093	0.3613
H211	0.9675	0.3221	0.1781
H222	0.9631	0.3932	0.0563
H231	0.7108	0.6103	0.0878
H232	0.8138	0.5289	-0.0088
H241	0.5922	0.6329	-0.0045
H242	0.6284	0.5021	-0.0153
H251	0.4450	0.7476	0.1633
H252	0.3551	0.7609	0.1028
H261	0.2044	0.8150	0.2475
H262	0.2120	0.7019	0.2023
H271	0.3865	0.7834	0.3147

TABLE XLVII (Continued)

H272	0.2319	0.8128	0.3886
H281	0.4025	0.7254	0.4467
H282	0.3415	0.6399	0.4305
H291	0.6205	0.5662	0.4297
H292	0.5723	0.4755	0.4042
H2101	0.8099	0.4981	0.2851
H2102	0.8275	0.4002	0.3397

TABLE XLVIII

ANISOTROPIC THERMAL PARAMETERS FOR ($Cu_4I_6K_2$ (15-Crown-5)$_2$) (XII)

ATOM	U11	U22	U33	U12	U13	U23
I1	34(1)	39(1)	32(1)	-7(1)	-12(1)	-4(1)
I2	34(1)	39(1)	36(1)	-20(1)	4(1)	-3(1)
I3	27	42(1)	30(1)	-17(1)	1(1)	0(1)
I4	34(1)	39(1)	30(1)	-10(1)	-6(1)	2(1)
I5	29	43(1)	28(1)	-16(1)	-7(1)	0(1)
I6	40(1)	38(1)	30(1)	-20(1)	-2(1)	1(1)
Cu1	55(3)	73(3)	70(3)	-25(2)	-3(2)	-31(2)
Cu2	42(2)	64(3)	70(3)	-10(2)	0(2)	-24(2)
Cu3	65(3)	49(3)	131(6)	0(2)	-42(3)	-33(3)
Cu4	44(2)	53(3)	138(6)	-14(2)	4(3)	-32(3)
K1	31(3)	45(4)	42(4)	-11(2)	-7(2)	8(3)
K2	49(4)	41(4)	36(3)	-27(3)	-9(3)	8(2)
O11	38(12)	58(16)	68(17)	-29(11)	-9(11)	13(13)
O12	52(14)	67(18)	34(13)	-26(13)	2(10)	-11(11)
O13	77(19)	70(20)	56(18)	-38(16)	-4(14)	-6(14)
O14	64(17)	75(19)	44(15)	-38(15)	-14(12)	23(13)
O15	78(19)	58(17)	50(16)	-24(14)	-23(14)	10(13)
O21	40(13)	57(16)	48(15)	-10(11)	2(10)	-10(12)
O22	59(16)	59(16)	42(14)	-28(13)	-2(11)	20(12)
O23	60(16)	75(20)	58(17)	-31(14)	-19(13)	32(14)
O24	58(16)	59(18)	72(20)	-15(13)	-9(14)	-2(14)

TABLE XLVIII (Continued)

O25	48(14)	75(19)	34(13)	-31(13)	7(10)	3(12)
C11	63(25)	54(25)	58(25)	-40(21)	2(18)	-8(19)
C12	29(16)	69(27)	97(33)	-33(17)	-33(18)	50(24)
C13	40(18)	88(30)	29(18)	-34(19)	3(13)	15(17)
C14	56(23)	109(38)	29(19)	-33(24)	7(15)	-34(21)
C15	90(34)	38(25)	135(49)	-11(23)	-47(34)	-31(27)
C16	122(46)	77(38)	111(49)	-76(36)	-29(38)	22(33)
C17	186(67)	33(27)	136(56)	-47(35)	-43(50)	33(30)
C18	65(28)	132(44)	38(23)	-44(29)	-3(19)	41(25)
C19	82(31)	94(37)	64(30)	-35(28)	-31(25)	47(27)
C110	63(24)	64(25)	44(21)	-35(20)	-18(17)	1(17)
C21	30(17)	52(22)	69(27)	-8(15)	0(16)	-3(19)
C22	31(17)	74(26)	46(21)	-17(17)	4(14)	9(18)
C23	54(25)	104(40)	44(23)	-36(25)	-2(18)	10(23)
C24	133(52)	124(49)	58(32)	-78(42)	-31(32)	66(33)
C25	167(64)	43(28)	112(54)	1(33)	-60(49)	30(31)
C26	71(30)	109(43)	53(29)	15(27)	-18(23)	12(27)
C27	65(30)	68(31)	111(44)	-23(25)	-14(29)	-37(29)
C28	55(26)	126(46)	56(28)	-28(28)	-6(20)	-32(28)
C29	76(27)	102(34)	6(14)	-57(25)	-4(14)	9(16)
C210	74(26)	70(27)	54(24)	-54(22)	-30(20)	30(19)

Anistropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^*$$

$$+2U13hla^*c^*+2U23klb^*c^*))\ X10^3.$$

compound may be a semiconductor, a possibility yet to be explored.

The use of a crown ether with large cavity, dibenzo-24-crown-8 (db-24-C-8), leads to the formation of Cu_3I_4K(dibenzo-24-crown-8) (XIII), which, like the other two members of this series, shows a novel structural geometry previously not known for CuI compounds. Compound XIII crystallizes in monoclinic space group, $P2_1$ (Table XLIX) and shows the basic polymeric backbone similar to $(CuI(MeCN))_x$. The interesting fact about this structure is that the basic polymeric back bone formed by edge sharing Cu_2I_2 rhombohedra, has an additional rhomb projecting perpendicular to the polymeric back bone at every other shared edge. These rhombs project from the chain back bone parallel to each other and are linked by an additional iodide atom (Figure 28) bridging copper atoms of the projecting rhombs. Unlike the other two members of this series, this compound has no close K-I distances which may be due to the fact that the crown ether cavity is large enough to completely encapsulate the K^+ ion and thus the potassium ion has no surface exposed to iodide. The potassium ion is bound to four oxygen atoms of the crown ether ring which has eight oxygen atoms in total (K-O distance less than 3.07(3) Å). The Cu-I distances vary between 2.66(1) Å and 2.74(1) Å and are comparable with other Cu-I distances. Two different types of Cu-Cu separations are seen in this molecule (Table L); a shorter one

TABLE XLIX

CRYSTAL DATA FOR ((Cu_3I_4)K(dibenzo-24-crown-8)) (XIII)

Formula	$Cu_3I_4KC_{24}H_{32}O_8$
M.W.	1185.866 g $mole^{-1}$
a	4.500(2) Å
b	20.217(6)
c	18.797(9)
$\alpha = \gamma$	90.0°
β	95.00(4)
V	1703.5(12) $Å^3$
F(000)	1116
μMoK_α	56.125 cm^{-1}
λMoK_α	0.71069 Å
D_{cal}	2.312 g cm^{-3}
Z	2
Meas refl	4718
Obs refl	2234
R	6.9%
R_w	9.8%
Space group	$P2_1$ (Monoclinic)
Octants meas	±h, +k, +l

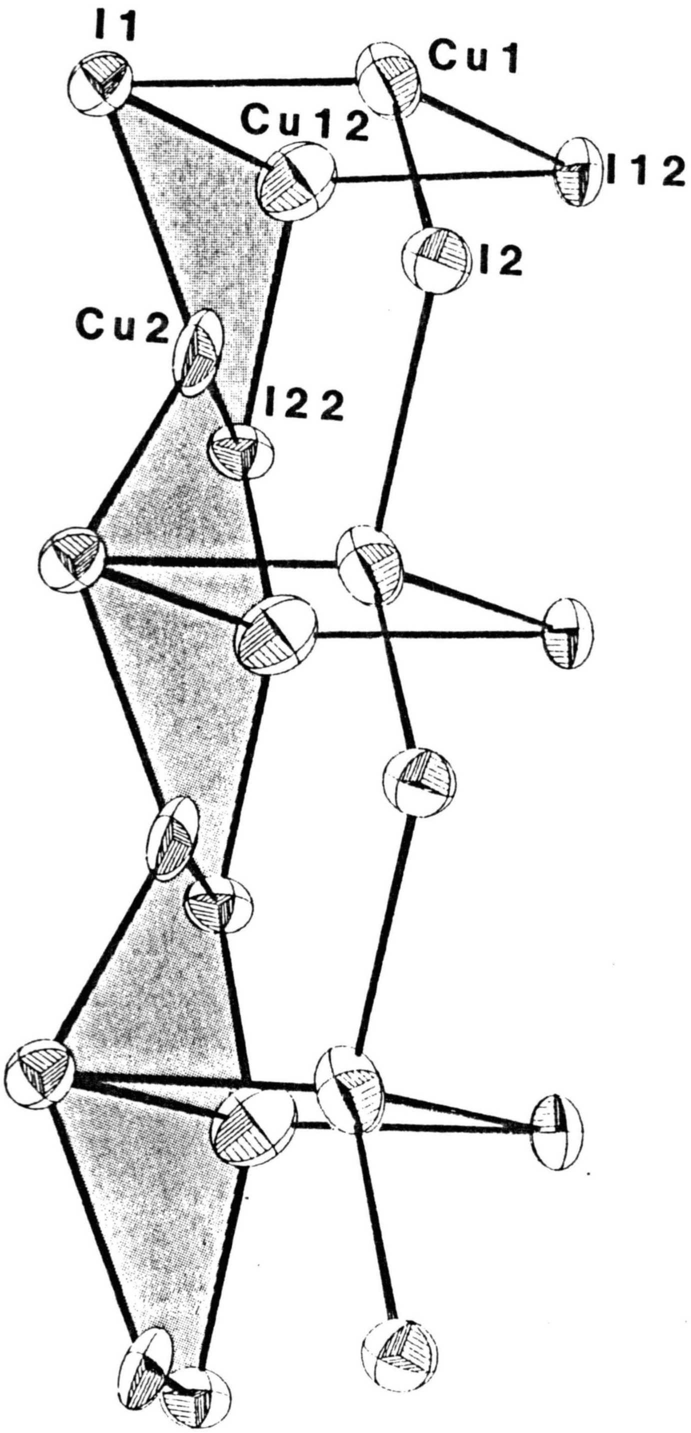

Figure 28. Projection View of XIII

TABLE L

BOND DISTANCES (Å) AND BOND ANGLES($^{\circ}$) FOR ((Cu_3I_4) K(Dibenzo-24-Crown-8) (XIII)

I1-I2'	4.211(6)	Cu1-I1-Cu12	60.5(3)
I1-I22'	4.305(7)	Cu1-I1-Cu2	69.1(4)
I12-I2	4.347(7)	Cu12-I1-Cu2	61.9(3)
I12-I22	4.259(6)	Cu2-I1-Cu2'	124.2(3)
I12-I2'	4.240(7)	Cu1-I12-Cu12	59.1(3)
I12-I22'	4.310(6)	Cu1-I2-Cu1''	114.9(3)
Cu1-I1	2.66(1)	Cu12-I22-Cu2	61.9(3)
Cu1-I12	2.74(1)	Cu12-I22-Cu12''	114.1(4)
Cu1-I2	2.68(1)	Cu2-I22-Cu12''	58.8(3)
Cu1-Cu12	2.69(1)	I1-Cu1-I12	119.8(4)
Cu1-Cu2	2.97(1)	I1-Cu1-I2	107.8(4)
Cu1-Cu2''	3.05(1)	I1-Cu1-I2'	104.6(4)
Cu12-I1	2.67(1)	I12-Cu1-I2	106.7(4)
Cu12-I12	2.71(1)	I12-Cu1-I2'	103.4(4)
Cu12-I22	2.68(1)	I2-Cu1-I2'	114.9(4)
Cu12-Cu2	2.80(1)	I1-Cu12-I12	120.5(4)
Cu12-Cu2'	2.67(1)	I1-Cu12-I22	105.4(4)
Cu2-I1	2.57(1)	I1-Cu12-I22'	107.0(4)
Cu2-I22	2.76(1)	I12-Cu12-I22	104.4(4)
Cu2-I1''	2.52(1)	I12-Cu12-I22'	114.1(4)
K1-O1	2.76(4)	I22-Cu12-I22'	125.7(4)
K1-O4	3.12(4)	O1-K1-O4	55(1)
K1-O7	3.25(4)	O1-K1-O7	109(1)

TABLE L (Continued)

K1-O19	2.82(5)	O1-K1-O19	120(1)
K1-O22	2.71(3)	O1-K1-O22	58(1)
O1-C2	1.04(6)	O4-K1-O7	55(1)
O1-C24	1.51(6)	O4-K1-O19	175(1)
O4-C3	1.29(5)	O4-K1-O22	111(1)
O4-C5	1.28(6)	O7-K1-O19	129(1)
O7-C6	1.52(9)	O7-K1-O22	152(1)
O7-C8	1.43(6)	O19-K1-O22	64(1)
O10-C9	1.65(8)	C2-O1-C24	116(4)
O10-C11	1.66(6)	C3-O4-C5	122(4)
O13-C12	1.15(8)	C6-O7-C8	116(4)
O13-C14	1.80(7)	C9-O10-C11	112(4)
O16-C15	1.51(6)	C12-O13-C14	118(5)
O16-C17	1.60(6)	C15-O16-C17	118(3)
O19-C18	1.43(7)	C18-O19-C20	97(4)
O19-C20	1.34(8)	C21-O22-C23	104(4)
O22-C21	1.48(4)	O1-C2-C3	123(4)
O22-C23	1.10(6)	O1-C2-C25	137(5)
C2-C3	1.66(6)	C2-C3-O4	112(3)
C2-C25	1.69(6)	C2-C3-C28	128(3)
C3-C28	1.59(6)	O4-C5-C6	100(4)
C5-C6	1.85(9)	C5-C6-O7	99(4)
C8-C9	1.22(9)	O7-C8-C9	108(5)
C11-C12	1.41(6)	C8-C9-O10	95(5)
C14-C15	1.01(6)	O10-C11-C12	111(3)

TABLE L (Continued)

C14-C29	1.33(8)	C11-C12-O13	106(5)
C15-C32	1.33(6)	O13-C14-C15	120(4)
C17-C18	1.40(6)	O13-C14-C29	101(4)
C20-C21	1.87(8)	C14-C15-O16	121(4)
C23-C24	1.66(7)	C14-C15-C32	127(5)
C25-C26	1.12(6)	O16-C17-C18	109(3)
C26-C27	1.75(8)	C17-C18-O19	118(4)
C27-C28	1.15(9)	O19-C20-C21	108(4)
C29-C30	1.97(8)	C20-C21-O22	108(3)
C30-C31	0.98(9)	O22-C23-C24	107(5)
C31-C32	1.51(8)	C23-C24-O1	103(3)
		C2-C25-C26	130(4)
		C25-C26-C27	121(4)
		C26-C27-C28	122(5)
		C27-C28-C3	114(5)
		C14-C29-C30	96(4)
		C29-C30-C31	118(6)
		C30-C31-C32	125(6)
		C31-C32-C15	114(4)

Symmetry operations :

' = 1.0+x, y, z

'' = -1.0+x, y, z

seen the for the copper atoms involved in the projecting rhombs (Cu1-Cu12 2.69(1) Å). The Cu-Cu separation of the edge sharing rhombs forming the chain backbone averages 3.01(1) Å which is large compared to that observed for members of the series with a polymeric structure i.e., XII. The packing diagram of the molecule (Figure 29) shows efficient filling of space between parallel polymeric chains by crown ether bound K atoms. The bulky crown ether rings are separated by distances greater than the sum of Van der Waal's radii. Only four of the eight oxygens are involved with the K^+ atom, the rest of the molecule displays significant disorder as can be noted from the thermal parameters (Table LI) and bond distances for parts of the ring. (Positional parametrs: Table LII)

This compound, like XI and XII, has no Cu-organic ligand interaction but exhibits thermochromic luminescence. The dry crystals luminesce yellow at room temperature and orange-red at liq. nitrogen temperature. The short Cu-Cu distances (less than 2.8 Å) may be considered to play a role in the thermochromicity.

The observation that compounds XI, XII, XIII exhibit thermochromic luminescence without direct Cu-organic ligand interaction eliminates the earlier idea of a Cu-electron donor organic ligand interaction being a 'precondition' for thermochromism. This conclusion is further augmented by the behavior of CuI(cyclam), (XVI), cyclam = 1,4,8,11-tetraazacyclo tetradecane, synthesized

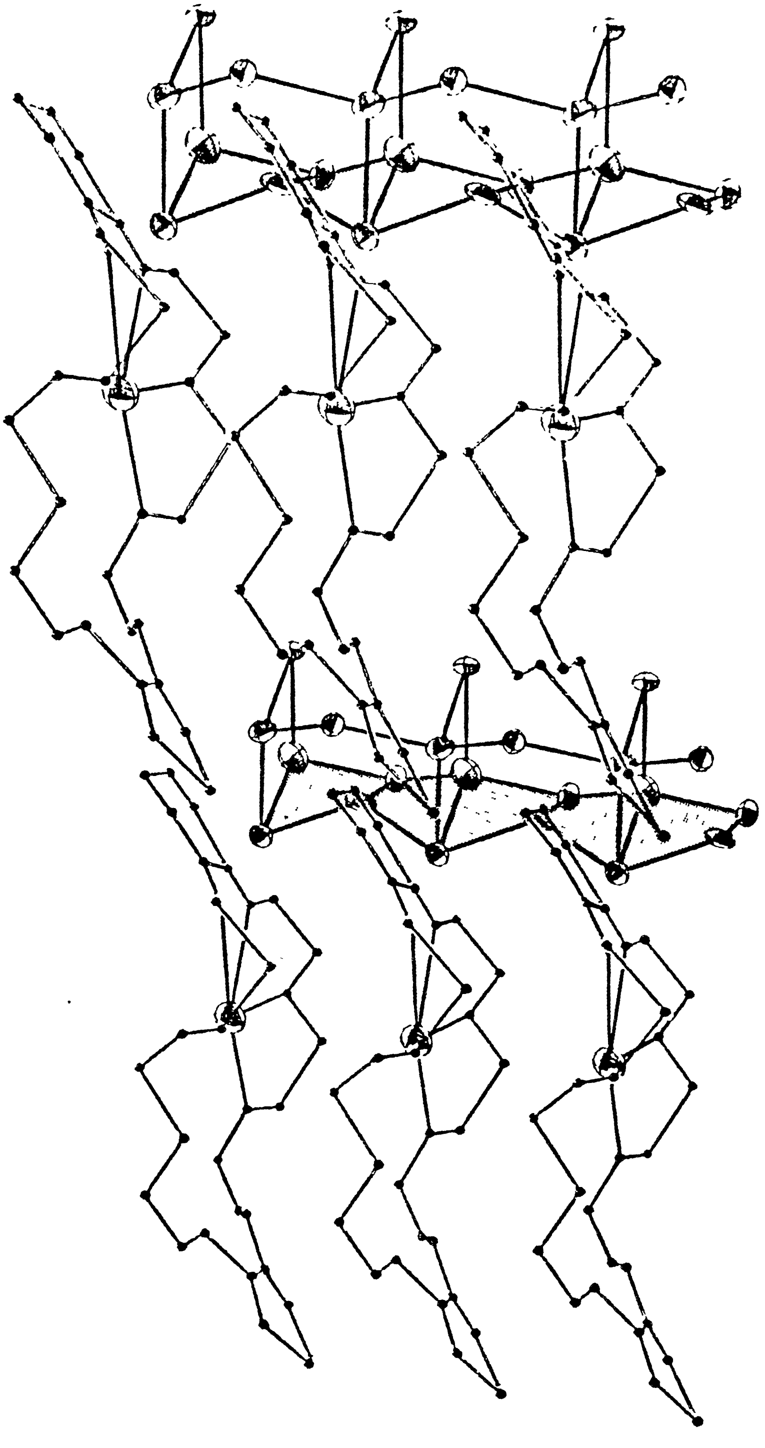

Figure 29. Packing Diagram of XIII

TABLE LI

ANISOTROPIC THERMAL PARAMETERS FOR ((Cu$_3$I$_4$) K(Dibenzo-24-Crown-8)) (XIII)

ATOM	U11	U22	U33	U12	U13	U23
I1	36(2)	30(3)	40(3)	-1(1)	8(1)	-2(1)
I12	44(2)	28(3)	32(3)	3(1)	2(1)	10(1)
I2	36(2)	44(3)	36(3)	-3(2)	4(1)	0(2)
I22	27(2)	47(3)	30(2)	0(2)	0(1)	-3(2)
Cu1	56(5)	36(5)	50(6)	-2(4)	-1(4)	2(4)
Cu12	58(5)	61(6)	42(5)	-3(5)	10(4)	-1(4)
Cu2	51(4)	88(6)	252(12)	0(4)	19(5)	51(7)
K1	72(7)	47(6)	47(6)	-14(5)	0(4)	0(4)
O1	41(15)	23(15)	16(15)	9(12)	-8(11)	-17(11)
O4	72(21)	31(19)	14(18)	1(14)	-14(14)	-19(14)
O7	54(20)	21(19)	44(19)	33(16)	-25(14)	-9(14)
O10	70(23)	49(23)	24(17)	11(17)	8(15)	-12(15)
O13	188(54)	90(45)	57(41)	-22(37)	-25(38)	25(32)
O16	55(18)	48(21)	7(169	2(15)	5(13)	-17(13)
O19	74(24)	144(45)	34(27)	-66(27)	42(20)	-22(25)
O22	48(16)	27(16)	22(16)	-27(13)	4(11)	0(11)
C2	75(28)	31(25)	74(29)	-22(20)	62(24)	-41(20)
C3	54(20)	5(18)	6(15)	11(14)	2(12)	-3(11)
C5	41(26)	51(34)	57(27)	-36(23)	2(209	-21(23)
C6	98(42)	116(69)	49(33)	5(41)	-3(28)	30(36)

TABLE LI (Continued)

C8	31(19)	21(30)	29(24)	-24(17)	-18(16)	9(17)
C9	104(52)	13(24)	175(53)	5(28)	109(44)	-6(28)
C11	51(23)	16(20)	69(31)	-17(16)	20(21)	16(18)
C12	36(24)	29(21)	45(27)	-5(179	30(21)	8(17)
C14	34(17)	35(21)	8(16)	1(14)	-15(12)	5(13)
C15	44(20)	38(27)	62(27)	-40(19)	9(18)	-17(21)
C17	50(21)	68(29)	26(19)	18(19)	7(15)	-28(18)
C18	12(16)	20(17)	51(25)	13(12)	14(14)	3(14)
C20	71(35)	95(47)	25(32)	26(31)	18(25)	34(29)
C21	52(26)	11(21)	8(16)	15(18)	-12(15)	3(14)
C23	168(56)	67(20)	19(28)	-14(24)	-28(30)	-9(16)
C24	36(22)	27(23)	68(34)	-27(17)	-5(20)	-18(20)
C25	29(22)	5(17)	40(26)	-9(14)	4(18)	6(15)
C26	41(20)	28(21)	2(20)	-7(15)	-8(15)	5(15)
C27	63(34)	73(51)	0(22)	-4(31)	-1(19)	-2(23)
C28	38(22)	63(33)	33(30)	-14(20)	-25(20)	40(27)
C29	16(21)	126(50)	33(27)	-25(24)	2(18)	-39(28)
C30	59(30)	101(51)	22(33)	-45(32)	-35(25)	19(33)
C31	47(27)	15(23)	45(24)	-2(17)	11(18)	-18(15)
C32	38(21)	43(25)	14(23)	-10(17)	-9(16)	24(19)

Anistropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^* +2U13hla^*c^*+2U23klb^*c^*))\ X10^3.$$

TABLE LII

POSITIONAL PARAMETERS FOR ((Cu_3I_4) K(Dibenzo-24-crown-8)) (XIII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.2360(9)	0.0991(0)	-0.3152(2)
I12	0.2839(9)	-0.0992(2)	-0.1868(2)
I2	-0.2158(10)	0.0721(4)	-0.1242(2)
I22	-0.2772(8)	-0.0712	-0.3788(2)
Cu1	0.2619(21)	0.0363(6)	-0.1904(5)
Cu12	0.2468(22)	-0.0331(7)	-0.3127(5)
Cu2	-0.2646(18)	0.0426(5)	-0.2971(7)
K1	-0.1420(26)	0.4420(6)	-0.2390(6)
O1	-0.0841(69)	0.3159(17)	-0.1826(17)
O4	-0.120(9)	0.408(2)	-0.077(2)
O7	-0.297(8)	0.545(2)	-0.114(2)
O10	-0.284(9)	0.671(2)	-0.164(2)
O13	-0.347(16)	0.697(2)	-0.303(3)
O16	-0.346(9)	0.601(2)	-0.403(2)
O19	-0.188(9)	0.462(3)	-0.388(2)
O22	-0.262(8)	0.333(2)	-0.320(2)
C2	0.029(11)	0.305(2)	-0.133(3)
C3	0.033(8)	0.355(2)	-0.063(2)
C5	-0.186(11)	0.448(3)	-0.027(3)
C6	-0.488(16)	0.496(5)	-0.076(4)
C8	-0.208(10)	0.603(3)	-0.076(2)

TABLE LII (Continued)

C9	-0.029(16)	0.633(2)	-0.109(4)
C11	-0.137(10)	0.731(2)	-0.210(3)
C12	-0.322(10)	0.746(2)	-0.272(2)
C14	-0.560(8)	0.698(2)	-0.389(2)
C15	-0.546(9)	0.659(2)	-0.423(2)
C17	-0.239(9)	0.557(2)	-0.467(2)
C18	-0.061(8)	0.506(2)	-0.437(2)
C20	-0.266(15)	0.414(4)	-0.435(4)
C21	-0.447(9)	0.346(2)	-0.387(2)
C23	-0.363(16)	0.288(2)	-0.298(3)
C24	-0.123(9)	0.259(2)	-0.234(3)
C25	0.279(9)	0.248(2)	-0.100(3)
C26	0.395(9)	0.242(2)	-0.045(2)
C27	0.363(16)	0.303(4)	0.020(3)
C28	0.178(11)	0.342(3)	0.016(3)
C29	-0.696(11)	0.756(4)	-0.387(3)
C30	-0.898(13)	0.751(4)	-0.484(3)
C31	-0.851(13)	0.714(3)	-0.514(3)
C32	-0.656(10)	0.656(3)	-0.491(2)

during the course of this investigation, which has four Cu-N bonds but no Cu-Cu or Cu-I bonding interactions. It is not luminescent. The copper atom radius is right for encapsulation of a single copper atom in the cavity of the ligand molecule. While the structure was solved, the ligand moeity could not be brought to a satisfactory refinement due to the highly disordered carbon positions. Recollection and refinement of data from a crystal crystallized from a mixture of solvents (alcohol-water) was also attempted and proved to be futile.

Whereas the mixing of KI and CuI in presence of a crown ether which has smaller or larger cavity than optimum for potassium complexation (80) leads to complexes of form $Cu_mK_xI_n$(crown ether)$_y$ where the I/Cu ratio is greater than one but less than two, the complexes formed when 18-crown-6 (18-C-6) or dicyclohexano-18-crown-6 (dch-18-C-6) is used are of stoichiometry I:Cu 2:1. The use of the 18-C-6 and dch-18-C-6 led to the isolation of two compounds with the previously unknown linear copper(I) species, CuI_2^- (81).

Symmetrical dicoordinated Cu(I) species have previously been identified with nitrogen (82), oxygen (83), carbon (84-86), sulfur (87), chlorine and bromine (88,89) donor ligands and in one case, a nonsymmetrical species (84) has received structural attention; Cu-$BrCH(SiMe_3)_2^-$. In those structures for which a linear arrangement is not dictated by the presence a symmetry element at the copper position, the L-Cu-L angle may differ somewhat from 180° : in the monoionic systems, an angle of 165.9(2)° was observed for Cu(2,6-dimethyl pyridine) (82), an angle of 178.6(1)° (87) in $Cu(SC_{10}H_{13})_2$ and 169.8(3)° (83) in $Cu(2,6\text{-dimethyl phenoxide})_2$. In other such systems the L-Cu-L angle is constrained by symmetry to be 180° : $Cu(mesityl)_2$ (86), $Cu(C(SiMe)_3)_2$ (85) and $CuPh_2$ (84).

CuI and KI in aqueous system with 18-C-6 forms the compound CuI_2K(18-crown-6) (XIV) which crystallizes in monoclinic space group, $P2_1/n$ (Table LIII). This structure contains the linear anion, CuI_2^- (Figure 30). Dicordinate copper is bonded to two iodide atoms at a remarkably short Cu-I separation of 2.383(1) Å. The I-Cu-I angle is linear (180°) as also I-K-I angle (180°). Both Cu and K lie on a symmetry element, $\bar{1}$, (Table LIV) thus constraining the geometry of the I-Cu-I and I-K-I angle. A 'Z' of two in the monoclinic space group $P2_1/n$ thus places the K and Cu atoms on center of inversion. The potassium atom shows ionic interaction with two iodide atoms (K-I distance 3.598(1) Å) and is bonded to a molecule of 18-C-6 through six oxygen atoms. The cavity of the 18-C-6 is of suitable size to accommodate K^+. The cation fits into the cavity and is coordinated to all six oxygens leading to crystalline order of the crown ether. The chain of I-Cu-I-K-I continues indefinitely (Figure 31) with I-Cu-I and I-K-I angles being 180° whereas the Cu-I-K angle is 92.33(3)°

TABLE LIII

CRYSTAL DATA FOR (CuI$_2$K(18-crown-6)) (XIV)

Formula	$CuI_2KC_{12}H_{24}O_6$
M.W.	620.771 g mole^{-1}
a	8.906(3) Å
b	8.791(4)
c	14.120(5)
$\alpha = \gamma$	90.0°
	104.04(3)
V	1072.4(7) Å^3
F(000)	596
μMoK$_\alpha$	40.826 cm^{-1}
λMoK$_\alpha$	0.71069 Å
D_{cal}	1.922 g cm^{-3}
Z	2
Meas refl	3076
Obs refl	1548
R	5.2%
R_w	6.6%
Space group	$P2_1/n$ (Monoclinic)
Octants meas	±h, +k, +l

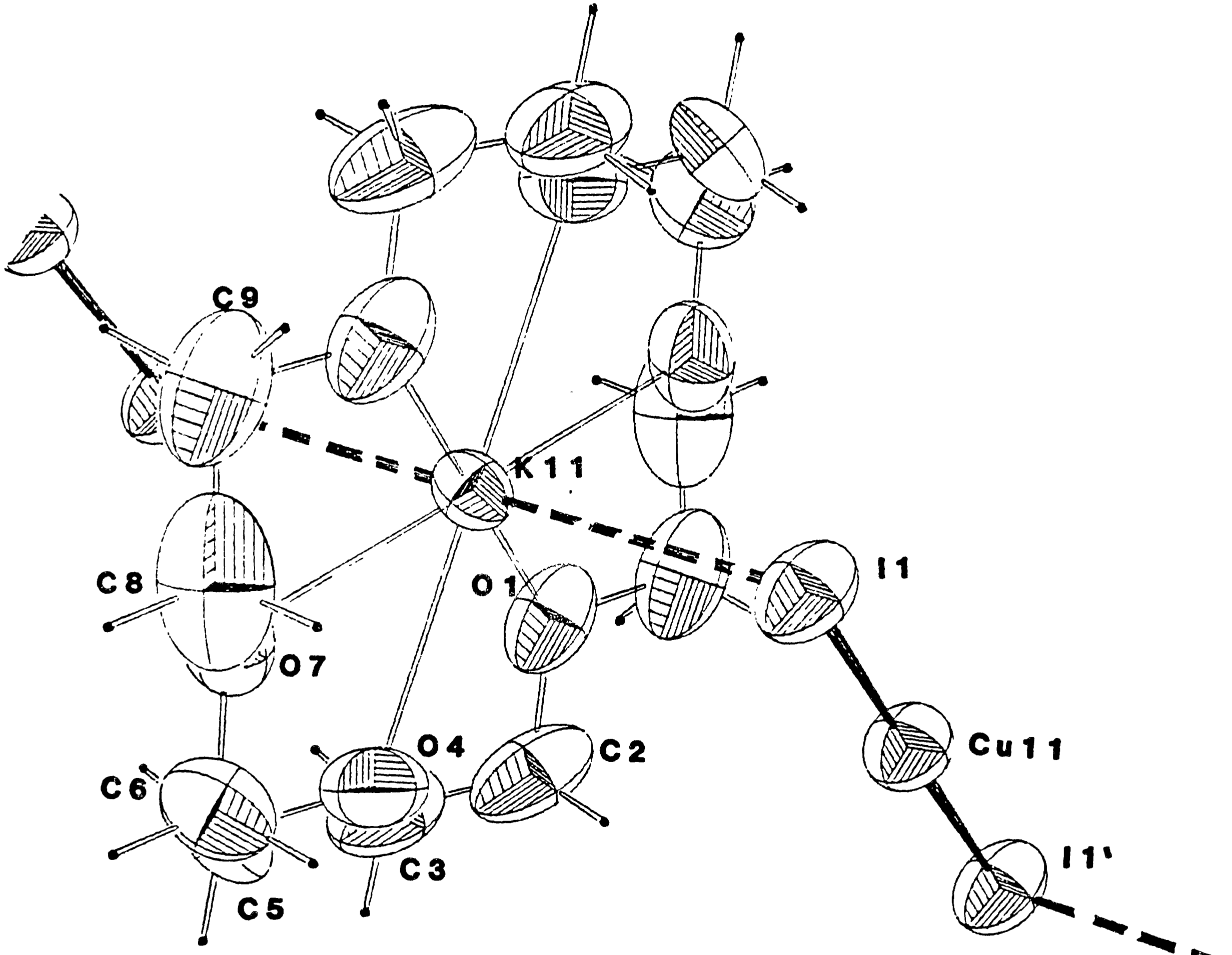

Figure 30. Projection View of XIV

TABLE LIV

POSITIONAL PARAMETERS FOR (CuI_2K(18-Crown-6)) (XIV)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.8135(1)	0.1559(1)	0.5491(1)
Cu11	1.0000	0.0000	0.5000
K11	1.0000	0.5000	0.5000
O1	1.2686(8)	0.3974(8)	0.4517(6)
O4	0.9973(10)	0.4390(9)	0.3046(5)
O7	0.7536(8)	0.6002(9)	0.3519(6)
C2	1.2398(17)	0.3329(15)	0.3554(14)
C3	1.1465(21)	0.4315(15)	0.2880(10)
C5	0.8958(28)	0.5315(17)	0.2392(8)
C6	0.7429(21)	0.5307(18)	0.2613(12)
C8	0.6089(13)	0.6072(18)	0.3827(15)
C9	0.6303(16)	0.6918(15)	0.4744(14)
H21	1.3390	0.3111	0.3371
H22	1.1842	0.2341	0.3532
H31	1.1967	0.5358	0.2957
H32	1.1436	0.3999	0.2195
H51	0.9312	0.6394	0.2430
H52	0.8867	0.4989	0.1695
H61	0.6627	0.5800	0.2068
H62	0.7074	0.4202	0.2605
H81	0.5278	0.6578	0.3301

TABLE LIV (Continued)

H82	0.5708	0.5026	0.3897
H91	0.6188	0.8041	0.4730
H92	0.5770	0.6540	0.5254

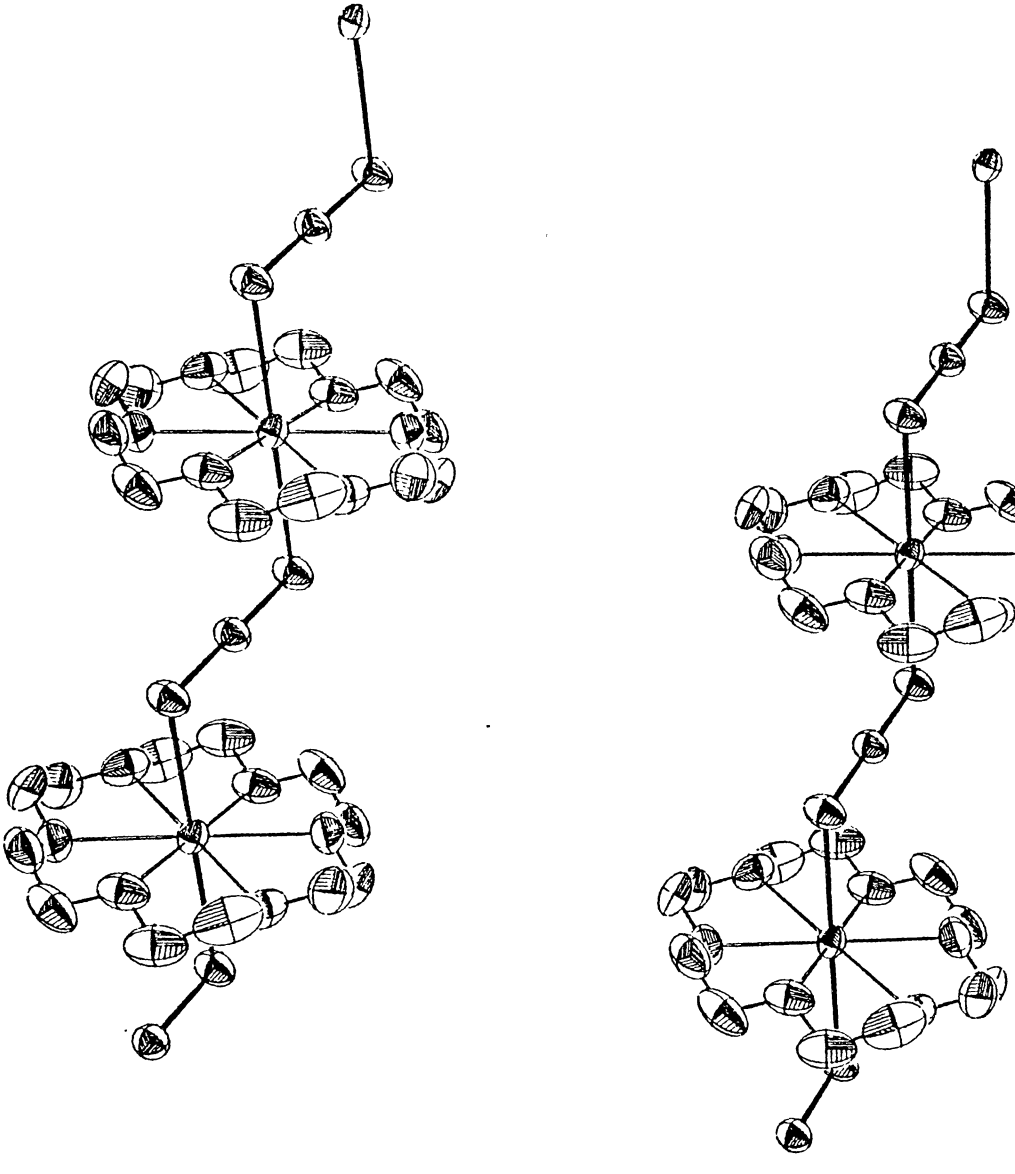

Figure 31. Packing Diagram of XIV

(Table LV). The crown ether lies in a plane perpendicular to the linear chain. Anisotropic thermal parameter for XIV are listed in Table LVI.

This compound (XIV) shows temperature independent luminescence, displaying light purple emission at both room and liq. nitrogen temperature. The luminescence may stem from excitation of pi electrons in the Cu-I bond which evidences considerable double bond charcter as seen in the very short Cu-I distance. The absence of thermochromism is probably due to the existance of a single excited state which involves the Cu-I bonding electrons. All previous observations of thermochromism involved multiple excited states whose population is temperature dependent.

Following the synthetic route which leads to XIV, but using the substituted 18-C-6, dch-18-C-6, a compound of the same general formula CuI_2K(crown ether) was obtained i.e., CuI_2K(dicyclohexano-18-crown-6) (XV). XV is similar in structure and properties to XIV. Compound XV, crystallizes in triclinic space group $P\bar{1}$ (Table LVII). The stricture of XV is similar to that of XIV in many respects as can be seen from a projection view of the molecule, Figure 32. The copper atoms are dicoordinated to two iodide atoms with an I-Cu-I angle of 180°. As in the previous compound, the Cu-I distance is short, 2.394(2) Å (Table LVIII). The copper and the potassium atoms sit on a $\bar{1}$ symmetry element (Table LIX), thus reducing the general

TABLE LV

BOND DISTANCES (Å) AND BOND ANGLES(°) FOR (CuI$_2$K(18-Crown-6)) (XIV)

I1-Cu11	2.383(1)	O4-C3	1.41(2)
I1-K11	3.598(1)	O4-C5	1.39(2)
K1-O1	2.791(8)	O7-C6	1.40(2)
K1-O4	2.805(8)	O7-C8	1.46(2)
K1-O7	2.782(7)	C2-C3	1.40(2)
O1-C2	1.44(2)	C5-C6	1.47(3)
O1-C9''	1.43(2)	C8-C9	1.47(3)
Cu11-I1-K11	92.33(3)	C2-O1-C9''	114.1(10)
I1-Cu11-I1'	180	K11-O4-C3	113.0(7)
I1-K11-I1''	180	K11-O4-C5	113.0(8)
O1-K11-O4	60.1(2)	C3-O4-C5	114(1)
O1-K11-O7	119.0(2)	K11-O4-C6	114.5(8)
O1-K11-O1''	180(2)	K11-O4-C8	112.5(8)
O1-K11-O4''	119.9(2)	C6-O4-C8	115(1)
O1-K11-O7''	61.0(2)	K11-O7-C6	114.5(8)
O4-K11-O7	60.3(2)	K11-O7-C8	114.9(11)
O4-K11-O4''	180(3)	O1-C2-C3	109.8(11)
O4-K11-O7''	119.7(2)	C2-C3-O4	110.2(13)
O7-K11-O7''	180(4)	O4-C5-C6	110.1(13)
K11-O1-C2	113.1(7)	C5-C6-O7	109.3(12)

TABLE LV (Continued)

K11-O1-C9''	115.0(9)	O7-C8-C9	110.5(10)
C8-C9-O1''	106.8(11)		

Symmetry Operations :

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

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

TABLE LVI

ANISOTROPIC THERMAL PARAMETERS FOR (CuI$_2$K(18-Crown-6) (XIV)

ATOM	U11	U22	U33	U12	U13	U23
I1	734(5)	596(4)	948(6)	22(3)	396(4)	-97(4)
Cu11	642(10)	605(10)	687(10)	63(8)	227(8)	-37(8)
K11	43(1)	65(1)	44(1)	3(1)	10(1)	3(1)
O1	77(4)	62(4)	124(6)	15(3)	47(4)	-1(4)
O4	132(7)	80(5)	61(4)	-27(5)	35(4)	-13(4)
O7	73(4)	86(5)	78(5)	-8(4)	-15(4)	11(4)
C2	121(10)	68(8)	185(15)	-30(7)	110(11)	-52(9)
C3	188(15)	62(7)	111(10)	-28(9)	103(11)	-32(7)
C5	250(20)	90(9)	41(6)	-7(13)	7(9)	11(6)
C6	145(13)	95(10)	91(10)	-12(10)	-49(10)	15(8)
C8	40(6)	112(11)	196(17)	-2(6)	-16(8)	56(11)
C9	79(8)	71(8)	176(15)	24(6)	49(9)	29(9)

Anisotropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^*$$

$$+2U13hla^*c^*+2U23klb^*c^*))\ X10^4 \text{ for I,Cu}$$

$$X10^3 \text{ for K, O, C.}$$

TABLE LVII

CRYSTAL DATA FOR (CuI_2K(dicyclohexano-18-crown-6)) (XV)

Formula	$CuI_2KC_{20}H_{36}O_6$
M.W.	728.954 g $mole^{-1}$
a	9.126(8) Å
b	9.211(6)
c	10.877(5)
α	103.37(5)°
β	93.40(6)
γ	126.86(4)
V	688.3(7) $Å^3$
F(000)	358
μMoK_α	31.939 cm^{-1}
λMoK_α	0.71069 Å
D_{cal}	1.758 g cm^{-3}
Z	1
Meas refl	3583
Obs refl	2088
R	6.7%
R_w	12.8%
Space group	$P\bar{1}$ (Triclinic)
Octants meas	±h, ±k, +l

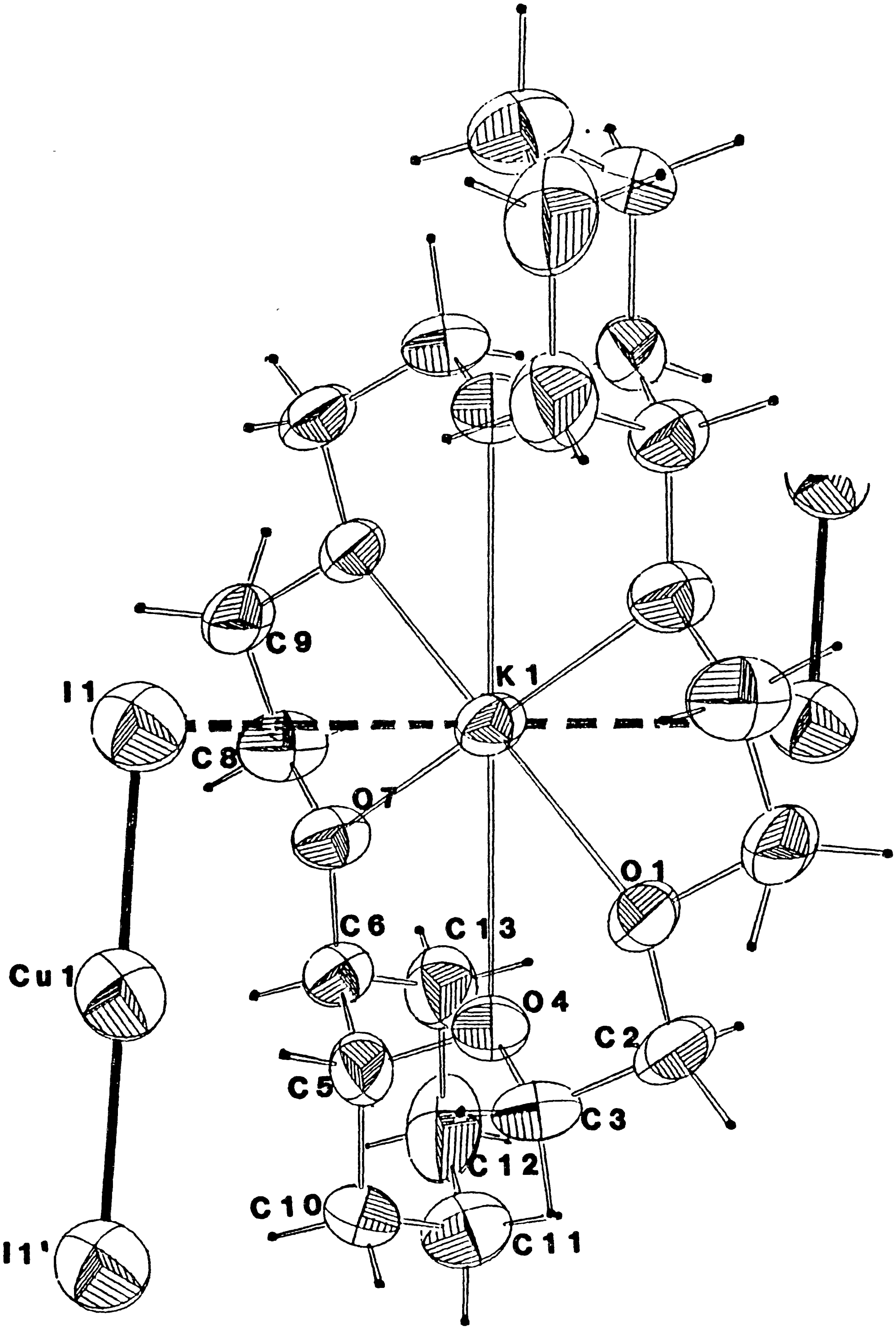

Figure 32. Projection View of XV

TABLE LVIII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR (CuI$_2$K (Dicyclohexano-18-Crown-6)) (XV)

I1-Cu1	2.394(2)	Cu1-I1-K1	96.93(5)
I1-K1	3.656(3)	I1-Cu1-I1''	180
K1-O1	2.78(1)	I1-K1-I1'	180
K1-O4	2.92(1)	O1-K1-O4	60.8(3)
K1-O7	2.72(1)	O1-K1-O7	118.4(4)
O1-C2	1.43(1)	O4-K1-O7	58.2(3)
O1-C9'	1.43(3)	C2-O1-C9'	112(2)
O4-C3	1.36(2)	C3-O4-C5	115(2)
O4-C5	1.43(3)	C6-O7-C8	113(1)
O7-C6	1.43(2)	O1-C2-C3	110(2)
O7-C8	1.49(2)	C2-C3-O4	110(2)
C2-C3	1.48(3)	O4-C5-C6	107(1)
C5-C6	1.54(2)	O4-C5-C10	113(1)
C5-C10	1.50(3)	C5-C6-O7	107.5(9)
C6-C13	1.58(2)	C5-C6-C13	115(1)
C8-C9	1.50(2)	O7-C8-C9	106(1)
C10-C11	1.57(3)	C8-C9-O1'	109(2)
C11-C12	1.58(3)	C5-C10-C11	110(2)
C12-C13	1.52(3)	C10-C11-C12	114(2)
		C11-C12-C13	111(1)
		C12-C13-C6	108(2)

TABLE LVIII (Continued)

Symmetry Operations :

' = -x, -y, -z

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

TABLE LIX

POSITIONAL PARAMETERS FOR (CuI$_2$K (Dicyclohexano-18-Crown-6)) (XV)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	-0.0590(2)	-0.4254(2)	-0.1842(1)
Cu1	0.0000	-0.5000	0.0000
K1	0.0000	0.0000	0.0000
O1	-0.2280(15)	-0.1678(16)	0.1635(9)
O4	0.1731(13)	0.0369(13)	0.2520(9)
O7	0.3672(13)	0.1475(15)	0.0645(9)
C2	-0.1192(23)	-0.0807(25)	0.2957(14)
C3	0.0377(22)	-0.0901(22)	0.3028(14)
C5	0.3239(24)	0.0284(26)	0.2437(15)
C6	0.4655(18)	0.1871(21)	0.1904(13)
C8	0.4959(21)	0.2664(26)	-0.0103(17)
C9	0.3826(25)	0.1641(31)	-0.1502(16)
C10	0.4245(26)	0.0595(27)	0.3735(16)
C11	0.5235(24)	0.2674(25)	0.4694(16)
C12	0.6642(29)	0.4317(34)	0.4140(19)
C12	0.5662(26)	0.4005(27)	0.2812(17)
H21	-0.0647	0.0561	0.3283
H22	-0.2018	-0.1455	0.3524
H31	0.0902	-0.0679	0.3939
H32	-0.0151	-0.2252	0.2506

TABLE LIX (Continued)

H51	0.2725	-0.0986	0.1809
H61	0.5752	0.1891	0.1820
H81	0.5370	0.3962	0.0198
H82	0.6090	0.2730	-0.0005
H91	0.3824	0.2382	-0.2020
H92	0.3953	0.0711	-0.2080
H101	0.3390	-0.0352	0.4122
H102	0.5285	0.0517	0.3633
H111	0.4214	0.2756	0.4868
H112	0.5899	0.2873	0.5554
H121	0.7173	0.5566	0.4762
H122	0.7687	0.4263	0.4040
H131	0.4653	0.4129	0.2915
H132	0.6542	0.4936	0.2426

equivalent positions for Cu and K from two to one (Z=1). Due to the positioning of the K and Cu atoms, the I-Cu-I and I-K-I angles are constrained to be 180°. The potassium ion shows ionic interaction with the iodide atoms (K-I distance 3.656(3) Å) and is encapsulated in the crown ether cavity being coordinated to the six oxygen atoms of the dch-18-C-6 ring. The crown ether ring with its cyclohexyl rings dictating crown ether packing, displays more order compared to the unsubstituted 18-C-6 of XIV. The cyclohexyl rings have chair confirmation. As in the previous case the crystallographic center of inversion relates the two halves of the crown ether molecule. The chain of -I-Cu-I-K-I- continues indefinitely (Figure 33) with the planes of the coordinated crown ether rings parallel to each other but perpendicular to the linear chain axis. The angle at iodine, K-I-Cu, is comparable to that of XIV (96.93(5)°). Final anisotropic thermal parameters for the nonhydrogen atoms are listed in Table LX.

Similar to XIV, compound XV also exhibits temperature independent luminescence. Dry crystals of XV luminesce sky blue at room temperature and at liquid nitrogen temperature. Further measurments are necessary before definite assignment of the emitting states can be made.

In XIV and XV, the Cu-I bonding distance is considerably shorter than the distances observed (79) in CuI complexes in which Cu is bound to four iodides,

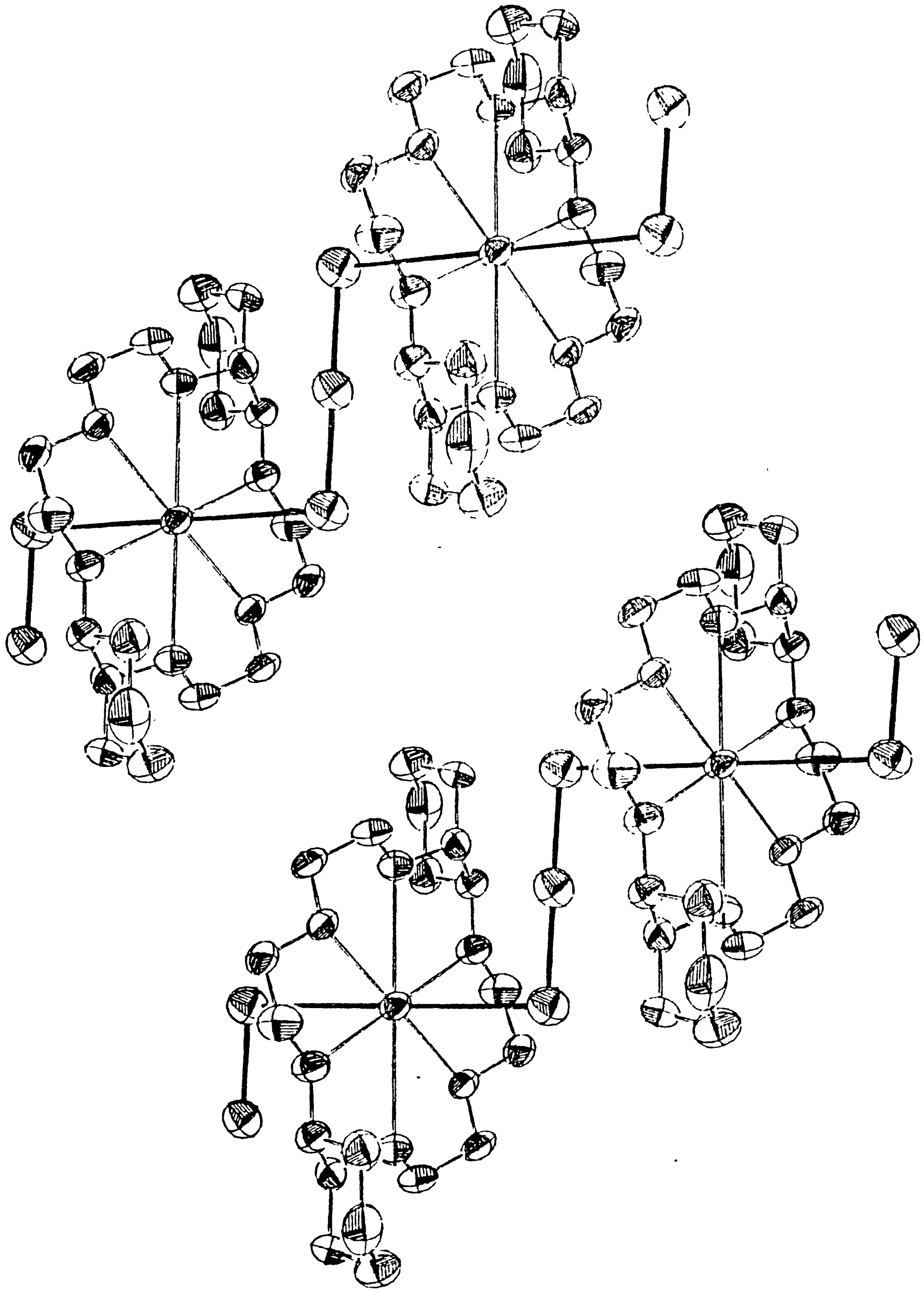

Figure 33. Packing Diagram of XV

TABLE LX

ANISOTROPIC THERMAL PARAMETERS FOR (CuI$_2$K(Dicyclohexano 18-Crown-6) (XV)

ATOM	U11	U22	U33	U12	U13	U23
I1	653(7)	622(7)	677(8)	364(6)	44(5)	154(5)
Cu1	58(1)	61(1)	71(2)	35(1)	7(1)	16(1)
K1	39(2)	68(2)	36(2)	35(2)	15(1)	22(2)
O1	56(5)	86(7)	34(5)	52(6)	14(4)	17(5)
O4	44(5)	42(4)	46(5)	22(4)	11(4)	20(4)
O7	37(4)	68(6)	44(5)	29(4)	11(4)	24(4)
C2	66(10)	83(11)	32(7)	49(9)	21(7)	23(7)
C3	58(8)	56(8)	41(8)	31(7)	13(6)	27(6)
C5	72(10)	83(11)	42(8)	63(10)	3(7)	6(7)
C6	35(6)	56(8)	40(7)	25(6)	7(5)	14(6)
C8	38(7)	81(11)	65(10)	27(8)	18(7)	40(9)
C9	67(10)	124(15)	52(9)	73(11)	34(8)	41(10)
C10	81(11)	95(13)	48(9)	69(11)	11(8)	28(8)
C11	53(9)	65(10)	51(9)	25(8)	0(7)	12(8)
C12	72(12)	113(16)	66(12)	63(13)	-24(9)	-35(11)
C13	67(10)	77(11)	61(10)	49(10)	6(8)	6(8)

Anisotropic thermal parameters in the form :

$$\exp(-2\pi^2(U11h^2a^{*2}+U22k^2b^{*2}+U33l^2c^{*2}+2U12hka^*b^* +2U13hla^*c^*+2U23klb^*c^*)) \times 10^4 \text{ for I,}$$

$$\times 10^3 \text{ for Cu, K, O, C.}$$

average distance 2.711 Å in XII or to three iodides, average 2.62 Å in $Cu_4I_62^-$ in XI. The shortening of the Cu-I distance, average 2.388 Å observed for XIV and XV, is consistant with the shortening of Cu-ligand distances observed in L-Cu-L complexes with other donor ligands and suggests considerable double bonding character between Cu and I in both cases (81).

Comparision of synthetic routes leading to XIV and XV with those reported for $CuMe_2^-$ and $CuPh_2^-$ (84) suggests a general reaction scheme (Equation 1) leading to dicordinate cuprous species :

$$2MZ + CuI + \text{Crown ether} \longrightarrow CuZ_2{}^{n-}M(\text{Crown ether}) \qquad (1)$$

(M= alkali metal ion, Z = X^- or R)

with alkali metal ion and crown ether chosen for optimum binding.

Conclusions and Scope of Further Studies :

This investigation has provided insight into understanding of the mechanism of luminescence and correlation of structural parameters with thermochromic luminescence behavior of CuI complexes. During the course of the investigation, structural motifs were observed, previously unknown for CuI systems. This investigation has laid the ground work and opened up a vast area of research to be conducted for nitrogen ligand systems as well as the CuI-KI water systems.

The CuI compounds formed from aqueous KI systems in presence of crown ethers of varying cavity size has has resulted in a series of novel structures, different from each other and previously unobserved. The isolation and structural elucidation of the linear CuI_2^- species, has led to the identification of a general synthetic route leading to the formation of CuZ_2^- linear species. Further syntheses in this field, with choice of alkali metal ion and crown ether for optimum fit of alkali metal to cavity may produce more linear dicoordinate species such as AgI_2^- , $AgBr_2^-$, $(CuBrI)^-$, which could be of interest as dopants for semiconductors (90). These linear species are used as spacers in the conductivity lattice. As such their ionic "thickness" and overall charge are of interest. Syntheses of the compounds of the type XI to XIII with change of halide, selecting halides of different ionic radii may lead to interesting structural results. Study of the luminescence properties of these materials will give further insight into the structure-emission property correlations by allowing observation of changes in emission bands with change of excited state due to halide. Life times of these compounds should be measured inorder to define the emission as fluorescence or phosphorescence. The possible occurance of a phase trasition must be investigated to rule out its importance in the thermochromism. Because the crystals were found intact before and after cooling the samples, only a non destructive phase change is a possibility. Because the change in emission with temperature appears contineous, a phase change appears unlikely, however the possibility needs to be investigated.

The following overall conclusions are drawn from the foregoing discussions about the correlation of the structures of the CuI complexes with their emission characteristics. The two types of systems investigated during the course of this study are 1. the CuI-nitrogen donor Lewis base ligand systems and 2. CuI-aqueous KI systems in presence of crown ethers of various sizes.

In the CuI-nitrogen donor Lewis base ligand systems the structural factors influencing the emission properties of these complexes, as concluded from this investigation, seem to be : Cu-Cu bonding interactions as seen for copper atoms with less than 2.8 Å separation, and close packing of planes of aromatic systems so as to have interactions between their nonhybridized p_z orbitals and the presence of bonds between copper and sp^2, or sp hybridized nitrogen atoms especially those which are components of aromatic rings. Factors such as the presence or absence of a crystallographic symmetry element, presence of Cu-saturated organic ligand interaction are shown to be irrelevant by these investigations. While detailed emission spectral studies were carried out on only representative complexes during the course of the investigation, they should be expanded to include other halide ions and aromatic ligand systems with activating substituents of varying efficiency.

From the CuI-aqueous KI, crown ether systems, in which only Cu-Cu interactions and Cu-I bonds provide possible excitement modes, it may be concluded that both may be involved to explain the multiplicity of emission bands observed. Complete characterization of the emission properties of XII and XIII in which there is less diversity of copper site, is necessary before the spectrum of XI may be fully understood. Thermochromism is not exhibited by the compounds XIV and XV which lack metal-metal interactions but display Cu-I bonds of multiple bond character. These compounds then are atypical of the systems produced in this investigation.

This study, then, has focused on an uncharted area of correlation of solid state emission spectra with solid state structure and has shown that the existance certain aspects of structure regularly manifest themselves in components of the emission spectra. It has shown that thermochromism of these compounds stem not from the shifting of the emission bands but rather from changing relative populations of excited states as temperature is lowered. It has shown that an understanding of the structural effects on thermochromic emission can lead in a simple way to the design of systems whose temperature dependent emission may be predictable.

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