LUMINESCENT COPPER(I) COMPLEXES - CORRELATION OF STRUCTURE AND PHYSICAL PROPERTIES

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PREFACE

The primary objective in this work has been to correlate emission of pure solids (cuprous iodide complexes) with the various electronic transitions possible in these systems in the same way that one correlates vibrations of the various functional groups of organic molecules with their infrared specta. In order to have information on the possible transitions of a complex, its structure must be known. Structures of single crystals were determined with a Nicolet P3 diffractometer, and from the quantitative structural information, electronic transitions could be inferred and correlated with emission spectra obtained from an Oriel Fluorescence Spectrophotometry system.

Until recently, a hand held black light giving off UV radiation at 366 nm (wavelength of maximun intensity of a mercury vapor lamp) has been the only excitation source and observed colors were recorded in a notebook. The Fluorescence Spectrophotometry system measures the total emission and does not differentiate between fluorescence and phosphorescence. Thus the sophistication of the correlations is proportional to that of the equipment.

I wish to thank Dr. Elizabeth M. Holt for her guidance, support, and patience throughout my stay at OSU,

and for her final push in the writing of this thesis. Also I extend my appreciation to Drs. Neil Purdie, Warren T. Ford, and Joel J. Martin for their help and direction. The friendship of the Holt family and that of the members of Dr. Holt's group is appreciated and their suggestions and help are recognised.

Financial support from the Department of Chemistry, Petroleum Research Fund, and National Science Foundation is greatly appreciated; this work and the realization of some personal goals would not have been possible without it.

Finally, the timely visit of Mrs. Elaine Tompkins, my mother, has been most instrumental in the revising of this thesis, seeing that to move on, this work must first be completed.

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CHAPTER I

INTRODUCTION

Luminescence of solid cuprous halides and of their complexes with Lewis base ligands was first reported by J. T. Randall (1,2). He reported that this luminescence was temperature dependent in many cases, that is when the temperature was lowered to that of liquid nitrogen (77K), the solid state emission changed color. Beginning in the 1970's, H. D. Hardt and co-workers reported numerous examples of luminescent complexes formed on copper iodide test papers whose emissions were temperature dependent and this phenomenon was termed "fluorescence thermochromism" (3,4). In these experiments, copper iodide is complexed to various aromatic and aliphatic amines such as pyridine, derivatives of pyridine, morpholine, piperidine, quinoline, pyrrolidine, and a variety of primary, secondary, and tertiary aliphatic amines. The fluorescence referred to is better designated "luminescence". This generic term includes both fluorescence which has a short lifetime and phosphorescence which has a much longer lifetime.

Not all copper(I) compounds emit, nor are all of those which do emit, thermochromic. For example solid copper iodide alkyl quinaldates (5) which are purple-brown in color, do not emit. An example of a copper(I) complex which is luminescent but not thermochromic is copper iodide quinoline ($(CuI(quin)_2)_2$) (6) which emits yellow at both room temperature and 77K. Other complexes made from 3-methylpyridine, 2-methylpyridine or 2,4-di-methylpyridine also emit non-thermochromically (7). Visually observed emission of CuXL compounds (X = Cl, Br, I) has ranged throughout the visible spectrum from violet to red. Compounds which emit thermochromically may emit at any wavelength in this range and at 77K. The observed color change can be to a longer wavelength (red shift) or to a shorter wavelength (blue shift). For example, copper iodide hexyl nicotinate emitted yellow at room temperature, and blue at 77K, while copper iodide dimethylamine emitted yellow at room temperature, but orange at 77K (4). Thermochromism in these complexes was reversible. For example, when the copper iodide hexyl nicotinate was cooled to 77K, the emission changed from yellow to blue but on warming to room temperature, the emission returned to yellow.

Some of the work of Hardt and co-workers involved copper(I) carboxylates (8,9,10,11). Most of these emit in the solid state and some are thermochromic although copper(I) 2-hydroxybenzoate does not emit at all (12).

Weber and Hardt (9) first explained temperature dependent luminescence by comparing the powder diffraction patterns of the formate, acetate, propionate, and butyrate salts of copper(I). All displayed a similar intense line corresponding to the 001 plane of the copper(I) acetate lattice whose structure had previously been determined (13,14). In the copper(I) acetate structure, copper atoms lie on the 001 planes and are bridged by carboxylates. They reasoned that since all of the carboxylate structures appeared to be of the same general motif, differences in emission properties, meaning thermochromicity, must be due to differences in packing. They observed that the differences in Stokes shifts between 300K and 77K for carboxylates with an even number of carbons tended to be greater than for those with odd numbers of carbon atoms. The results are illustrated below:

$C_5H_{11}COOCu$ $E_{77K} - E_{300K} = 0.28$ eV (higher)

C_6H_{14} Melting Point = $-92^{\circ}C$ (higher)

while

C_4H_9COOCu $E_{77K} - E_{300K} = 0.1$ eV (lower)

C_5H_{12} Melting Point = $-143^{\circ}C$ (lower)

and

C_3H_7COOCu $E_{77K} - E_{300K} = 0.9$ eV (higher)

C_4H_{10} Melting Point = $-137^{\circ}C$ (higher)

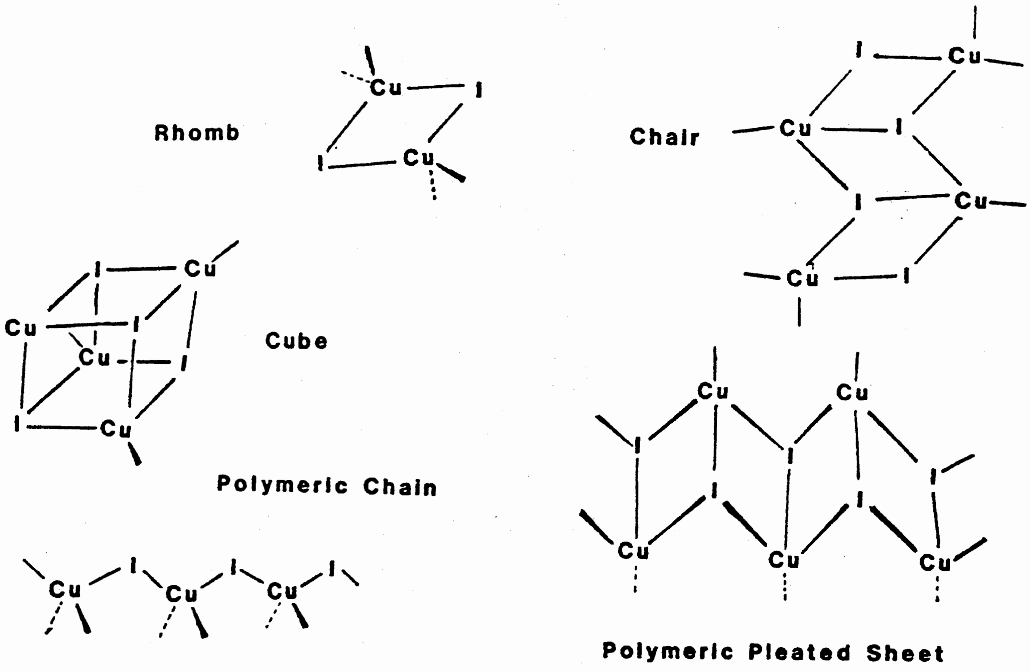
where E is the Stokes shift. The Stokes shift is the difference between the maximum absorption and the wavelength of maximum emission for a compound. For carboxylates whose change in Stokes shift was lower, the melting points of their parent alkanes were also lower, and those with the lower melting points or lower Stokes shifts had odd numbers of carbons. Weber and Hardt explained that those carboxylates with odd numbers of carbon atoms pack more loosely while those with even numbers of carbon atoms pack closely. Tight packing leads to thermochromic emission while loose packing leads to greater oscillation among molecules and non-thermochromic emission because molecules are more free to oscillate and some of the excitation energy may be dissipated non-radiatively.

Comparisons of thermochomic behavior of aromatic carboxylates were also made. The benzoate and 4-hydroxybenzoate of copper(I) both emitted yellow non-thermochromically, while the 3-hydroxybenzoate emitted yellow at room temperature and green at 77K. Hardt and Weber proposed a decrease in the crystallographic symmetry to explain the thermochromic emission for these cases (8).

A possible connection between thermochromism and symmetry was observed in the comparison study among three tetrameric CuI complexes of morpholine, pyridine, and piperidine (25). Hardt and Weber found that the tetramer with the lowest internal symmetry was the most thermochromic and from this observation emerged the hypothesis that if the point symmetry of a $(CuI)_4$ cluster is four-fold, thermochromic luminescence will not be observed (25).

The number of structural studies on cuprous carboxylates is limited because of their air sensitivity (13,14, 15), but cuprous iodide complexes of various aliphatic or aromatic nitrogen donor Lewis bases offer the potential of increased stability since the cuprous oxidation state is stabilized by iodide in the solid state. Synthetic processes carried out in saturated aqueous KI solutions or in acetonitrile, which tend to stabilize Cu(I) in the presence of iodide, are possible.

The complexes of cuprous iodide crystallize in a variety of structural motifs and stoichiometries. A common stoichiometry is 1:1:1, copper:iodide:ligand. Stoichiometries of 1:1:0.5, 1:1:1.5, 1:1:2, and 1:1:3 have also been observed. Polymeric pleated sheets, cubes and rhombs are common motifs as well as chairs and polymeric chains. These motifs are illustrated in Figure 1.



Rhomb

Chair

Cube

Polymeric Chain

Polymeric Pleated Sheet

Figure 1. Motifs (Structural for $CuI(L)_x$)

Monomers of stoichiometry 1:1:3 or 1:1:2 (16,17), rhombs of stoichiometry 1:1:1, or 1:1:2 (5,18,19,20), chairs of 1:1:1.5 or 1:1:2 (19), polymeric chains (5,19,20,21) and cubes (16,17,18,23) of 1:1:1 are described in the literature. In these complexes, Cu(I) is normally four coordinate although three coordinate copper has been noted (18). Inclusion compounds are also described in the literature (12). One such compound consists of molecules of quinaldic acid included between $(Cu_2I_3)_x$ chains and has a stoichiometry of Cu:I:quinaldic acid, 1:1.5:1.5 (12). The ligand was not coordinated to the copper.

Early reports of emission properties of $CuIL_x$ complexes were merely the noting of the observed color at room temperature and that at 77K. The eye sees the average of the radiation emitting from the substance but it cannot resolve the spectrum into its various maxima. Correlation studies of luminescent substances depend on the ability to resolve a spectrum into its various emission maxima and thus to allow assignment of an electronic transition to each one. Thus, further correlation of structure with emission properties depends upon quantitative as opposed to qualitative characterization.

Emission in copper iodide complexes originates from three sources (6);

1) Metal to Ligand Charge Transfer (MLCT)
2) Ligand - Ligand interaction (LC)
3) Metal - Metal interaction (MC)

Metal to Ligand Charge Transfer in these $CuXL_x$ systems describes a $3d^{10}$ - $3d^9pi^*$ transition, transfer of an electron from a d orbital of the metal to a pi* orbital of the ligand. This assignment is appropriate for the numerous complexes in which copper is ligated to a nitrogen donor which is part of an aromatic system. An interesting example is the copper(I) iodide pyridine system which has been identified in three different solid motifs; polymeric pleated sheet and cube with stoichiometry 1:1:1, as well as rhomb with stoichiometry 1:1:2 (22,24,26).

Hardt and Pierre (22) first reported that the emission for the cubic complex (Cu_4I_4(pyridine)$_4$) (23) was due solely to MLCT. At 293K the emission was yellow (560 nm) but at 77K, the emission was dual, luminescing at 610 nm and 440 nm. They observed also that the excitation maxima were different for each emission maximum and concluded that there were copper ions in two separate environments with respect to symmetry. The red shift in the low energy peak was attributed to the increase in Cu - Cu interactions as the substance was cooled. Eitel et al. (25) similarly reported that this cubic complex emitted yellow only (585 nm) at 295K; orange (613 nm) and blue (439 nm) at 70K; and blue only (437 nm) at 15K. The polymeric complex emitted blue only at 295K and emitted practically the same at 15K (449 nm). Metal to ligand charge transfer was assigned to the blue emission only.

For the complexes (CuI(quinoline)$_2$)$_2$ and Cu_4I_4(quinoline)$_4$ emission was observed at 620 and 615 nm. respectively and MLCT was assigned to these wavelengths (6). Metal to ligand charge transfer has been assigned to emission between 500 and 600 nm for $Cu(PPh_3)_2(phen)^+$ and for solid $Cu(dmp)_2{}^+$ where phen is phenanthroline and dmp is 2,9-diphenyl-1,10-phenanthroline (26,27,28). The MLCT band increases in wavelength with the extent of conjugation in the aromatic system.

Three $CuIL_x$ complexes which do not emit have been studied by Tompkins et al. (5). Copper iodide methyl quinaldate, was previously prepared and studied by Goher and Hafez (29). The crystalline powder (dark brown, mp 205°C) mixed with nujol showed a broad absorption band at 520 nm and this wavelength was assigned to MLCT. Absorbances in the ultra-violet region were observed for ethanol and DMSO solutions of this complex at 240 and 290 nm with a shoulder at 315 nm. Pi - pi* transitions were assigned to these UV absorbances. The complex studied by Tompkins et al. was purple-brown in color, melted at 180°C and was of stoichiometry 1:1:1, crystallizing as a polymeric chain. Luminescence was not observed for this complex nor for similar ones made from isopropyl quinaldate and n-butyl quinaldate, both of stoichiometry 1:1 and crystallizing as rhombs. The earlier paper (29) suggested that there was no coordination between copper and the carbonyl oxygen of the ester group because of the small change in the C=O stretching vibration in the IR spectra of complexed vs. uncomplexed quinaldates. Structural studies showed that there was indeed coordination with a Cu - O distance of 2.33(1) Å for the methyl quinaldate complex (5). The bonding of oxygen to copper(I) apparently affects the energy levels of the copper atom making relaxation through non-radiative processes more favorable than relaxation through emission. Metal to ligand charge transfer processes thus do not result in emission.

Ligand centered interactions are described electronically as pi - pi* transitions. They have been reported in luminescence studies of frozen solutions (77K) of pure quinoline in ethanol (30) and in solid copper iodide quinoline complexes also at 77K (6). The low temperature (77K) emission spectrum of the copper iodide quinoline has fine structure which matches that of the quinoline alone in the frozen ethanol solution. In the $(\mathrm{CuI(quinoline)})_4$ the ligands are lined up in a parallel fashion and the distances between ligands within each tetramer are 3.325(12) Å and 3.279(10) Å. At temperatures below 77K the separation between ligands is apparently lessened giving rise to inter-ligand interactions of the type pi - pi*. Buchner et al. (26) assigned a pi - pi* transition to emission at 470 nm and d - pi* to a more intense peak at 600 nm in the total emission spectrum of $(\mathrm{Cu(PPh_3)(phen)})^+$ at 77K. This spectrum was run at an excitation of 370 nm and was time resolved to separate the long-lived component from the short lived component. The long-lived component (600 nm) was assigned MLCT and the short-lived component (470 nm) was assigned LC. In the total emission spectrum, the peak at 470 nm was much less intense than that at 600 nm but the spectrum observed through a phosphoroscope showed a multiplet covering a broad range from 445 to 650 nm.

In the copper(I) complexes, one notable feature of the single crystal structure is the variability of the distance between copper atoms. The distances range from 2.42 Å (31) to 3.58 Å (32) with 2.83 Å being a common Cu...Cu separation (33). With the shorter distances, possibilities for Cu...Cu interactions cannot be ignored (33). Molecular orbital calculations (33) have shown that for Cu_4^{4+} clusters, the overlap population is great enough for "soft attractive Cu(I) - Cu(I) interactions" (33). Considering d orbitals alone, the population overlaps become increasingly negative (unfavorable) as the atoms are brought closer but if s and p orbitals are included in the MO calculations, the overlap populations become more positive, meaning an increase in the attraction among the atoms. For example, in isolated Cu_4^{4+} clusters, as the inter-copper distances decrease from 2.83 Å to 2.44 Å the overlap population increases from 0.032 to 0.124 corresponding to bond energies ranging from -0.417 eV to -1.469 eV. For Cu_2^{2+}, as the inter-copper distance is decreased from 3.18 Å to 2.58 Å, the bond energies increase from -0.026 eV to -0.228 eV. These values, although small, represent attractive forces or metal - metal interactions.

The third transition associated with these solid materials is a metal - metal interaction represented electronically as $3d^{10}$ - $3d^9 4s^1$. The existence of MC interactions in cuprous complexes is illustrated by the CuI complexes of piperidine and morpholine. Both have non-aromatic ligands bound to copper through the nitrogen atoms and both are luminescent in the solid state. The morpholine complex emits orange at room temperature (lambda$_{max}$ - 625 nm) while the piperidine emits yellow at room temperature (lambda$_{max}$ - 570 nm). Hardt and Pierre (25) examined the emission spectra of these complexes and observed a red shift of the emission maximum for each on going from room temperature to 77K. The Cu...Cu separations for piperidine, morpholine, and pyridine are 2.63-2.67, 2.59-2.71, and 2.62-2.72 Å respectively and Cu(I) - Cu(I) interactions are likely to exist for all three complexes. The copper iodide complex of pyridine emits yellow at room temperature (lambda$_{max}$ - 560 nm) changing to purple at 77K. The emission spectrum at 95K showed the emergence of a second smaller peak with a wavelength near 400 nm which red shifted slightly and increased in intensity as the temperature was lowered. The maximum at 77K was at 440 nm. The peak at 560 nm red shifted also by 50 nm to 610 nm but diminished in intensity. The emission at 440 nm had a different excitation maximum (lambda$_{ex}$ 270, 295, 364 nm) than the one at 610 nm (lambda$_{ex}$ 317 nm) suggesting that luminescence was from two different emitting centers, copper ions in two different environments (25).

Work by Tanimura et al. (31) seems to support this thesis. Crystals of $RbMgF_3$ doped with Cu^+ emitted at 450 nm ("blue" copper centers) when excited at 305 nm but when excited at 364 nm, the emission maximum was 575 nm ("green" copper centers). The reported excitation maxima for the pyridine complex was similar to those of Tanimura et al. In the $RbMgF_3$ crystals, the origin of the blue emission was a copper ion with D_{3h} symmetry while the green emission was due to a copper ion with C_{3v} symmetry. But these copper ions are isolated from each other and are not pairs or aggregates (31). Emission is due to an electronic transition of a Cu^+ ion itself or an interaction with a neighboring anion rather than one with neighboring copper atoms or ions. The single crystal X-ray structure determinations of $(CuIL)_4$ where L = pyridine (21), morpholine (31) or piperidine (32) show the presence of a Cu_4 cluster. The origin of the luminescence in the morpholine and the piperidine can only be metal - metal interactions (d - s), there are no pi orbitals in either of these two ligands, but for pyridine there is the added mechanism of MLCT (d - pi^*).

Below 100K, the emergence of the second maximum at 440 nm for the pyridine complex is observed and the spectrum at 84K is like that observed for the $Cu(PPh)_2(phen)^+$ species reported by Buckner et al. (26) who assigned a pi - pi^* transition to the small peak in the 450-500 nm range. Blasse and McMillin, however, observed only one emission band for $Cu_4I_4(pyridine)_4$ which changed from yellow at room temperature and red-shifting with decreasing temperature. Pyridine, therefore, has at least two sources of emission; metal to ligand charge transfer, and Cu(I) - Cu(I) interactions. The emergent high energy peak for the spectrum of

(CuI(pyridine))$_4$ prepared by Hardt and Pierre may be due to interligand interactions but since there is no parallel stacking of ligands as in the (copper iodide quinoline)$_4$ (6), the origin of this emission is not clear.

Vogler and Kunkley (34) reported that copper iodide pyridine, which emits at 585 nm (20) at room temperature, emitted at 610 nm when incorporated in a methyl methacrylate resin and at 698 nm in benzene solution. An excited state distortion was given as the explanation (34). The Franck-Condon rule would apply in this case, and changes in the positions of atoms would not be observed. This rule states that the electronic transitions occur at a much faster rate than does movement of atoms which would arise from such transitions (47). Distortion of the tetrameric complex in the excited state may occur more readily in a fluid lattice such as benzene, less readily in a lattice which is only somewhat fluid such as a resin and not at all in a rigid lattice such as a crystal or a glass. Vogler and Kunkely have suggested that distortion of the emitting center affects the wavelength of the luminescence. Distorting the crystal enough to bring about an inter-ligand interaction has been described earlier for the complex of quinoline (6), but distortion may also bring about a change in symmetry about the emitting metal center.

Thus the thermochromism reported in these complexes is of two types. One involves the emergence at low temperatures of one or more peaks in the emission spectrum as in that of copper iodide quinoline (6) and for copper iodide pyridine (25) on cooling. The second kind is an actual shift in the maximum to a different wavelength. It was this shift which Hardt and Pierre correlated with the symmetry of the cluster (25).

In recent work (37), two tetrameric complexes of copper iodide containing mixed ligands were studied with the intention of determining the importance of $\bar{4}$ symmetry to the thermochromicity of these compounds as proposed by Hardt and Pierre (25). $Cu_4I_4(ligand)_2(acetonitrile)_2$ complexes; bis-(p-toluidine)bis(acetonitrile)tetraiodotetracopper (i) and bis((p-chloroaniline)(acetonitrile)diiododicopper))$_2$ (ii) were studied. Both emitted yellow non-thermochromically and showed no shift of emission maxima; one complex (i) had no internal symmetry and, according to the thesis that absence of crystallographically related Cu - I bonds leads to thermochromism, should emit thermochromically (lambda$_{max}$ 586 nm). The other complex (ii) had two-fold symmetry but its emission behavior (lambda$_{max}$ 628 nm) was the same as that of (i). Rath et al. showed that internal symmetry in $CuIL_x$ complexes was not a factor in temperature dependent luminescence. For these two tetrameric aggregates the average Cu...Cu separations averaged 2.699(3) and 2.682(7) Å respectively. Thus the two emission maxima were most likely due to metal centered interactions.

Many structures of copper iodide complexes have been solved, but there have been no crystallographic studies made at low temperature. Crystallographic studies at both room and low temperature represent a significant step to more complete understanding of these systems. The primary reason for low temperature studies is to observe the differences in structural details at the two extremes of temperature, especially for those complexes which emitted thermochromically. Both room and low temperature emission studies on these kind of complexes have been made (25) but there are few instances in the literature where both crystallographic and luminescence studies occur together in one work.

Willett et al. (38) have studied crystals of tetramethylammonium trichlorocuprate(II) and were able to ascertain three separate phases due to variation of Jahn-Teller distortion patterns at three separate temperatures. The complex at 405K had $P6_3/mmc$ hexagonal symmetry, at 323K, $P\bar{1}$ triclinic symmetry and at 213.2K it had $P2_1$ monoclinic symmetry. The sequence of Jahn-Teller elongated bonds changed from a spiral progression to an alternating one to disorder and was reflected in changes in the magnetism from ferromagnetic to ferrimagnetic to non-magnetic. Although Jahn-Teller distortions are not expected in copper(I) systems, phase changes may be related in some manner to thermochromic luminescence. McMillin and coworkers (39) have suggested a pseudo Jahn-Teller effect involving a d^9 metal center in the triplet d - pi^* state to explain dual emission in rigid low temperature glasses containing copper(I) complexes of the type $(Cu(biL)(PPh)_2)^+$ where biL is 2,2'-

bipyridyl, 1,10-phenanthroline, or 2,9-dimethyl-1,10-phenanthroline.

CHAPTER II

X-RAY CRYSTALLOGRAPHY

From the crystallographic point of view, a single crystal is made up of repetitions of a single volume of space which is called the unit cell. Each unit cell contains the same molecules arranged in the same way. Unit cells must be lined up in an ordered fashion in order for the material to be truly crystalline. The edges of the unit cell are designated $\underline{a}$, $\underline{b}$, and $\underline{c}$ and the angles between edges; α, β, and γ. The relationships between these cell edges and angles determine the crystal class to which the unit cell belongs (40).

There are seven classes of crystals:

1) triclinic $\underline{a} \neq \underline{b} \neq \underline{c}$, $\alpha \neq \beta \neq \gamma$.
2) monoclinic $\underline{a} \neq \underline{b} \neq \underline{c}$, $\alpha = \gamma = 90^{\circ}$, $\beta \neq 90^{\circ}$
3) orthorhombic $\underline{a} \neq \underline{b} \neq \underline{c}$, $\alpha = \beta = \gamma = 90^{\circ}$
4) tetragonal $\underline{a} = \underline{b} \neq \underline{c}$, $\alpha = \beta = \gamma = 90^{\circ}$
5) cubic $\underline{a} = \underline{b} = \underline{c}$, $\alpha = \beta = \gamma = 90^{\circ}$
6) hexagonal $\underline{a} = \underline{b} \neq \underline{c}$, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$
7) rhombohedral $\underline{a} = \underline{b} = \underline{c}$, $\alpha = \beta = \gamma \neq 90^{\circ}$

The molecules within a unit cell may be related to each other by symmetry elements such as 2, 3, 4 and 6 fold rotation axes; $\bar{1}$, $\bar{3}$, $\bar{4}$, and $\bar{6}$ fold inversion axes; mirrors;

glide planes; and screw axes. In addition there may be a repetition of motif in the center of particular faces of the unit cell, called face centering; or in the center of the volume of the unit cell, called body centering. The absence of centering renders the cell primitive.

The optimum crystal contains ordered unit cells and is of optimum dimensions 0.2 mm x 0.2 mm x 0.2 mm. The crystal is visually chosen on the basis of well defined edges and faces without cracks or obvious cleavage planes. Smaller crystals will usually yield a successful determination if sufficient time is devoted to data collection. Crystals which are too large can be cut to the appropriate size.

None of the compounds examined was sensitive to air or moisture within the time required for X-ray data collection so crystals were attached to a glass fiber using epoxy glue and the fiber affixed to a brass nib without any attempt to isolate the sample from the environment. The brass nib is inserted into a goniometer head which was then positioned on a four circle Syntex P3 automated diffractometer. The mounted crystal is visually centered at the crosshairs of a microscope focused on the center of the instrument circles and a rotation photograph taken to provide a starting point for the unit cell determination sequence of the diffractometer. The quality of the crystal may also be ascertained from a brief examination of the photograph with high crystalline quality giving rise to a sharp and extensive diffraction pattern whereas poor crystallinity is indicated by a fuzzy or diffuse appearance of the pattern.

Diffraction occurs where the conditions of the Bragg equation are met:

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

where λ is the wavelength of the radiation θ is the angle of incidence of the X-ray beam on the set of planes diffracting and d is the spacing between the planes. The planes may be imagined as parallel and successive slices of the unit cell. They are designated by the hkl indices where h designates that the set of planes cuts the a cell edge every 1/h. Similar relationships to the b and c cell edges are designated by k and l.

The photograph consists of a diffraction pattern which is symmetrical about both "x" and "y" axes. A strong reflection was chosen such that $\chi > 75^{\circ}$ and $2\theta < 20^{\circ}$. (ω and ϕ are angles of rotation about the center of the crystal.) This reflection was used to adjust the height of the crystal more accurately. Fifteen independent reflections are centered to determine the optimum 2θ, ω, ϕ, and χ angles for each reflection. An indexing routine provides possible cell edges from which a set with maximum symmetry and minimum volume is chosen (41). A least squares fit of the diffractometer centered angles for the fifteen reflections to the cell edges gave the final cell dimensions, their associated errors, and an orientation matrix to be used for data collection (41). If the errors (standard deviations) of the cell dimensions are unacceptably high a fast data scan may be carried out to find fifteen intense reflections with 2 values which are consistantly greater than 20°. The cell determination procedure is then repeated to yield a cell with acceptable errors. In some cases a cell with greater symmetry may be found using cell vector programs NEWLAT(42) and TRACER(43). TRACER indicates the reduced primitive cell and may indicate the presence of higher symmetry. A set of data is collected such that the diffraction symmetry of the cell generates a complete sphere of data (44). Thus the minimum diffraction symmetry of the crystal must be considered in selecting parameters for data collection.

The diffractometer records the intensity data, I_{hkl}, associated with each reflection in the following format: sequence number, h, k, l, 2θ, ω, ϕ, χ, 2θ scan range, scan speed, peak profile, left background, peak count, right background, scaled net count on a 1°/minute basis, standard deviation and exposure hours of the crystal.

The diffraction data is reduced by a computer program called DATRDN which reduces the data by applying four corrections (45). These four corrections are for background, polarization, Lorentz effect, and crystal decomposition.

Correction for left and right background is calculated as follows:

$$I_{int} = (I_{meas} - Lbg - Rbg) \times \text{Scan speed} \qquad (2)$$

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

where:

I_{int} = Integrated Intensity

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

I_{meas} = Measured Intensity

Lbg = Left Background

Rbg = Right Background

The reflection is considered observed if:

$$I_{int} \geqslant 3\sigma(I_{int}) \qquad (4)$$

The polarization term arises because of the nature of the X-ray beam and the manner in which its reflection varies with the reflection angle. The unpolarized vector of the X-ray beam has a parallel component and a perpendicular component. Because of the greater efficiency of the diffraction of the parallel component (parallel to the surface of the reflecting plane) it will be represented to a greater extent in the reflected beam than will the perpendicular component, and so the diffracted beam is partially polarized. The correction for the polarization is:

$$p = (1 + \cos^2 2\theta)/2 \qquad (5)$$

(p is thus a simple function of 2θ and is independent of the method of collection).

The Lorentz effect is a geometrical factor which accounts for the fact that when the crystal is rotated at a constant speed, reflections with low 2θ spend more time in the beam than those reflections with high 2θ. The Lorentz factor (L) is given by:

$$L = (\sin 2\theta)^{-1} \qquad (6)$$

Thus, the Lorentz-polarization factor (Lp) is given by:

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

A final correction must be applied in those cases in which the crystal decomposes. This correction assumes that decomposition is linear with respect to time and is indicated by:

$$I_{orig} \,/\, I_{ave} \qquad (8)$$

where:

I_{orig} = original intensity of the std. reflection

I_{ave} = Average current intensity of the std reflection

These four corrections are combined to form the following expression:

$$I_{cor} = I_{int} \times (Lp)^{-1} \times (I_{orig}/I_{ave}) \qquad (9)$$

The structure factor $|F|$ is determined as the square root of the corrected integrated intensity, I_{cor}:

$$|F_{hkl}| = (I_{cor})^{1/2} \qquad (10)$$

This is the observed structure factor and is usually designated F_{obs}. The error in $|F_{hkl}|$, is σF and is calculated according to the following (50):

$$\sigma F = (1/2)(k/Lp)^{1/2}((N_t + N_{Rbg} + N_{Lbg} + (0.01N_{pk})^2)/(N_t - N_{Lbg} - N_{Rbg})^{1/2} \qquad (11)$$

where

N_t = no. of counts

N_{Lbg} = no. of left background counts

N_{Rbg} = no. of right background counts

$N_{pk} = N_t - N_{Rbg} - N_{Lbg}$

The algebraic repesentation for two waves is represented:

$$x_1 = a_1\cos(\phi + \alpha_1) \qquad (12)$$

$$x_2 = a_2\cos(\phi + \alpha_2) \tag{13}$$

where

x = the displacement of the wave on the "x" axis

a = amplitude of the wave

ϕ = an angular variable proportional to time and frequency

α = the phase

When these two waves are superposed the result is:

$$x_r = x_1 + x_2 = a_1\cos(\phi + \alpha_1) + a_1\cos(\phi + \alpha_2) \tag{14}$$

or

$$x_r = (a_1\cos\alpha_1 + a_2\cos\alpha_2)\cos\phi$$

$$- (a_1\sin\alpha_1 + a_2\sin\alpha_2)\sin\phi \tag{15}$$

$$= a_r\cos(\phi + \alpha_r) \tag{16}$$

The amplitudes are related to the phases such that

$$a_r\cos\alpha_r = a_1\cos\alpha_1 + a_2\cos\alpha_2 = \sum_j a_j\cos\alpha_j \tag{17}$$

$$a_r\sin\alpha_r = a_1\sin\alpha_1 + a_2\sin\alpha_2 = \sum_j a_j\sin\alpha_j \tag{18}$$

Equations (17) and (18) can be abbreviated as A and B respectively

Thus:

$$A = \sum_j a_j\cos\alpha_j \tag{19}$$

$$B = \sum_j a_j\sin\alpha_j \tag{20}$$

and

$$a_r = (A^2 + B^2)^{1/2}. \tag{21}$$

This can be represented in complex form as:

$$a_r\exp(i\,\alpha_r) = A + iB \tag{22}$$

The complex form is especially adaptable to computer programs and the only reason for using this notation is convenience.

The structure factor is a function of the amplitude and the phase and is expressed as:

$$F(hkl) = |F(hkl)| \exp(i\alpha(hkl)) = A(hkl) + iB(hkl) \qquad (23)$$

where:

$$A(hkl) = \sum_j f_j \cos\alpha_j \qquad (24)$$

and

$$B(hkl) = \sum_j f_j \sin\alpha_j . \qquad (25)$$

where f_j represent individual atomic scattering factors. The phases $_j$ are expressed by:

$$\alpha_j = 2pi(hx_j + ky_j + lz_j) \qquad (26)$$

Thus, to obtain a three dimensional electron density map one needs to know amplitudes of the structure factors and their phases

$$\rho(XYZ) = (|F(000)|/V_c) + (2/V_c) \sum \sum^{\infty} \sum F \cos(\phi - \alpha) \qquad (27)$$

where $\rho(xyz)$ is the electron density at some point xyz in the cell and V_c = unit cell volume. However, the structure factors F derived from the measurements made from the diffractometer, contain no information about the phase (α), because phases cannot be measured (44). The 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 scattering at the origin. To find the atomic positions in a model, information about the phases of at least some reflections is required so that a Fourier transform or summation of the ΣF leads to an interpretable electron density showing the atomic positional parameters.

The amplitude $|F_{hkl}|$ (unphased) may be used to find the co-ordinates of atoms by Direct methods or by Patterson techniques. The older method which may be used only for structures which contain heavy atoms is a Patterson synthesis, calculated by squaring the amplitudes of the structure factors $|F|^2$ which eliminates the phase. Interpretation of the Patterson map locates the positions of the ends of vectors between heavy atoms. Use of the knowledge of the space group general equivalent positions allows calculation of heavy atom positional parameters.

Direct Methods may be used for heavy or light atom structures. The principle underlying this approach is that relationships between intensities themselves (50) can give an indication of the phases of enough reflections to allow a Fourier transform of a limited set of phased structure factors to display the molecule. Normalizing these factors eliminates the effects of thermal vibration
and are found using using the following expression:

$$E^2_{hkl} = |(F_{hkl})^2| / \Sigma f_i^2 \qquad (28)$$

Normalizing the sructure factors eliminates the effects of decline in atomic scattering power with increasing 2θ.

At any point in a crystal the electron density can only be positive, never negative. The principle of symbolic addition or positivity of electron density allows the determination of the phases of many hkl planes by knowing the phases of a few. For example if the 100 reflection is large it may have a maximum at x = 0 and a minimum at x = 0.5, ie the sign of the structure factor is positive (the phase angle is zero). Conversely, if the maximum is at x = 0.5, then the sign is negative (the phase angle is zero). If the 200 reflection is strong, then it is related to the 100 reflection by the Harker-Kaspar inequality (46).

$$U_h^2 \leqslant 1/2(1 + U_{2h}) \qquad (29)$$

where U is the unitary structure factor found by dividing the structure factor F by the scattering factors for the atoms. This can be rearranged and becomes:

$$2U_h^2 \leqslant U_{2h} + 1. \qquad (30)$$

or

$$U_{2h} \geqslant 2U_h^2 - 1 \qquad (31)$$

To illustrate its use, consider the 100 peak and the 200 peak whose unitary structure factors $| U_h |$ and $| U_{2h} |$ are 0.6 and 0.5 respectively. Using the inequality, the right side becomes -0.28. Only if the sign of U_{2h} is positive is this inequality satisfied. If the 100 reflection has a peak (positive) or a valley (negative) at x = 0.5, it follows that the 200 will have a peak at x = 0.5 in order to be consistant with the observation of the 100 peak. If the 200 reflection had a negative phase, then the maximum would be at x = 0.25 and x = 0.75 which is <u>not</u> consistent with 100. Therefore if both the 200 and 100 reflections are intense, the phase of the 200 must be positive to agree with the phase of the 100 reflection.

Symbolic addition then can be used to expand the number of phases using the triplet relationship:

$$s(h_1,k_1,l_1) \cdot s(h_2,k_2,l_2) \simeq s(h_1 + h_2,\ k_1 + k_2,\ l_1 + l_2) \qquad (32)$$

where s is "sign of". Once a significant number of phases is known, a trial structure can be determined and the phased structure factors (F_{cal}) can be calculated and compared with those that have been measured (F_{obs}).

The correctness of the model is indicated by the "Residual Factor", (R_f), which is defined as:

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

After this initial R factor is determined a structure refinement and completion procedure is followed using least squares and difference Fourier methods. The least squares program fits the observed structure amplitudes to the calculated amplitudes. Then the parameters of the calculated structure factors are altered so that the least squares fit improves. The difference Fourier synthesis ($||F_o| - |F_c||$) allows location of missing atoms. When the structure is complete, only peaks of low intensity will remain on this map. As the model approaches completion, the difference between F_{obs} and F_{calc} is reflected in a lower value of R_f.

The motion of the atoms is expressed in the temperature factor or thermal parameter. This factor is responsible for an decrease in the atomic scattering factors as 2θ increases. It is written:

$$f\exp(-B_{iso}(\sin^2\theta/\lambda^2) \qquad (34)$$

where B_{iso} is the isotropic thermal parameter. The atomic scattering factor is then replaced by a new term which incorporates the anisotropic thermal parameter and is written:

$$f\exp(-b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}kl + b_{13}hl + b_{23}kl \qquad (35)$$

where b is the individual anisotropic thermal parameter.

Single crystal structure determinations at low temperature offers the possibility of damping all thermal vibration and thus improving the diffraction from a crystal. Experimentally, cooling is accomplished by passing nitrogen gas generated by boiling liquid nitrogen over the crystal. Low temperature structure determinations also provide the opportunity to observe any structural changes in the copper iodide complexes which emit differently at lower temperatures.

When the R factor ceases to decrease and all atoms have been located, the refinement is considered complete. Tables of positional parameters, anisotropic thermal parame ters, bond distances and angles, and a table showing the F_{obs} and F_{calc} structure factors are drawn up. A projection view of the molecule is prepared showing atoms as ellipsiods of 90% probability. From these data, bonding type, atom hybridization, and electron location may be inferred.

CHAPTER III

LUMINESCENCE

Luminescence is defined as emission of photons in excess of energy losses due to thermal agitation in a substance which follows the absorption of photons by that same substance (47). Typically, for materials which are considered to be luminescent, emission of visible light results from excitation by ultra-violet radiation. Photoluminescence is a more precise term for this phenomenon which distinguishes it from cathodoluminescence, the result of electron bombardment, triboluminescence, due to mechanical forces, and chemiluminescence, which is luminescence resulting from a chemical reaction (47). Emission which persists after the excitation is turned off is called phosphorescence, while emission which does not persist is called fluorescence. Phosphorescence is a delayed release of photons which has a lifetime of 10^{-6} to 100 seconds, while fluorescence is immediate or delayed, with a lifetime of 10^{-8} seconds or less (48).

These three classes of emission are also defined in terms of the electronic transitions which give rise to this phenomenon. Excitation of an electron to a singlet excited state followed by nonradiative decay to an intermediate triplet state and emission from that triplet state is phosphorescence, while fluorescence is emission from the first singlet excited state. Delayed fluorescence is similar to phosphorescence involving an intermediate state but that intermediate state is a singlet state and emission to the ground state follows (48).

In the singlet state (ground or excited), electrons are spin coupled, the spin orientation of one electron being opposite to that of the other. The triplet excited state arises when the spin of one electron is re-oriented such that the orientations become parallel. There are two possibilities for parallel spin, plus two possibilities for spin coupled oriention (which are equal in energies). Thus in the triplet state, there are three energy levels.

The aim in all luminescence research is to find the source of the emission and to understand the mechanism which gives rise to it. Emission by a substance depends on how well the absorbed energy can be protected from nonradiative losses such as thermal motion. This means that unless the absorption and emission occur at the same place, there must be a way for energy to be transported from the place of absorption to the place of emission. Such places, where electronic transitions occur without disturbances from the surroundings are called emitting centers (48). Disturbances by the surroundings which increase the probability for thermal (non-radiative) vibrations often cause a decrease of the emission intensity. Substances which are capable of decreasing the emission intensity are called quenchers. True quenchers actually alter the electronic density of the emitter. Quenching will occur most easily in very fluid substances because emitting centers will encounter quenchers more often. Not all reductions in luminescence intensity are due to true quenching however and any encounter between an emitting center and some other molecule can lead to such a reduction. Phosphorescence is especially sensitive to these collisional effects and it follows that in a rigid system such as in a frozen solution at 77K or a glass, phosphorescence will be greatly enhanced. Typical of this phosphorescence is that of frozen quinoline in ethanol at 77K showing a fine structure in its emission spectrum. The transition responsilble for this is from a triplet pi^* excited state (48).

A model for a characteristic emitting system starts with a ground state electronic potential energy curve for the system in which the emitting center is bound in an unspecified manner. The lower potential energy curve in Figure 2. represents the electronic bond energy of an emitting center within a lattice, as a function of the bond distance. Within this curve are the characteristic quantitized vibrational states. When the center is excited with a quantum of energy, a new potential energy curve (higher in energy) can be drawn with its own set of quantized vibrational states. In the excited state, the center will be in some excited vibrational state of this excited electronic state and will relax to the lowest vibrational state within the excited electronic state. At this point, the system returns to the ground state giving off a quantum of energy in the form of visible light. Some of the excitation energy is given off as vibrational or thermal energy and the remainder as electromagnetic radiation which is of lower energy than the excitation energy (49).

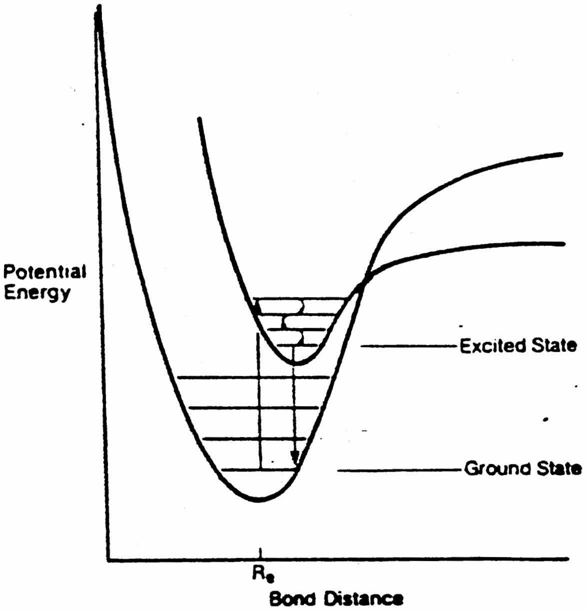


Figure 2. Potential Energy Diagram Illustrating Excitation/Emission (49)

Only a few pure substances emit in their solid state and they include manganous halides, uranyl salts, platinocyanides, some rare earth salts and some copper(I) complexes. For manganous salts in their ground state, the d electrons occupy all five d orbitals and all five electrons have the same spin. In the excited state, the $d_{x^2-y^2}$ or d_{z^2}

is promoted to a d_{xy}, d_{yz} or d_{xz} orbital and its spin is reversed. Emission thus arises from a reversed spin excited state. Emission arises from incomplete f orbitals in the case of the actinide and lanthanide materials. For copper(I) complexes the emission arises from d orbitals which are incomplete in their excited states (47). A typical mechanism for Cu(I) emission is illustrated below.

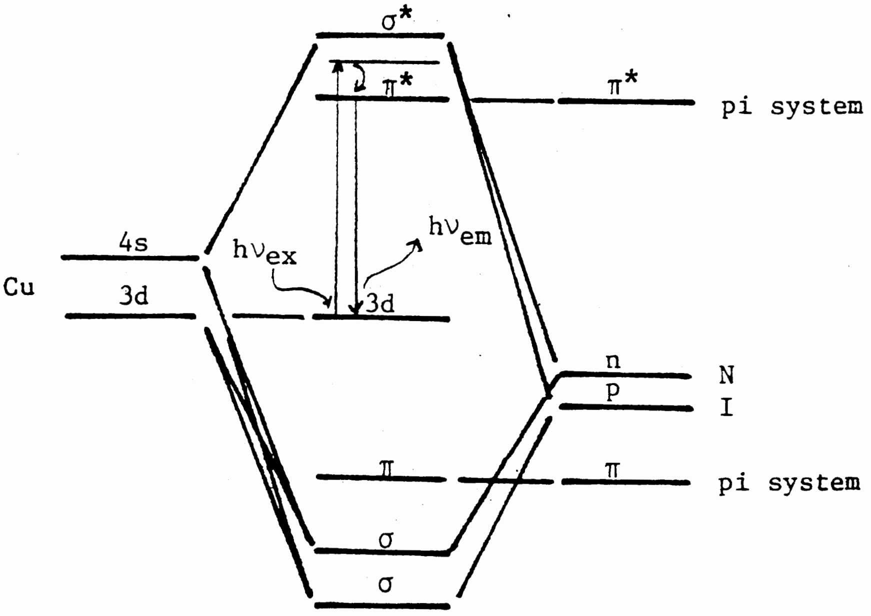


Figure 3. Simplified Energy Level Diagram Illustrating MLCT in Cu_4^{4+} system.

In a typical luminescent $CuIL_x$ system, UV radiation (200 - 400 nm) is absorbed and an electron from the d orbital (HOMO) is excited and promoted to the pi^* orbital at an unspecified excited vibrational state. The electron then undergoes radiationless relaxation to the lowest unoccupied molecular orbital (LUMO) and emits visible radiation (luminescence) in relaxing to the ground state.

Copper(I) complexes have a potential for practical applications, namely as sensitizers for semiconductors used in solar energy conversion (28). The way a sensitizer works in semi-conductors can be illustrated by examining their use with phosphors.

The emitting center for a solid-state luminescent substance or phosphor is usually an impurity which has been deliberately incorporated into the lattice of the phosphor. A second substance added to the host lattice which has an excited state which is similar in energy to that of the activator may serve as a sensitizer. The energy from the sensitizer is transferred non-radiatively to the activator, which in turn is excited. The activator emits as it returns to its ground state. The advantage to using a sensitizer is that the energy of excitation does not need to be specific, so that a phosphor containing a sensitizer can be excited with a broad range of excitation energy and still luminesce satisfactorily. In some cases, as in commercial fluorescent lamps, a sensitizer serves as an activator as well. For example, a host lattice, calcium halophosphate, may be doped with both Mn^{2+} and Sb^{3+}. Antimony emits blue over a broad range and can transfer its energy, non-radiatively, to manganese which then emits yellow. An emission spectrum shows a maximum at 600 nm with a minor peak at 475 nm (49).

The problem of impurities in luminescent materials is important in their syntheses. Most phosphors consist of a parent or host material (not necessarily luminescent by itself) doped with a measured amount of impurity, to make it luminescent. DeLuca stated "A cavalier attitude toward attention to the details of careful sample preparation can greatly minimize the chances of discovering a superior phosphor (49)." The presence of impurities has a marked effect on luminescence and is relevant to this work. The examination of inorganic complexes containing organic ligands using emission spectrophotometry is a relatively recent development. It has not been common in the past to examine first row transition element complexes this way because only a few are luminescent.

The bulk of the emitting transition metal complexes emit in the red or infrared region making their study difficult because the sensitivities of most detectors are low in these regions. Although better results can be obtained at liquid nitrogen temperature, most laboratories are not equipped to measure luminescence at this temperature. In the studies of these complexes, the possibility of both fluorescence and phosphorescence exists with the latter arising most often at low temperature (77K). In non-rigid or fluid lattices, most phosphorescence is quenched as discussed above, but as the lattice becomes more rigid (frozen solutions or glasses) the intensity of the phosphorescence increases.

CHAPTER IV

EXPERIMENTAL

Syntheses

$\underline{(\mathrm{CuI(n\text{-}butylnicotinate)})_x}$. Nicotinic acid (1 g) was dissolved in 10 mL n-butanol followed by addition of 1 mL conc. sulfuric acid, in a procedure similar to that of Mills and Hamer (47) and the resulting solution was heated under reflux for twenty-four hours. A Dean - Stark apparatus was used to trap water which was azeotropically distilled from the refluxing mixture. The solution was then poured into distilled water and neutralized with solid Na_2CO_3 until effervescence ceased. The n-butyl ester was extracted with three 10 mL portions of diethyl ether, isolated by evaporation of the diethyl ether from the combined extracts and used without further purification. Copper iodide (0.15 g) and n-butyl nicotinate (0.5 mL) were dissolved in acetonitrile/ benzene (30 mL) giving a yellow solution. The solution was filtered. Clear crystals suitable for single X-ray analysis were obtained upon slow evaporation of the solvent (mp 135-6°C decomp). The short needlelike crystals emitted pale blue upon excitation at 366 nm both at room temperature and at 77K.

$\underline{\mathrm{Cu_4I_4(isopropylnicotinate)_4}}$. The isopropyl ester of nicotinic acid was prepared by an acid catalysed esterification procedure as above and used as isolated without further purification. The ester (0.5 mL) and CuI (0.6 g, slight excess) were dissolved in acetonitrile and filtered. Yellow brown octahedral crystals were obtained upon slow evaporation of the solvent (mp. 135-137^{o}C decomp). The crystalline material emitted dull green-brown at room temperature upon excitation at 366 nm changing to intense pale green at 77K. A few of these crystals were dissolved in benzene forming a cloudy solution which was filtered and set aside for a few days growing large clear octahedral crystals which emitted yellow-blue at room temperature and sky blue at 77K. The carbon-13 NMR spectrum indicated the presence of isopropanol in the crystalline substance (^{13}C NMR DMSO-d^{6} 21.47, 68.903 ppm) A second motif (polymeric pleated sheet) was formed when Cu_4I_4(isopropylnicotinate)$_4$ was recrystallized in acetonitrile containing water. It decomposed at 130-133^{o}C. Crystals suitable for X-ray analysis (blue needles) were formed by slow evaporation of the solvent. The excess ligand was washed from the external surface of the crystals with a small amount of cold acetonitrile. These crystals emitted intense pale green-blue at both room temperature and 77K. They emitted light brown (similar to the first motif) after they had been heated to 130^{o}C, at 77K, this residue emitted intense pale green-blue under UV excitation at 366 nm.

(CuI(n-propylnicotinate)$_n$. Nicotinic acid (1 g) was dissolved in 10 mL of methanol to which was added 3 mL of conc. sulfuric acid. The resulting mixture was heated under reflux with stirring for six hours. The solution was poured into water and neutralized with solid Na_2CO_3 until effervescence ceased. The n-propyl ester was extracted into 30 mL of diethylether, isolated upon distillation of the organic solvent and used without further purification. The crude n-propyl nicotinate (0.4 mL) was dissolved in acetonitrile and a slight excess of copper(I) iodide was added (0.1 g). The solution was filtered and set aside for a few days. Crystals (pale green needles) suitable for X-ray analysis were formed upon slow evaporation of the solvent (decomp. 148-50^{o}C). The solid crystalline material emitted pale green-blue under UV radiation of 366 nm both at room temperature and at 77K with no visible change in intensity.

(CuI(methylnicotinate)$_x$. Nicotinic acid (1 g) was dissolved in 10 mL of methanol to which was added 3 mL of conc. sulfuric acid. The resulting mixture was heated under reflux with stirring for three hours. The solution was poured into water and neutralized with solid Na_2CO_3 until effervescence ceased. The methyl ester was extracted into 30 mL of diethyl ether, isolated upon distillation of the organic solvent and used without further purification. The crude methyl nicotinate (0.4 g) was dissolved in acetonitrile and a slight excess of copper(I) iodide was added

(0.1 g) The yellow precipitate which formed was dissolved in acetonitrile and crystals suitable for X-ray analysis were formed upon slow evaporation of the solvent (yellow needles decomp. 250°C). The solid crystalline material emitted pale green-blue under UV radiation of 366 nm at room temperature; at 77K the emission was more intense but the observed color was not significantly different.

$\underline{\text{(CuI(benzylnicotinate)}_x}$. The benzyl ester of nicotinic acid was prepared by heating stoichiometric quantities of the acid and benzyl alcohol followed by distillation of the water. This was a modification of the method used by Thompson and Leuck (48). Two grams (16.8 mmol) of nicotinic acid and of benzyl alcohol (2 mL) were heated together in a 10 mL round-bottom flask fitted with a condenser. As the mixture refluxed, a quantity of water was observed to condense into the receiving flask. The temperature remained at 100° C. for several minutes and then dropped to 80°C. At this point the characteristic odor of pyridine was detected and heating was discontinued. The residue (yellow oil) was set aside in the fume hood overnight allowing the pyridine to evaporate. A small quantity of this oil (0.5 mL) was dissolved in acetonitrile (30 mL) and copper iodide (0.2 g) was added with stirring. When most of the copper iodide was dissolved, the yellow solution was filtered. Long yellow needles (mp 160-3°C decomp) formed after slow evaporation of the solvent. The crystals emitted yellow at room temperature and blue at 77K under UV excitation at 366 nm.

$\underline{(\mathrm{CuI(phenylnicotinate)})_4}$ Two grams of nicotinic acid (16.8 mmol) was dissolved in twenty grams of phenol (21.3 mmol). Concentrated sulfuric acid (3 mL) was added to the solution. The reaction was carried out in a 50 mL round-bottom flask fitted with a condenser and a Dean and Starkes trap. The solution heated under reflux. After a few minutes, toluene (8 mL) was added to the reaction and heating was continued for twelve hours. After this time, the crimson liquid was poured into cold distilled water (100 mL) and neutralized to pH of 7 with solid sodium carbonate. This mixture was extracted with two 10 mL portions of ether and the organic portion set aside in the fume hood to allow the ether to evaporate. To remove excess phenol, sodium hydroxide solution (10 mL of 3 M approx.) was added to the extract. This mixture was extracted twice with two 10 mL portions of ether. The combined extracts, after evaporation of the ether, were used without further purification, the main impurity being unreacted phenol. The crude phenyl nicotinate (0.5 mL) was dissolved in acetonitrile (30 mL) and copper iodide (0.1 g) was stirred into the solution until most of the copper iodide was dissolved. The mixture was filtered and set aside. Large clear prisms (mp 209-11^{o}C) formed over night after slow evaporation of the solvent. The crystals emitted blue non-thermochromically under UV excitation at 366 nm.

$(CuI(ethylnicotinate)_x$ The ester was prepared in the same way as the methyl ester and a complex was prepared on combination of the ester and copper iodide in acetonitrile. After slow evaporation of the solvent, long fibers, not suited for X-ray analysis, formed. The fibers emitted blue under UV excitation at 366 nm non-thermochromically.

$(CuI(3\text{-cyanopyridine}))_x$ The complex was formed by dissolving 3-cyanopyridine in acetonitrile and adding excess copper iodide. Copper iodide (0.2 g, 1.05 mmol) and 3-cyanopyridine (0.1 g, 0.96 mmol) were mixed together in acetonitrile (30 mL) and heated for approximately 15 minutes. Long yellow luminescent needles (decomp. 224-6°C) formed after slow evaporation of the solvent. Under UV excitation at 366 nm. the crystals emitted yellow at room temperature and orange at 77K. When this substance was recrystalized from acetone/KI(sat.) the crystals emitted orange at both room temperature and 77K. When recrystallized from acetonitrile/benzene (50:50) the resulting crystals emitted yellow in non-thermochromic fashion.

$CuI(3\text{-cyanopyridine})_2$ 3-Cyanopyridine (0.4 g, 3.84 mmol) was dissolved in acetonitrile (30 mL). Copper iodide (0.1 g, 0.525 mmol) was added and the solution stirred for five minutes. The pale green solution was filtered. Pale green rhombic crystals (mp 219-22° decomp.) formed overnight after slow evaporation of part of the solvent. The mother liquor was decanted from the crystals. These pale green crystals were highly luminescent even in visible light. They emitted pale green under UV excitation of 366 nm non-thermochromically. A solution of this complex, after heating or extended stirring, turned yellow, and upon evaporation of the solvent, yellow needles which emitted yellow under UV excitaion at 366 nm formed. At 140°C, the pale green crystals began to lose their crystallinity and their color changed to yellow. This yellow substance melted at a temperature similar to that of the polymeric complex above.

$\underline{(\text{CuI}(\text{3-pyridylacetonitrile}))_x}$ A few drops of 3-pyridyl-acetonitrile were dissolved in acetonitrile (20 mL). Copper iodide (0.1 g, 0.525 mmol) was stirred into the solution until most of the copper iodide had dissolved. The solution was then filtered. Short yellow needles formed after slow evaporation of the solvent (mp. 194-6°C decomp) The emission from the solid was yellow at both room temperature and 77K. When this substance was recrystallized from benzene, short clear needles formed which emitted yellow at room temperature and blue at 77K under UV excitation at 366 nm. This thermochromism was most pronounced when the crystals were fresh. After several months the change in luminescence was not as sharp and the apparant color of the emission was brown at both temperatures with yellow predominating at room temperature, and blue predominating at the lower temperature.

(CuI(iso-nicotinic acid))$_x$ Copper iodide (0.1 g, 0.525 mmol) was dissolved in acetonitrile (30 mL). Excess iso-nicotinic acid (0.2 g) was added and the mixture stirred for 1 hour and then filtered. The first crystals which formed appeared to be those of the acetonitrile complex of copper iodide because they began to disintigrate upon exposure to air and turned to powder after a few hours. Just prior to the solvent being completely evaporated, a brown crystalline material began to form inside crevasses of the decomposing crystals. Excitation under at 366 nm. gave no emission. The amount of complex isolated was insufficient for a melting point determination but was enough for an X-ray structure determination.

(CuI(isonicotinamide))$_x$ Copper iodide (0.1 g, 0.525 mmol) and isonicotinamide (0.1 g, 0.820 mmol) were stirred together in acetonitrile (30 mL) for one hour and then filtered. Pale yellow plates (mp 150-55°C decomp) formed after slow evaporation of the solvent. These crystals emitted blue non-thermochromically under UV excitation at 366 nm. After standing for several months, crystals emitted green at 77K.

Cu_4I_4(4-cyanopyridine)$_5$ Copper iodide (0.2 g, 1.050

mmol) and 4-cyanopyridine (0.1 g, 0.961 mmol) were stirred together until both reagents dissolved and the resulting orange solution filtered. Large, flat orange crystals (decomp. 240°C) formed overnight after slow evaportion of the solvent. These crystals emitted orange non-thermochromically under UV excitation at 366 nm.

$\underline{(\text{CuI(methylisonicotinate)})_x}$ Isonicotinic acid (1.0 g), methanol (10 mL), and conc. sulfuric acid (3 mL) were refluxed together for 6 hrs. The mixture was cooled, added to 100 mL of cool distilled water, neutralized with solid Na_2CO_3 until effervescence ceased, and extracted with three 10 mL portions of ether. The ether was removed from the combined extracts by evaporation. Copper Iodide (0.1 g) and some of the crude methyl iso-nicotinate (0.5 mL) were mixed in acetonitrile (40 mL). The orange solution was filtered and set aside. Long pale orange crystals (mp 187-90°C decomp) were isolated after slow evaporation of the solvent. They emitted orange non-thermochromically under UV exitation at 366 nm.

$\underline{(\text{CuI(nicotinamide)}_2)_2}$ Copper iodide (0.2 g, 1.050 mmol) and nicotinamide (0.128 g, 1.050 mmol) were stirred together in acetonitrile (30 mL) with heating. Colorless crystals suitable for X-ray diffraction formed after slow evaporation of the solvent (mp 150-55°C). The observed emission was blue on the ends of some of the crystals but pale yellow in the middle. Other crystals emitted pale yellow throughout. However, when these crystals were powdered, the overall emission was blue under excitation at 366 nm. The emission was non-thermochromic.

(CuI(methyl 2-pyridylacetate)$_2$ 2-pyridylacetic acid hydrochloride (0.5 g), methanol (5 mL), and conc. sulfuric acid (1.5 mL) were refluxed together for 1 hour. The mixture was cooled and added to 100 mL of cool distilled water and neutralized with solid Na_2CO_3 until effervescence ceased. It was extracted with three 10 mL portions of ether. Ether was removed from the combined extracts by evaporation to give the crude ester which was used without further purification. Copper iodide (0.095 g) was suspended in 2.5 mL of acetone. Saturated aqueous potassium iodide was added dropwise until the CuI dissolved. An excess of the ester (0.1 g) dissolved in 3 mL of acetone was added to the solution and the mixture was refluxed for 24 hours. Heating was stopped and the apparatus left for 48 hours. Large clear crystals (mp. 84-7°C) formed in the bottom of the flask. These crystals emitted non-thermochromically.

(CuI(benzylnicotinamide))$_4$ Nicotinic acid (1.0 g, 0.813 mmol) and benzylamine (0.087 g, 0.813 mmol) were heated together in a well vented hood (185°C approx); the resultant liquid was boiled to remove water formed during the amidization. Heating was continued for approximately 20 minutes. The mixture was allowed to cool. After cooling, acetonitrile was added to the solid in the bottom of the beaker and stirred for ten minutes to dissolve some of this material. The liquid was decanted, filtered, and used without further purification. Copper iodide (0.1 g) was added to 3 mL of the amide solution and the mixture stirred until most of the copper iodide was dissolved and then filtered. Small short yellow crystals formed after very slow evaporation of the solvent. One crystal suitable for X-ray analysis was found among the small crystals, but there was not enough material to allow the taking of a melting point. The crystals emitted yellow at room temperature and orange at 77K. There was no gradual changing of colors with this complex (as was the case with some of the ester complexes) There was instead, a sharp transition from yellow to orange on cooling.

CHAPTER V

RESULTS AND DISCUSSION

The goal of this research has been to find correlations between structural details and emission properties of copper iodide ligand complexes. A secondary goal has been to correlate structural changes with temperature changes for those complexes which have been observed to exhibit thermochromic emission. Efforts have been focused on the polymeric pleated sheet, $(CuIL)_x$ and cube, $Cu_4I_4L_4$ complexes in which L is an aromatic heterocycle having donor electron pairs located on nitrogen. Eleven new polymeric complexes $(CuIL)_x$ have been prepared and structurally characterized by X-ray diffraction techniques. None of these compounds was submitted for elemental analysis. Of the eleven, three emit thermochromically and eight emit in non-thermochromically. Four of these have been characterized at both room and low temperatures. $(CuI(3\text{-pyridylacetonitrile}))_x$ was observed to vary in emission properties with solvent of crystallization. Thus, samples of this material crystallized from benzene/ CH_3CN or from acetonitrile alone were studied both at room and low temperature. Three new cubic complexes $(CuIL)_4$ have been prepared and characterized, two of which whose structures have been determined at both room and low temperature.

In addition, three other new solid state Cu(I) materials of other structural motifs have been synthesized and characterized. The solid state emission spectra of all of these materials have been determined.

A polymeric pleated sheet of $(CuIL)_x$ may be viewed as a series of edge sharing rhombohedra of Cu_2I_2, fan folded to allow tetrahedral coordination of copper. The rhombohedra are distorted with angles approaching 60° at iodide and 116° at copper to bring copper atoms into proximity with each other. A structural description of a polymeric pleated sheet includes Cu - I distances across the rhomb, and along the polymeric direction; I - Cu - I angles within rhombohedra and along the polymeric chain; Cu - I - Cu angles within the rhombohedra and along the chain; and Cu...Cu distances across the rhomb (Figure 4a).

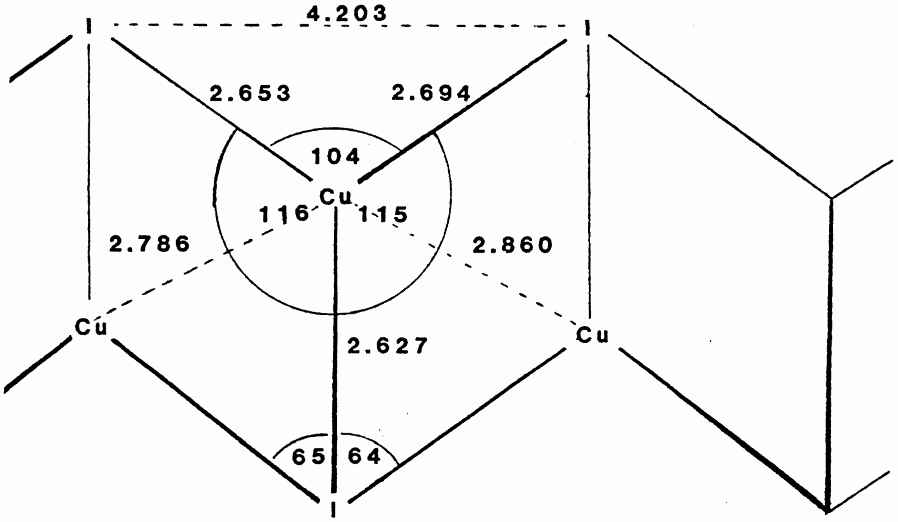


Figure 4a. Standard Polymeric Pleated Sheet

Complex	Cu - I across rhomb	Cu - I along chain	Cu...Cu across rhomb	Cu...Cu along chain	I - Cu - I along fold	I - Cu - I within rhomb	Cu - I - Cu along fold	Cu - I - Cu within rhomb
Ave.	2.627(31) Å	2.653(35) Å 2.694(25)	2.786(64) Å 2.860(36)	4.203(77) Å	104(3)°	115(1)° 116(1)	104(3)°	64(1)° 65(1)
1.	2.65(2)	2.619(2) 2.673(2)	2.736(2) 2.856(2)	4.161	103.67(5)	115.10(5) 117.45(6)	103.67(5)	62.55(5) 64.90(4)
2.	2.644(2)	2.616(2) 2.666(2)	2.705(2) 2.802(2)	4.131	102.89(6)	116.30(7) 118.11(7)	102.89(6)	61.89(5) 63.70(5)
3.	2.634(3)	2.651(3) 2.671(3)	2.829(2)	4.308	108.07(8)	115.1(1) 115.7(1)	108.07(8)	64.46(9) 64.73(9)
4.	2.648(2)	2.662(2) 2.684(2)	2.869(2)	4.330	108.17(3)	114.37(5) 115.10(6)	108.17(4)	65.11(4) 65.41(4)
5.	2.626(3)	2.641(3) 2.708(3)	2.795(4) 2.902(5)	4.254	105.36(9)	113.1(1) 116.8(1)	105.36(9)	63.17(9) 66.7(9)
6.	2.631(7)	2.626(7) 2.706(7)	2.744(5) 2.860(6)	4.233	105.1(2)	114.1(2) 118.1(2)	105.2(2)	61.8(2) 66.4(2)
7.	2.627(3)	2.632(3) 2.700(3)	2.786(4) 2.897(5)	4.231	105.04(9)	113.1(1) 116.9(1)	105.04(9)	63.05(9) 66.89(9)
8.	2.632(2)	2.638(1) 2.721(2)	2.814(2) 2.892(2)	4.259	105.27(4)	113.44(6) 116.50(5)	105.27(4)	63.40(5) 66.57(4)
9.	2.624(2)	2.628(1) 2.708(1)	2.757(2) 2.867(2)	4.235	105.05(4)	113.84(4) 117.85(5)	105.05(5)	63.25(4) 66.16(8)
10.	2.649(2)	2.654(2) 2.692(2)	2.804(3) 2.880(2)	4.171	102.57(8)	114.75(7) 116.17(8)	102.57(8)	63.83(6) 65.24(6)
11.	2.645(2)	2.652(2) 2.676(2)	2.783(2) 2.814(2)	4.136	101.83(7)	116.15(6) 116.61(7)	101.84(6)	63.39(5) 63.85(5)
12.	2.618(2)	2.688(2) 2.695(2)	2.842(3) 2.855(3)	4.316	106.62(8)	115.01(8) 115.25(6)	106.6(6)	64.99(6) 65.75(6)
13.	2.629(2)	2.693(2)	2.828(2) 2.928(2)	4.215	103.01(4)	115.80(5) 115.82(7)	103.00(5)	64.18(5) 64.20(5)
14.	2.616(4)	2.682(3) 2.686(3)	2.823(4) 2.830(4)	4.259	105.01	115.43(9) 115.69(8)	105.0(1)	64.30(8) 64.56(8)
15.	2.650(4)	2.649(5) 2.686(4)	2.762(6) 2.888(5)	4.04(5)	98.6(1)	114.5(1) 117.2(1)	98.6(1)	62.8(1) 65.5(1)
16.	2.645(2)	2.600(2) 2.711(2)	2.891(3)	4.116	101.62(7)	112.03(7) 115.73(8)	101.62(7)	65.30(6) 66.88(6)
17.	2.658(4)	2.628(5) 2.634(5)	2.876(6)	4.121	103.1(1)	114.0(2) 114.1(1)	103.1(1)	65.8(1) 65.9(1)
18.	2.544(4)	2.725(5) 2.743(4)	2.748(6) 2.811(7)	4.164	99.3(2)	115.9(1) 117(2)	99,3(2)	62.8(1) 64.1(1)
19.	2.544(5)	2.729(4) 2.743(4)	2.758(6) 2.811(7)	4.167	99.2(1)	115.0(2) 117.1(1)	99.2(1)	62.9(1) 64.1(1)

1. $(\mathrm{CuI(3\text{-}cyanopyridine)})_x$ RT
2. $(\mathrm{CuI(3\text{-}cyanopyridine)})_x$ LT
3. $(\mathrm{CuI(benzylnicotinate)})_x$ LT
4. $(\mathrm{CuI(benzylnicotinate)})_x$ RT
5. $(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ RT - benzene
6. $(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ LT - benzene
7. $(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ RT, UV - benzene
8. $(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ RT - acetonitrile
9. $(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ LT - acetonitrile
10. $(\mathrm{CuI(methylnicotinate)})_x$ RT
11. $(\mathrm{CuI(methylnicotinate)})_x$ LT
12. $(\mathrm{CuI(isopropylnicotinate)})_x$
13. $(\mathrm{CuI(n\text{-}butylnicotinate)})_x$
14. $(\mathrm{CuI(n\text{-}propylnicotinate)})_x$
15. $(\mathrm{CuI(nicotinamide)_2})_x$
16. $(\mathrm{CuI(isonicotinamide)})_x$
17. $(\mathrm{CuI(isonicotinic\ acid)})_x$
18. $(\mathrm{CuI(methylisonicotinate)})_x$
19. $(\mathrm{CuI(methylisonicotinate)})_x$

Bond Distances and Angles Between Copper and Iodide in Polymeric CuIL Complexes
RT is room temperature, LT is low temperature, UV is ultra-violet.
"benzene" and "acetonitrile" stand for "crystallized from ..."

Figure 4b. Standard Polymeric Pleated Sheet.

Figure 4c. Standard Polymeric Pleated Sheet

Complex	Cu - I across rhomb	Cu - I along chain	Cu...Cu across rhomb	Cu...Cu along chain	I - Cu - I along fold	I - Cu - I within rhomb	Cu - I - Cu along fold	Cu - I - Cu within rhomb
RT Ave.	2.624(36) Å	2.660(39) Å 2.698(28)	2.813(49) Å 2.871(34)	4.201(80) Å	103(3)°	114(1)° 116(1)	103(3)°	64(1)° 65(1)
$3s/N^{1/2}$	0.03	0.032 0.023	0.041 0.028	0.066	2.50	0.83 0.83	2.50	0.83 0.83
$(\mu - \bar{x})_1$	0.027	0.041 0.025	0.077 0.015	0.04	0.67	1.1 1.45	0.67	1.50 0.10
$(\mu - \bar{x})_4$	0.038	0.002 0.014	0.056 0.002	0.129	5.17	0.37 0.90	5.17	1.11 0.41
$(\mu - \bar{x})_5$	0.002	0.019 0.010	0.018 0.031	0.053	2.36	0.90 0.80	2.36	0.83 1.70
$(\mu - \bar{x})_{10}$	0.025	0.006 0.006	0.009 0.009	0.03	0.43	0.75 0.17	0.43	0.17 0.24
$(\mu - \bar{x})_{13}$	0.005	0.03 0.005	0.015 0.057	0.014	0.01	1.80 0.18	0	0.18 0.20
$(\mu - \bar{x})_{15}$	0.026	0.011 0.012	0.051 0.017	0.156	4.40	0.50 1.20	4.40	1.20 0.50
$(\mu - \bar{x})_{17}$	0.034	0.032 0.064	0.010 0.005	0.08	0.10	0 1.90	0.10	1.80 0.90
$(\mu - \bar{x})_{18}$	0.10	0.065 0.045	0.065 0.06	0.03	3.70	1.90 1.0	3.70	1.20 1.0

$|(\mu - \bar{x})| = 3s/N^{1/2}$ where μ is an actual value, $\bar{x}$ is an average of μ's, s is the sample std. deviation, and N is the degrees of freedom. If the left side of the this equation is larger than the right side, the real value in question differs significantly from the mean and warrants further investigation.

The Standard Polymeric Pleated Sheet was constructed from the dimensions of eighteen structure determinations giving rise to nineteen sets of distances and angles (Figure 4b). With this standard motif, it is possible to apply statistics to determine if any of the values observed for any particular material is unusual.

In a statistical analysis the null hypothesis says that every sample drawn from a population is the same. When various measurements of these samples are taken, they are averaged, and the standard deviations are assumed to arise from experimental error. To test this, each sample is compared using a set criteria to check whether it deviates significantly from the average. If it does, then it violates the null hypothesis, and the difference from the mean is significant.

For example, in the complexes which are thermochromic, do the angles at the copper atoms deviate significantly from the average ones? To determine this, use the expression:

$$(\mu - \bar{x}) = \pm 3s/\sqrt{N}. \qquad (36)$$

where μ is a single true value, $\bar{x}$ is the average of a sample of measured values, s is the sample standard deviation, and N is the degrees of freedom or the number of samples minus one. If the left side of this equation is larger than the right side, then the measured value is significantly different from the average of the sample values. Figure 4c is a standard polymeric pleated sheet like that in Figure 4a but is constructed from the room temperature measurements only. It statistically compares measured angles and distances of selected complexes with the average of all the room temperature measurements. For example, the average for the Cu - I distance across the rhomb for a sample of fourteen complexes is 2.624 Å with a sample standard deviation of 0.036. The right side of equation (36) equals 0.03 and the absolute value for the difference between the mean of the distances and the true measured distance in entry 1 (L = 3-cyanopyridine) is 0.027. Since this is smaller than $3s/N^{1/2}$, the measured value is not significantly different than the mean distances of the sample. In entry 18 of Figure 4b, this difference is larger than $3s/N^{1/2}$, meaning that this particular complex (L = methylisonicotinate) violates the null hypothesis

An examination of Figure 4c shows that the null hypothesis is violated for certain complexes with respect to the angle and distances along the chain or the fold of the pleated sheet. For example, $(\mu - \bar{x})_{18}$ is entry 18 of Figure 4a $((\mu - \bar{x})_4)$ in Figure 4c refers to entry 4 in Figure 4b, etc.) It shows that the bond angles about copper or iodide along the fold are significantly different from normal for entry 18, although the distances between the copper atoms are not unusual. Entries 1,4, and 5 in Figure 4b are room temperature structure determinations of $(CuI(3\text{-cyanopyridine}))_x$, $(CuI(\text{benzylnicotinate}))_x$, and $(CuI(3\text{-pyridylacetonitrile}))_x$ crystallized from benzene, all of which are thermochromic. (These are the first three entries in Figure 4c). While all three show significant deviations from the mean with respect to the I - Cu - I and Cu - I - Cu angles within the rhomb, the complexes with nicotinamide, isonicotinic acid, and methyl isonicotinate do so also (entries 15, 17, and 18 respectively in Figure 4b). The angles at these atoms are neither consistently the largest, nor the smallest within their categories nor do they show a pattern of alternation from rhomb to rhomb. Similarly, the Cu...Cu distances across adjacent rhombs, Cu - I distances along rhombs, and Cu...Cu distances across folds are not consistently larger or smaller than those of non-thermochromic materials. It is not possible to look at room temperature structural data and differentiate between a material that will be thermochromic and one that will emit independent of temperature.

Entries 5 and 8 in Figure 4b show structural data for $(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ crystallized from benzene (entry 5) which is a thermochromic material and from acetonitrile (entry 8) which is a non-thermochromic material. While there are differences in Cu - I distances for the two structure determinations, they are not in excess of experimental error, for example Cu - I 2.708(3) Å for entry 5 and 2.721(2) Å for entry 8. Interpretation of such differences would have to take into account the fact that the two measurements were made on different crystals. Repeated measurements of data sets on a single crystal will show some deviations due to diffractometer error. Certainly data sets measured on different crystals will show deviations in results due both to diffractometer error and to differences in crystal quality. Thus the differences between entries 5 and 8 appear insignificant.

The difference in the behavior of the crystal with solvent of crystallization may be due to molecules of the solvent included in the unit cell. The planes of 3-pyridylacetonitrile rings are separated by 4.254 Å (entry 5). While it seems unlikely for a benzene molecule to be included between planes of bound pyridyl ligands in regular fashion (a minimum separation between planes of aromatic rings in solid materials is approximately 3.2 Å) there appears to be the possibility of insertion of an occasional benzene molecule in the volume between polymeric pleated sheets. If the benzene molecule were present in less than 15% of the unit cells, its presence would be undetected crystallographically since the presence would amount to less than one electron per atom on the average. X-ray crystallography has difficulty detecting the presence of hydrogen atoms, thus a lesser electron density could easily go undetected. Alternately, benzene may be present in a high number of unit cells, however its position may change from cell to cell creating the same sort of undetectable disorder.

The same single crystal of $(CuI(3\text{-pyridylacetonitrile}))_x$, crystallized from benzene, which was measured at room temperature (entry 5) was remeasured while the crystal was bathed in UV radiation. Thus a UV lamp emitting at 366 nm was positioned inside the diffractometer hood to determine if the structural data collected on the emitting crystal (excited state) would differ from that of the crystal in the ground state. Entry 7 in Figure 4a gives the results for this experiment. A comparison of entries 5 and 7 shows no differences in structural details in excess of standard deviations associated with these values. Thus, in accordance with the Franck-Condon rule, the electronic changes which occur on excitation were not reflected in gross structural changes.

Crystals of $(CuI(3\text{-cyanopyridine}))_x$, $(CuI(\text{benzylnicotinate}))_x$, and $(CuI(3\text{-pyridylacetonitrile}))_x$, all of which are thermochromic, were structurally characterized at room temperature and at low temperature (in a stream of chilled nitrogen gas from a nitrogen storage dewar). Using an estimate supplied by Nicolet of a 5^{o} loss per joint between storage dewar and crystal, the temperature of the crystal during low temperature data collection may be estimated to be about 100K. For all three crystals the volume decreased from 0.5 to 2.6% on cooling. Cell dimensions also contracted. Shrinkage was observed to be 2.7% across the short cell dimension (across the fold of the polymeric pleated sheet) and a maximum of 1.5% in other cell dimensions. Changes in angles were 0.9%. Errors in cell dimensions increased with a drop in temperature to 100K. The derived structural details for room temperature structures of these three materials show significantly better standard deviations from those derived from low temperature structure determinations. In many cases the standard deviation is doubled on cooling the crystal. For example, for (CuI(3-pyridylacetonitrile))$_x$ crystallized from benzene, the Cu - I distances along the chain are 2.642(3) and 2.708(3) Å at room temperature but 2.626(7) and 2.706(7) Å at low temperature. Consistant with the shrinkage of the unit cell, distances at lower temperature are shorter. There is not a discernable pattern in changes in angle. The R factors of the low temperature structures were worse than those at room temperature; for example the benzylnicotinate complex, 3.0% at room temperature but 6.0% at low temperature; the 3-pyridylacetonitrile complex, 8.5% at room temperature but 12.6% at low temperature. The poorer R factors at low temperature and the increase in standard deviations of atomic parameters and unit cell dimensions (which are also atomic parameters) all point to a disordering of the crystals and a possible phase change.

A single crystal of (CuI(methylnicotinate))$_x$, a non-thermochromic material, was measured at room temperature and low temperature. This crystal showed a smaller volume and 0.9, 0.2, and 1.1% shrinkage in the three cell dimensions. Details of the structure (entries 10, room temperature and 11, low temperature, Figure 4b) show a pattern of somewhat better errors at low temperature than at room temperature.

The magnitude of cell edges and angles change slightly on cooling as well, reflecting the expected shrinkage of unit cell with cooling. The refinement at room temperature was completed at a final agreement factor of 5.2% whereas that at low temperature reached 5.3%. Thus while the differences in behavior between thermochromic and non-thermochromic materials on cooling are not large, decrease in quality of refinement for thermochromic materials seems consistent. This suggests that a phase change may occur below 100K. The onset of such a phase change is normally sharply defined (by temperature) for a first order phase change and gradual for a second order phase change. Thus the disorder suggested by the behavior of these solid materials at 100K would seem to suggest a second order phase change, but other behavior cannot be ruled out.

Entries 15, 16, and 17 in Figure 4b represent data on polymeric pleated sheet structures in which hydrogen bonding interactions link ligands bonded to adjacent polymeric pleated sheets. These unit cells then involve a positive interaction between adjacent polymeric sheets. These three materials are non-thermochromic and are thus similar to the non-thermochromic complexes in which pyrazine, quinoxaline, and phenazine serve as bidentate ligands bridging adjacent polymeric sheets.

Crystallographic data for the nineteen entries in Figure 4b can be found at the end of this thesis in the tables shown.

1)	$(\mathrm{CuI(3\text{-}cyanopyridine)})_x$ RT	Table XXXIX - XLIV
2)	$(\mathrm{CuI(3\text{-}cyanopyridine)})_x$ LT	Table XLV - L
3)	$(\mathrm{CuI(benzylnicotinate)})_x$ LT	Table XXXIII - XXXVIII
4)	$(\mathrm{CuI)benzylnicotinate)})_x$ RT	Table XXVII - XXXII
5)	$(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ RT - benzene	Table CI - CIV
6)	$(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ LT - benzene	Table XCVII - C
7)	$(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ RT, UV benzene	Table CV - CVIII
8)	$(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ RT acetonitrile	Table LI - LVI
9)	$(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ LT acetonitrile	Table LVII - LXI
10)	$(\mathrm{CuI(methylnicotinate)})_x$ RT	Table XXI - XXVI
11)	$(\mathrm{CuI(methylnicotinate)})_x$ LT	Table XV - XX
12)	$(\mathrm{CuI(isopropylnicotinate)})_x$	Table VII - X
13)	$(\mathrm{CuI(n\text{-}butylnicotinate)})_x$	Table I - VI
14)	$(\mathrm{CuI(n\text{-}propylnicotinate)})_x$	Table XI - XIV
15)	$(\mathrm{CuI(nicotinamide)_2})_x$	Table XCI - XCVI
16)	$(\mathrm{CuI(isonicotinamide)})_x$	Table LXIX - LXXIV
17)	$(\mathrm{CuI(isonicotinic\ acid)})_x$	Table LXIII - LXVIII
18)	$(\mathrm{CuI(methylisonicotinate)})_x$	Table LXXV - LXXIII
19)	$(\mathrm{CuI(methylisonicotinate)})_x$	Table LXXV - LXXIII

The ORTEP drawings for the above entries are illustrated in the following figures:

1) $(\mathrm{CuI(3\text{-}cyanopyridine)})_x$ RT Figure 5a and 6.

2)	$(\mathrm{CuI(3\text{-}cyanopyridine)})_x$ LT	Figure 5b.
3)	$(\mathrm{CuI(benzylnicotinate)})_x$ LT	not shown.
4)	$(\mathrm{CuI(benzylnicotinate)})_x$ RT	Figure 7 and 8.
5)	$(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ LT benzene	not shown but see 8).
6)	$(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ RT benzene	not shown but see 8).
7)	$(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ RT, UV benzene	not shown but see 8).
8)	$(\mathrm{CuI(3\text{-}pyridylscetonitrile)})_x$ RT acetonitrile	Figure 9a and 10.
9)	$(\mathrm{CuI(3\text{-}pyridylacetonitrile)})_x$ LT acetonitrile	Figure 9b.
10)	$(\mathrm{CuI(methylnicotinate)})_x$ RT	Figure 11a and 12.
11)	$(\mathrm{CuI(methylnicotinate)})_x$ LT	Figure 11b.
12)	$(\mathrm{CuI(isopropylnicotinate)})_x$	Figure 13.
13)	$(\mathrm{CuI(n\text{-}butylnicotinate)})_x$	Figure 14 and 15.
14)	$(\mathrm{CuI(n\text{-}propylnicotinate)})_x$	Figure 16.
15)	$(\mathrm{CuI(nicotinamide)_2})_x$	Figure 17 and 18.
16)	$(\mathrm{CuI(isonicotinamide)})_x$	Figure 19.
17)	$(\mathrm{CuI(isonicotinic\ acid)})_x$	Figure 20.
18)	$(\mathrm{CuI(methylisonicotinate)})_x$	Figure 21 and 22.

The emission spectra of the polymeric pleated sheets with esterified nicotinic acid groups as ligand all show peaks in the 481 - 500 nm region (Figure 26 and 27). The band is broad and highly shifted from the 366 nm excitation. The consistancy of the position of this band is to be expected since the ligands differ only in the identity of the esterification group (methyl, isopropyl, n-propyl, n-butyl). Cu...Cu distances (Figure 4b, entries 10, 12, 13, and 14) show a range 2.804(3) - 2.928(2) Å and thus this emission may be assigned to MLCT. The influence of the meta- ester group thus lowers the electron density of the aromatic ring, shifting the charge transfer band to lower energies than that seen for MLCT for Cu(I) complexed to pyridine (436 nm). $(\mathrm{CuI(benzylnicotinate)})_x$, which is a thermochromic material, also shows this MLCT band at approximately 500 nm although it is a shoulder on a larger emission; similarly 3-pyridylacetonitrile shows MLCT at 490 nm and another maximum at lower energy. The emission maximum for the nicotinamide polymeric pleated sheet is 485 nm and may be assigned to MLCT and supports the view that the replacement of an esterified carboxylate group with an amide in the meta- position should not alter the electron density of the aromatic ring significantly and thus the energy level of the pi^* excited states for ester and amide substituted rings should be similar.

The removal of ester or amide groups to the para-position causes a greater change in the position of the MLCT band, (600 nm when the ligand is methylisonicotinate but 541 nm when the ligand is isonicotinamide). Thus, the influence of position of the withdrawing group parallels the resonance influence of a withdrawing group and that the creation of a partially positive charge on the bonded nitrogen atom lowers the energy levels of the pi* orbital and thus moves the MLCT band to lower energies. The withdrawing effect of the para-amide group is less than that of the para- methyl ester.

The failure of the isonicotinic acid CuI complex to emit is not understood. Unlike the esters of quinaldic acid which were earlier observed to be non-emitting, the isonicotinic acid is bound to copper only through nitrogen and not through oxygen as well. Both isonicotinic acid and isonicotinamide are involved in interpolymer hydrogen bonds. There are no apparent differences in structural details for these two materials (entries 16 and 18 of Figure 4b, Figures 19 and 20).

The two polymeric pleated sheet structures in which the ligand is benzyl nicotinate and 3-pyridylacetonitrile each show an additional lower energy band of greater intensity in the 565 - 583 nm region in addition to the MLCT band. While this band is in the range where metal centered emission is commonly expected, (Figure 26) this phenomenon is observed when the Cu...Cu separations across rhombs fall in the 2.647(4) - 2.699(3) Å range, but those of the two thermochromic of these two materials range from 2.736(2) - 2.902(5) Å. The two thermochromic materials differ from the ester and amide substituted pyridine groups in an important way; each has a second chromophore. The benzyl of benzyl nicotinate and the cyano- group of 3-pyridylacetonitrile are not in conjugation with the bound pyridine ring. Potentially, these groups are additional emitting centers.

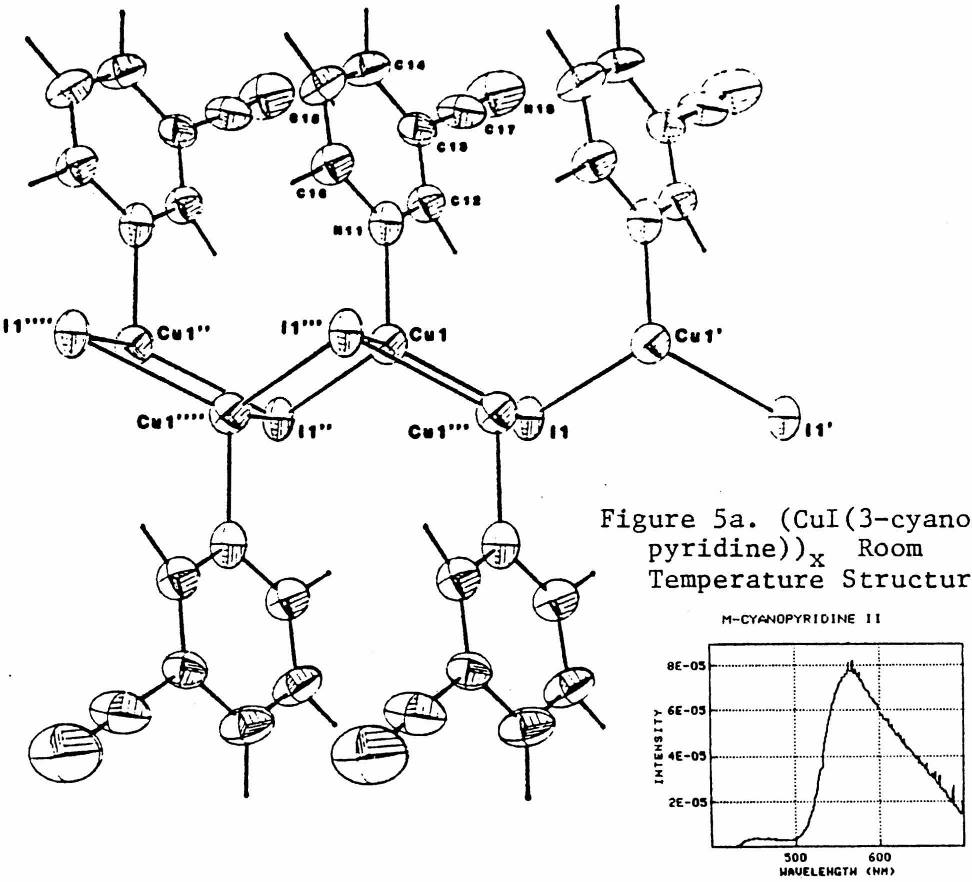


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Figure 5a. (CuI(3-cyano-pyridine))$_x$ Room Temperature Structure.

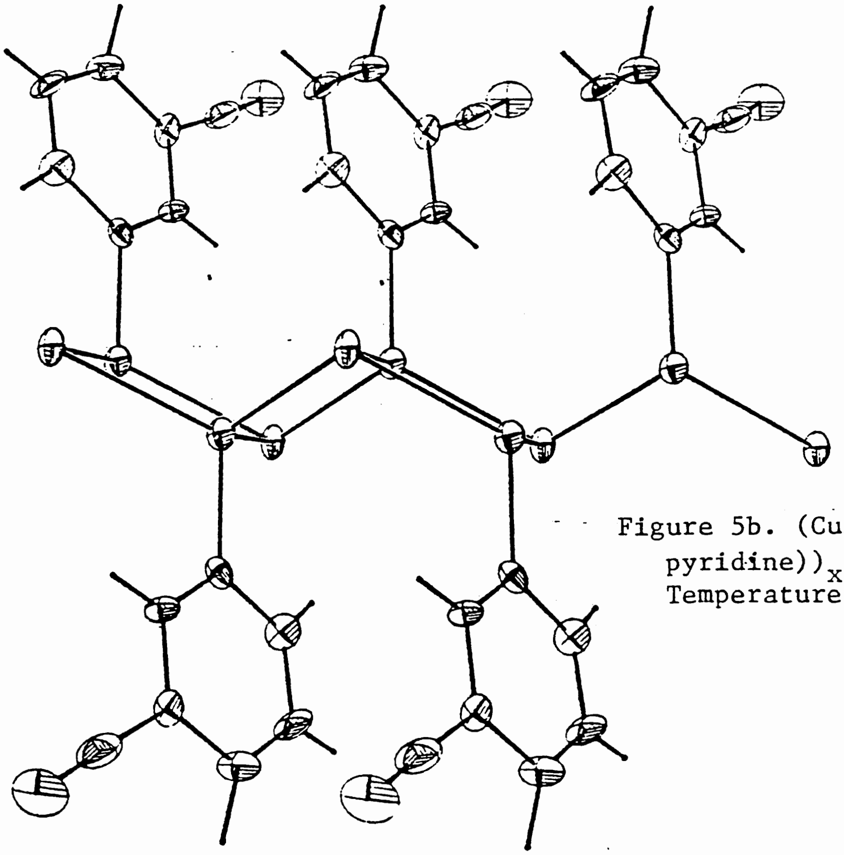


Figure 5b. (CuI(3-cyano-pyridine))$_x$ Low Temperature Structure.

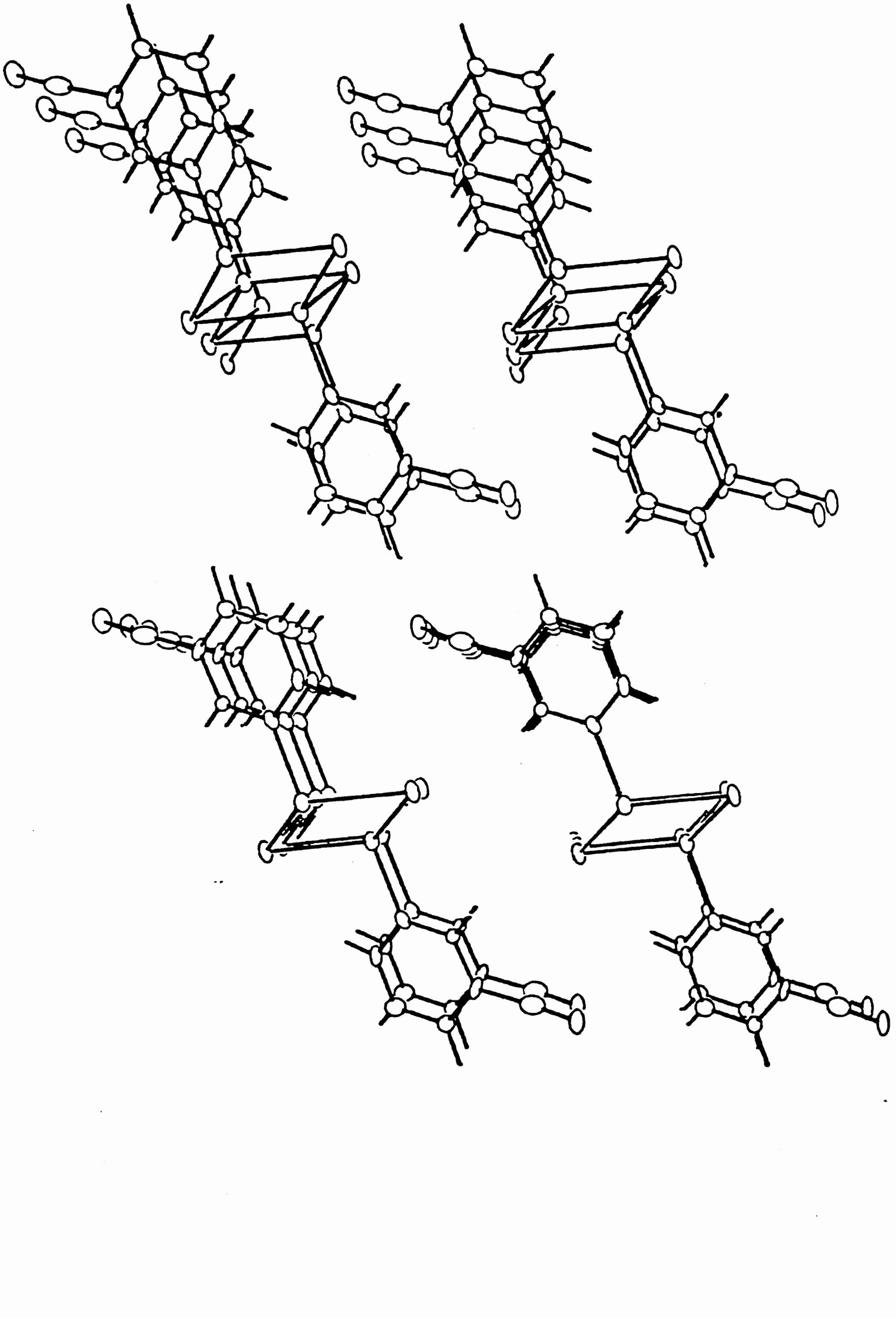
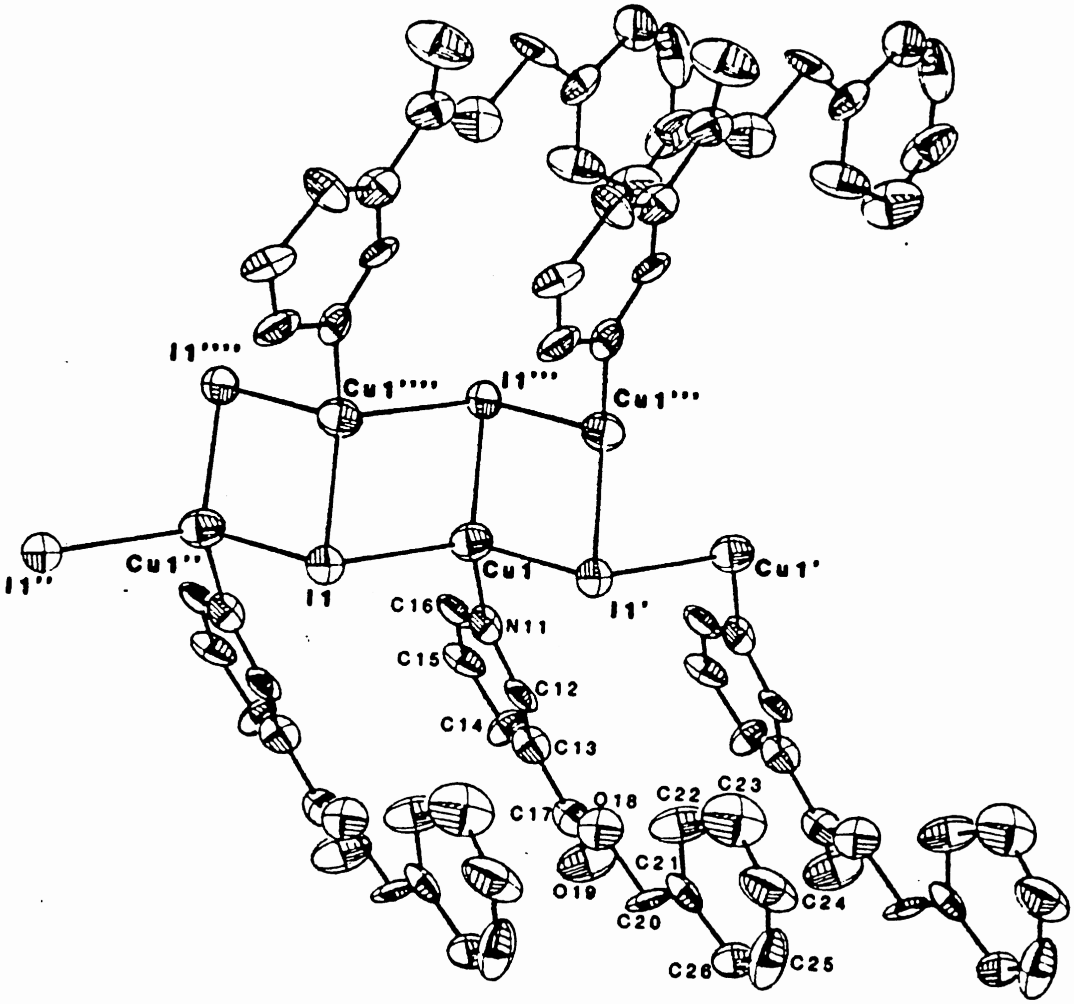


Figure 6. Packing Diagram for $(CuI(3\text{-cyanopyridine}))_x$



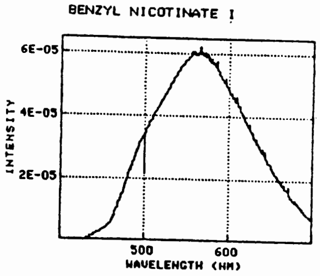


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Figure 7. (CuI(benzylnicotinate))$_x$ Room Temperature Structure.

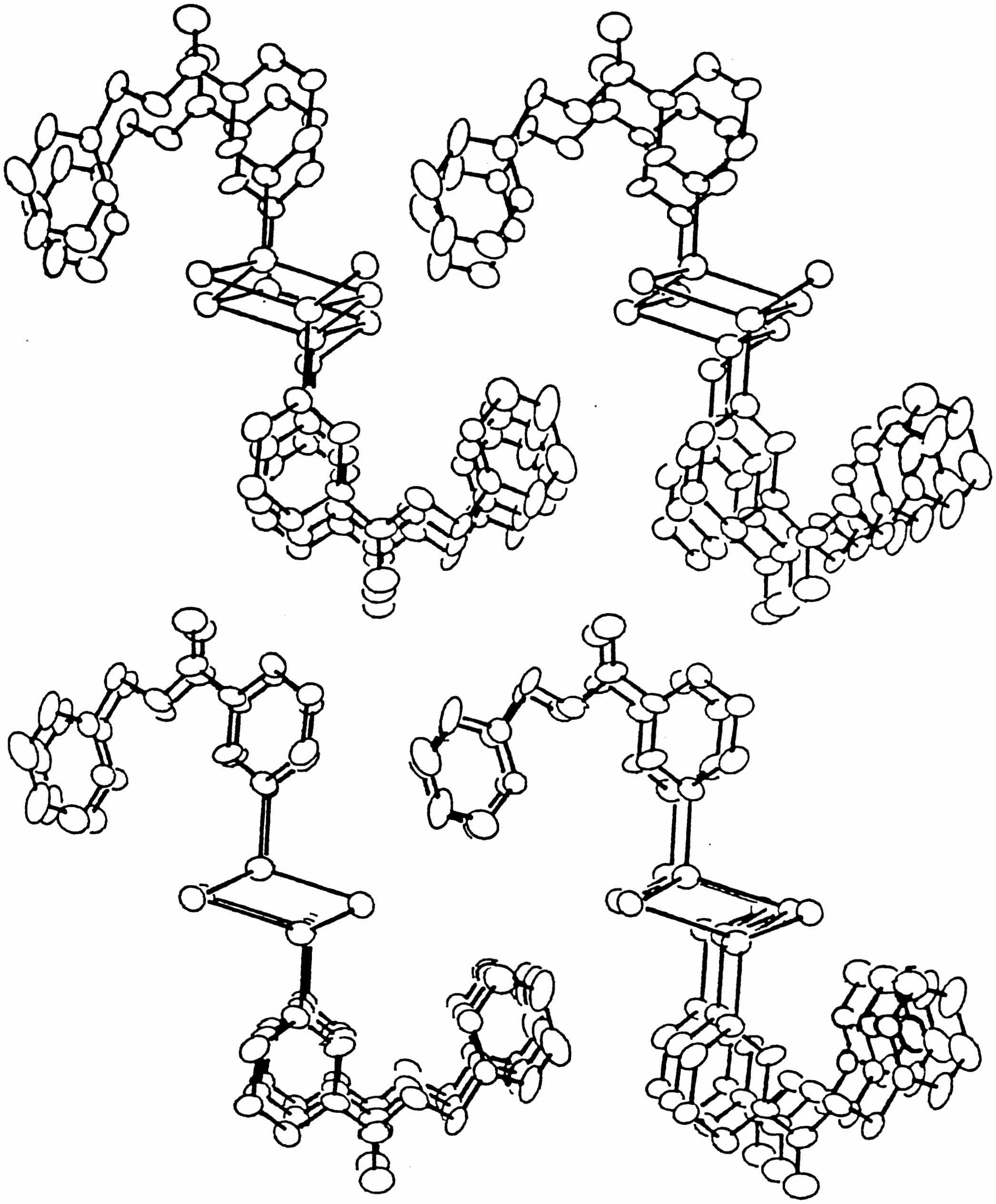


Figure 8. Packing Diagram for (CuI(benzynicotinate))$_x$

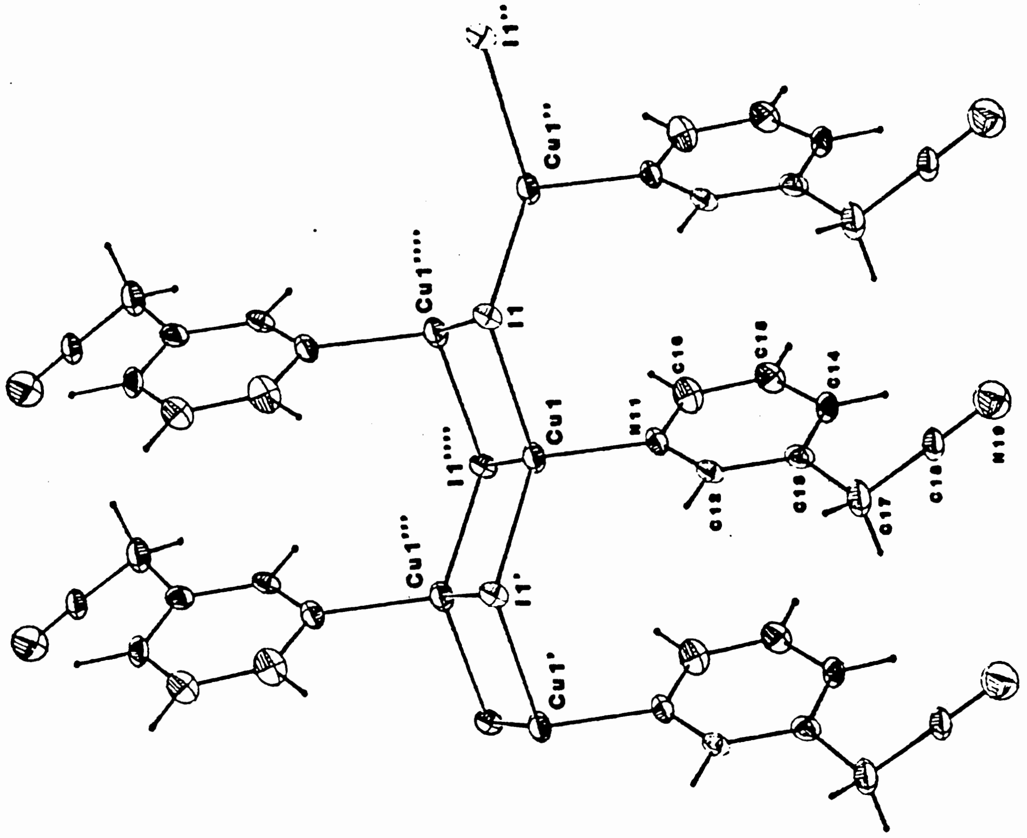


Figure 9a. (CuI(3-pyridylacetonitrile))$_x$
Low Temperature Structure.

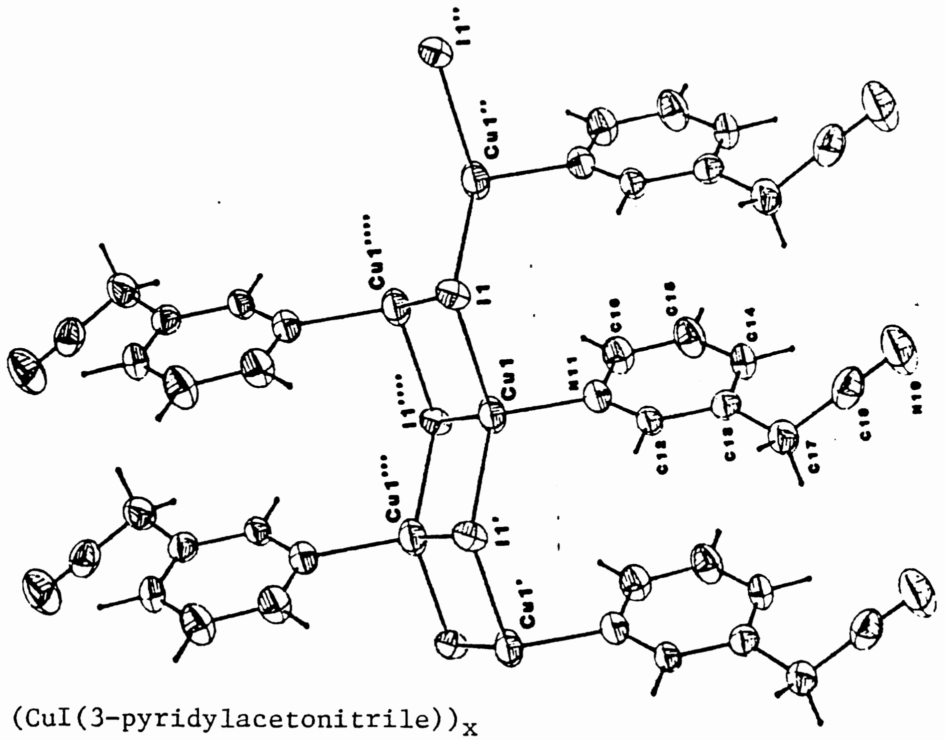


Figure 9b. (CuI(3-pyridylacetonitrile))$_x$
Room Temperature Structure.

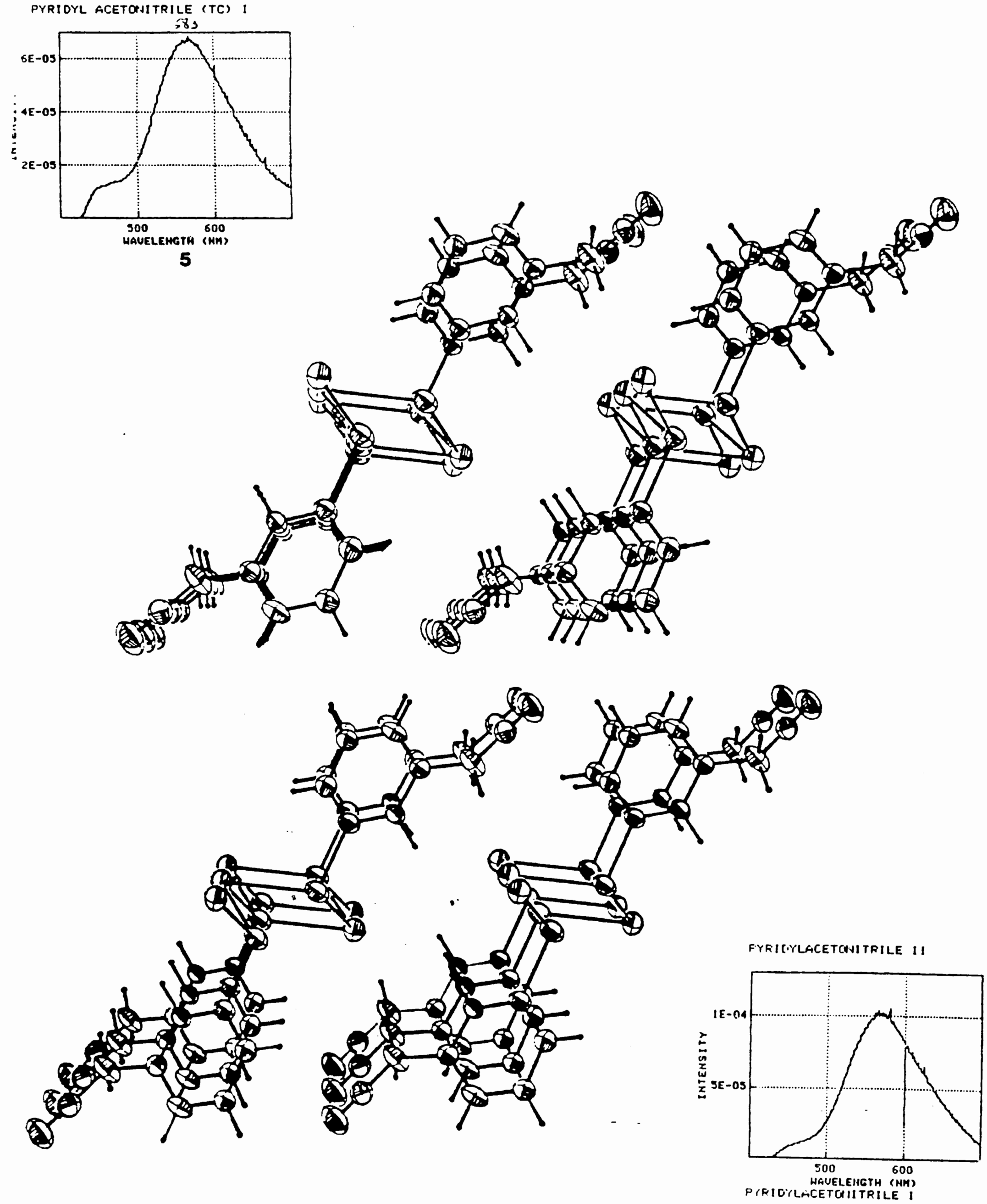


Figure 10. Packing Diagram for $(\text{CuI(3-pyridylacetonitrile)})_x$ RT.

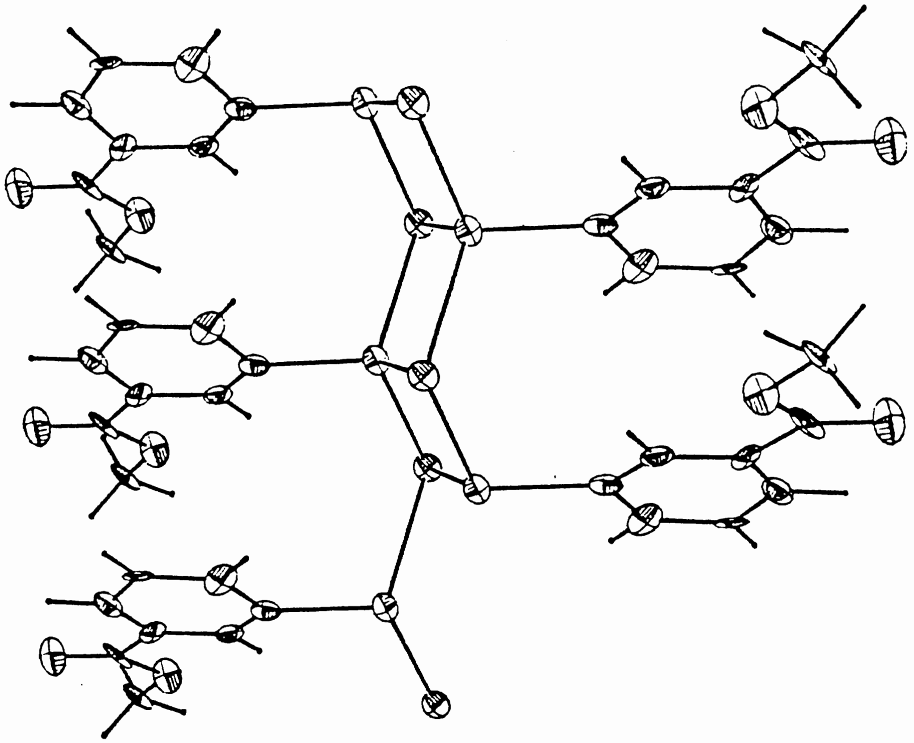


Figure 11a. (CuI(methylnicotinate))$_x$ Low Temperature Structure.

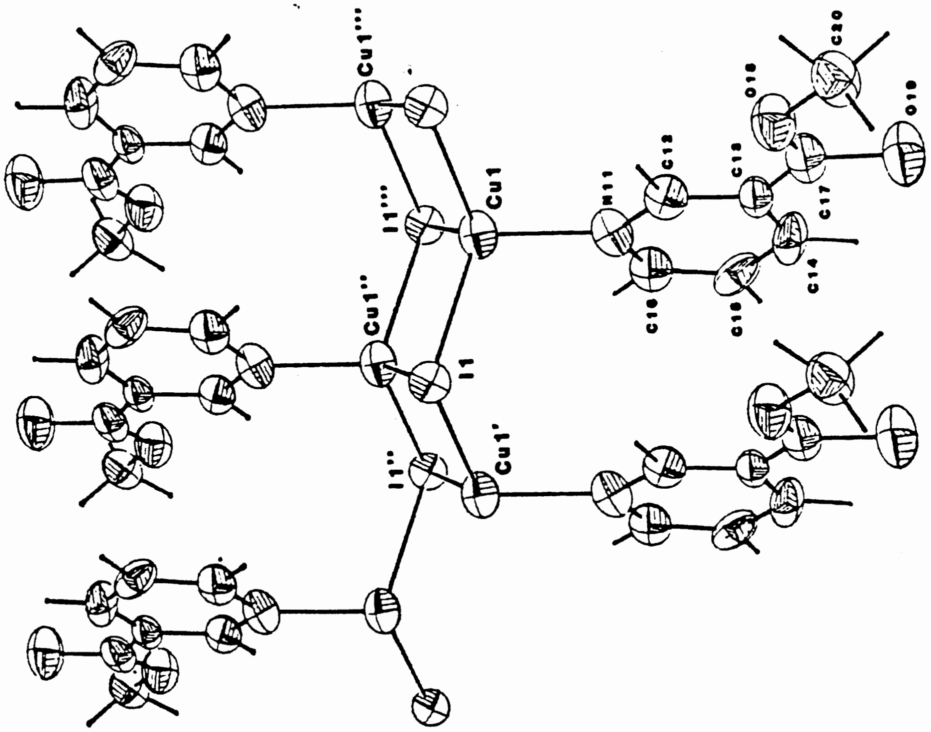


Figure 11b. (CuI(methylnicotinate))$_x$ Room Temperature Structure.

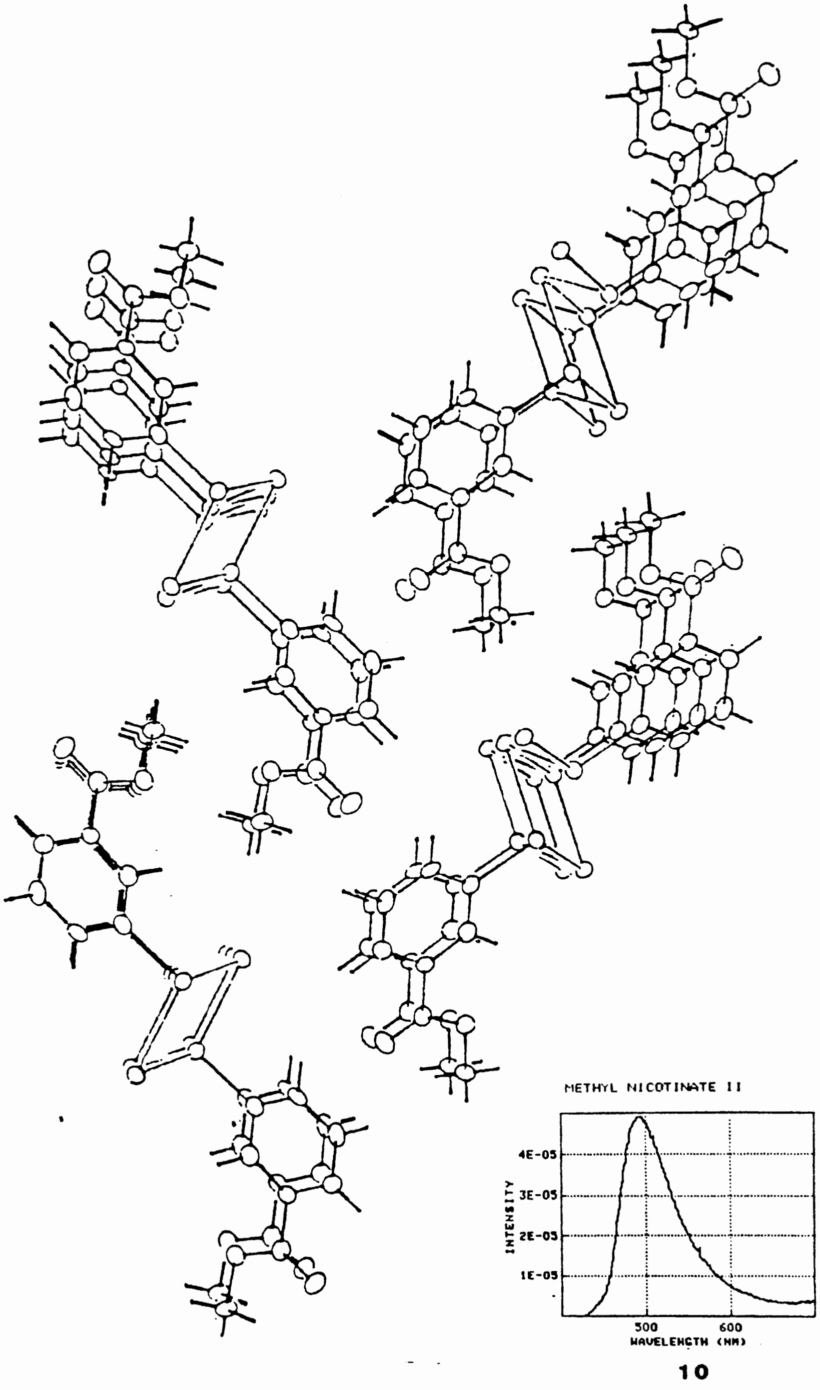


Figure 12. Packing Diagram for (CuI(methylnicotinate))$_x$

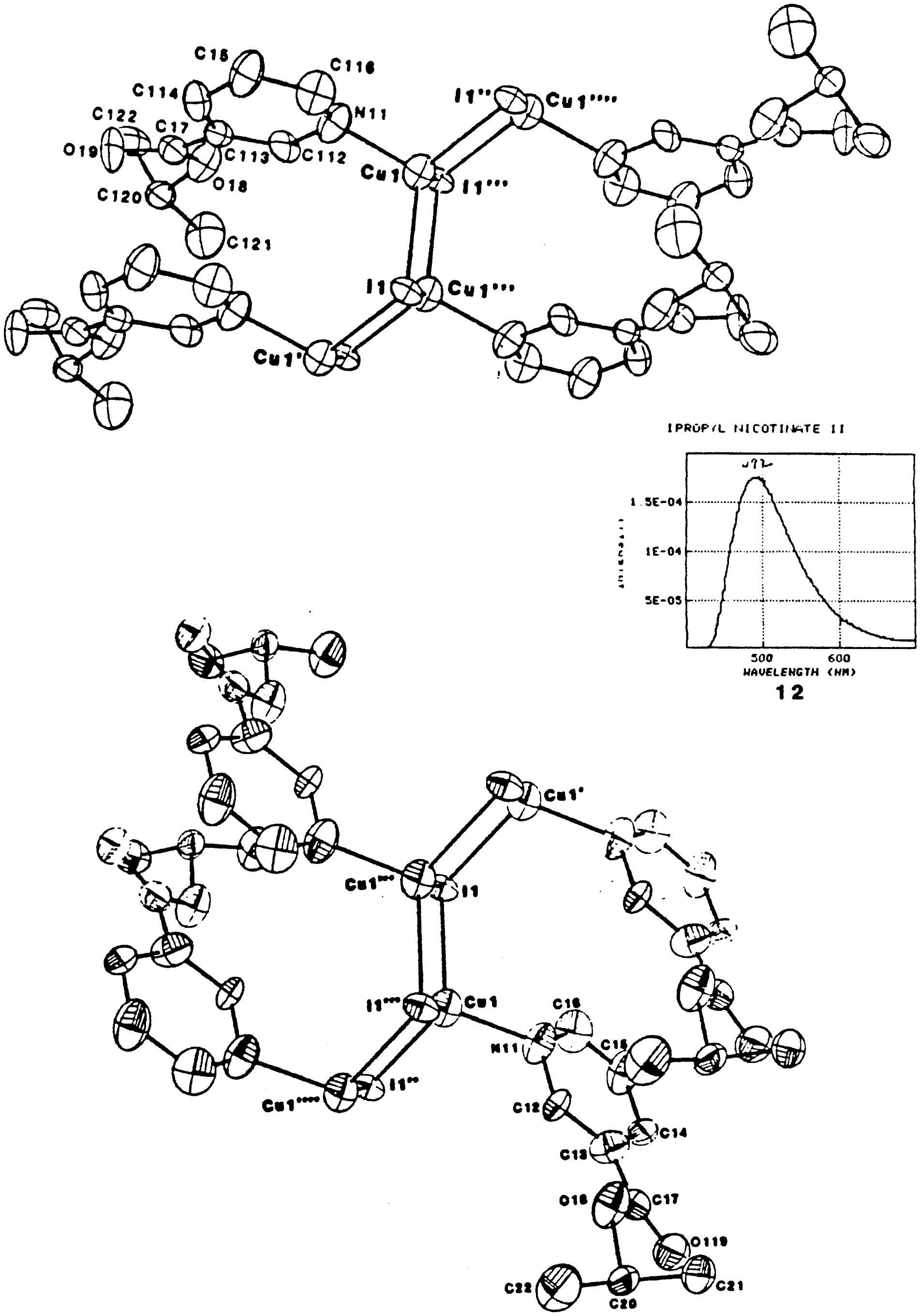
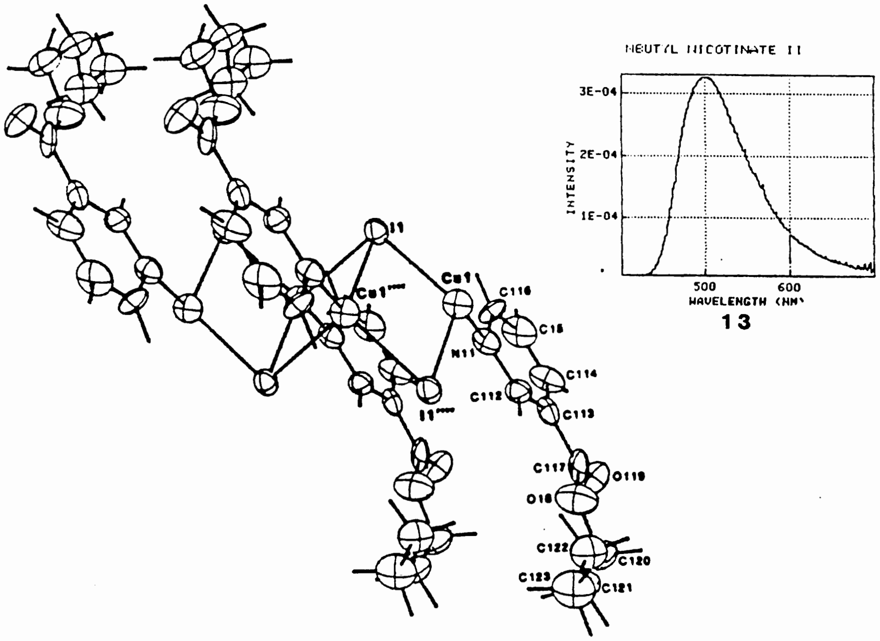


Figure 13. (CuI(isopropylnicotinate))$_x$ 2-Fold Disordered Structure.



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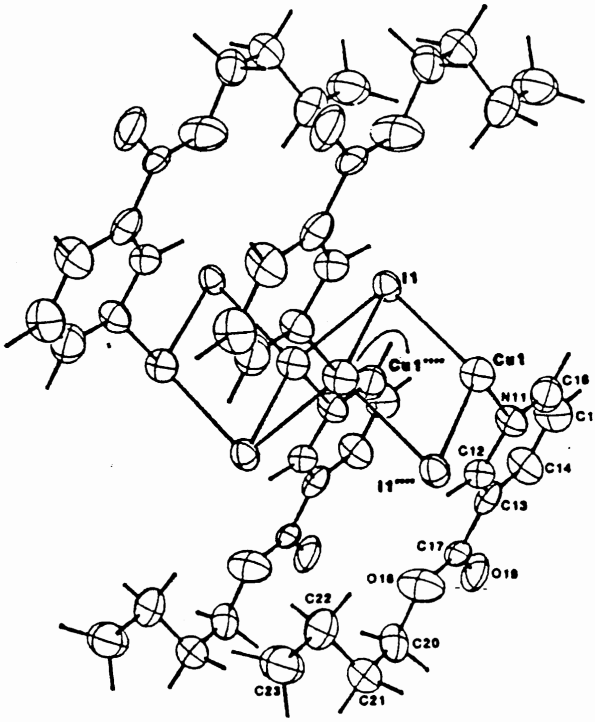


Figure 14. (CuI(n-butylnicotinate))$_x$ 2-Fold Disordered Structure.

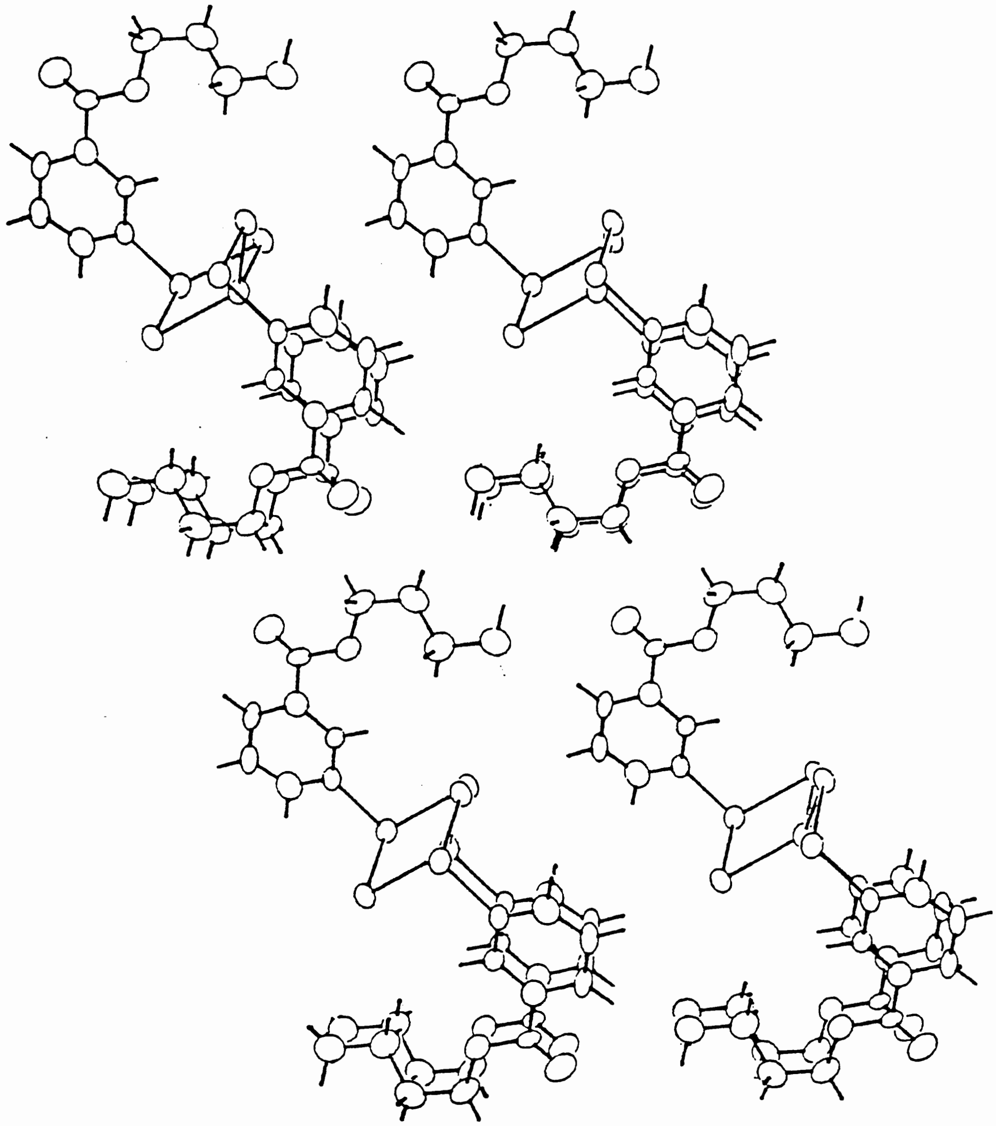


Figure 15. Packing Diagram for (CuI(n-butylnicotinate))$_x$

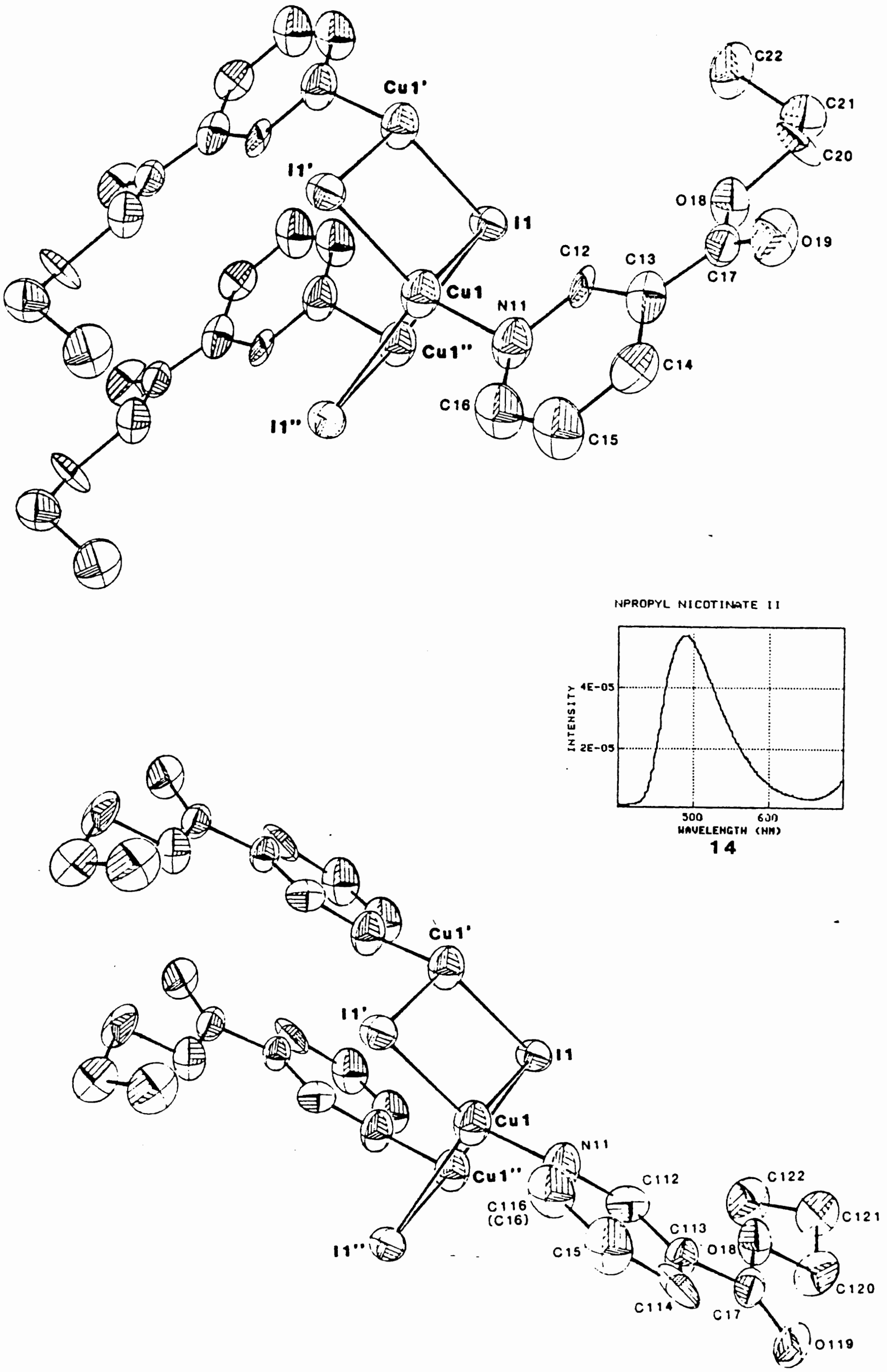
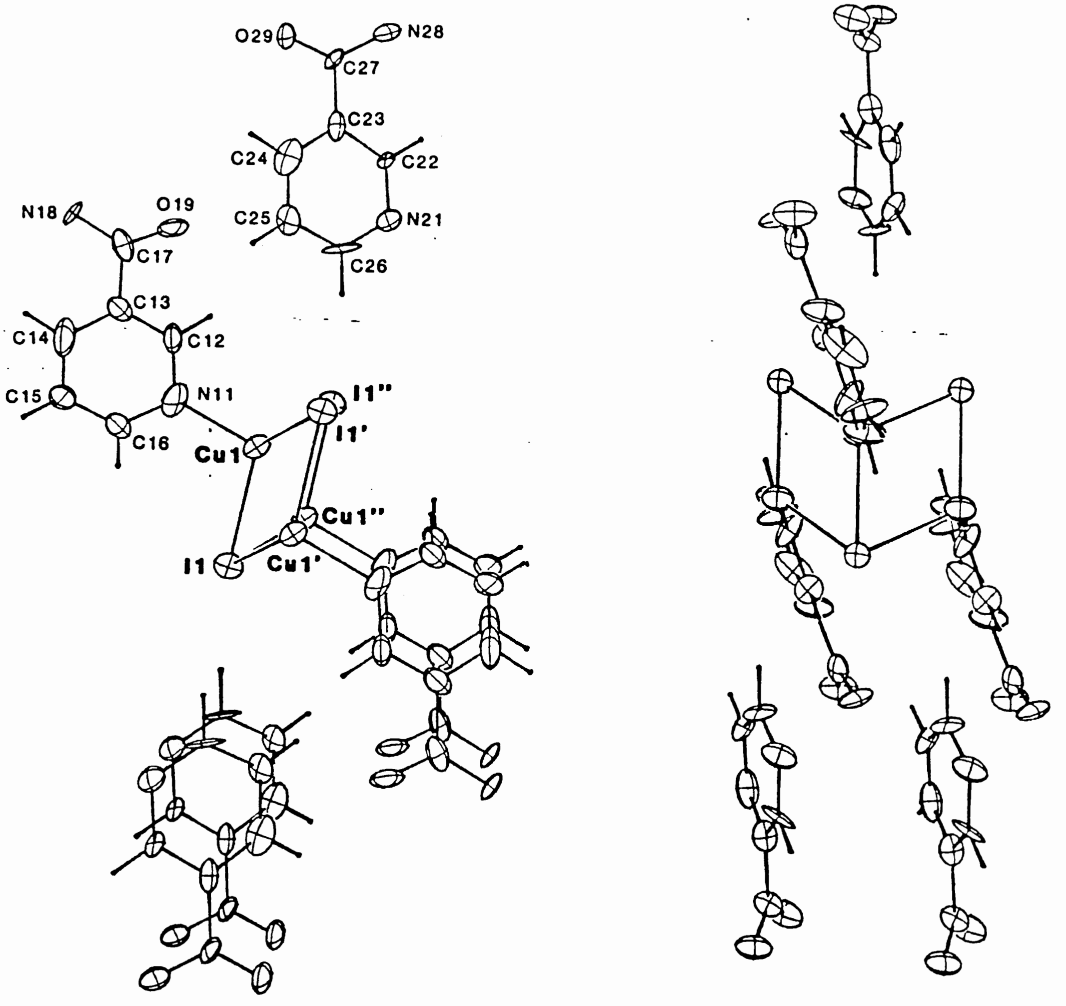


Figure 16. $(\mathrm{CuI(n\text{-}propylnicotinate)})_x$ 2-Fold Disordered Structure.



(a) (b)

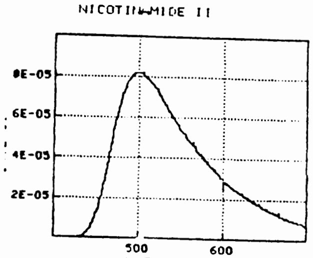


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Figure 17a. $(CuI(nicotinamide)_2)_x$ View Down c Axis.
Figure 17b. $(CuI(nicotinamide)_2)_x$ View Down a Axis.

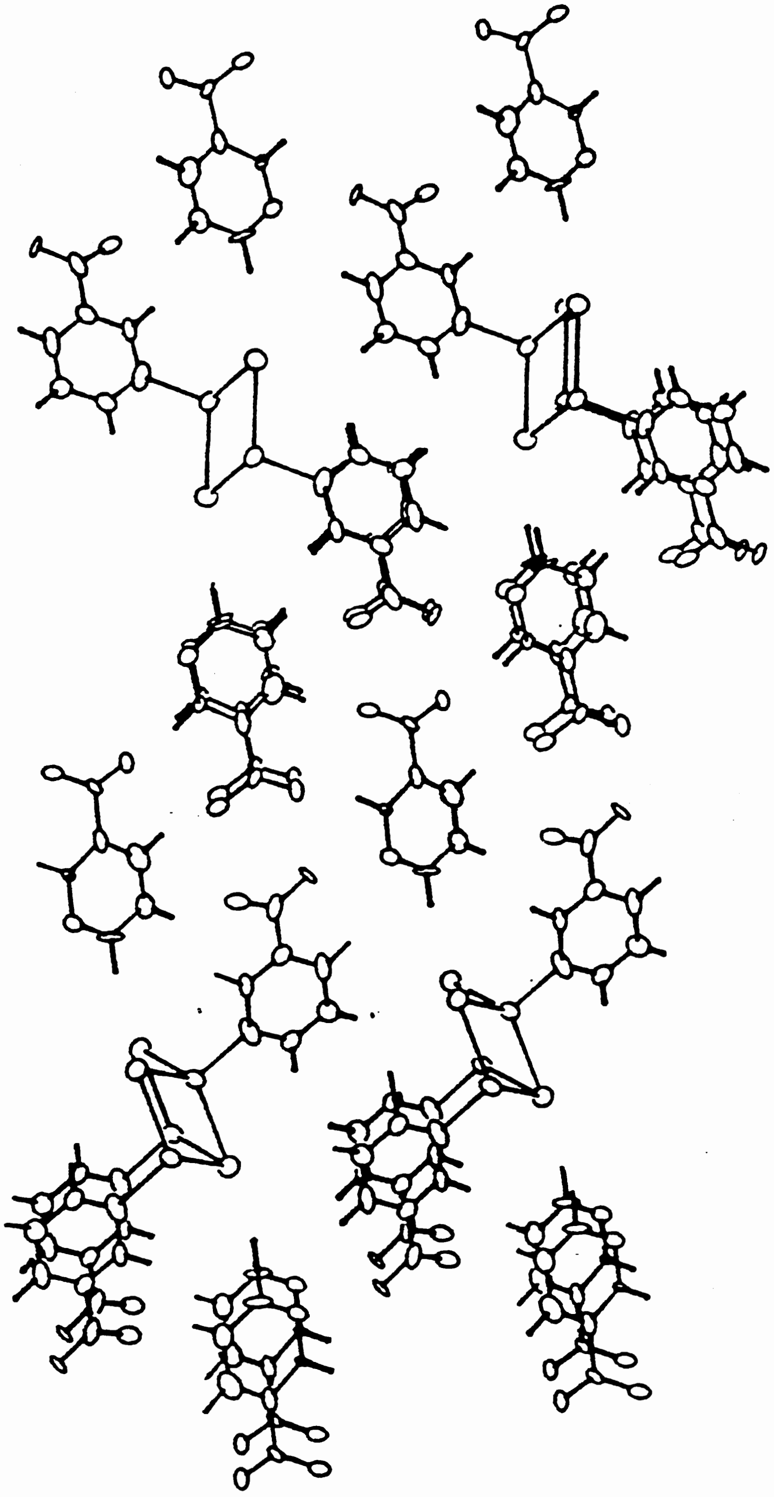


Figure 18. Packing Diagram for $(CuI(nicotinamide)_2)_x$

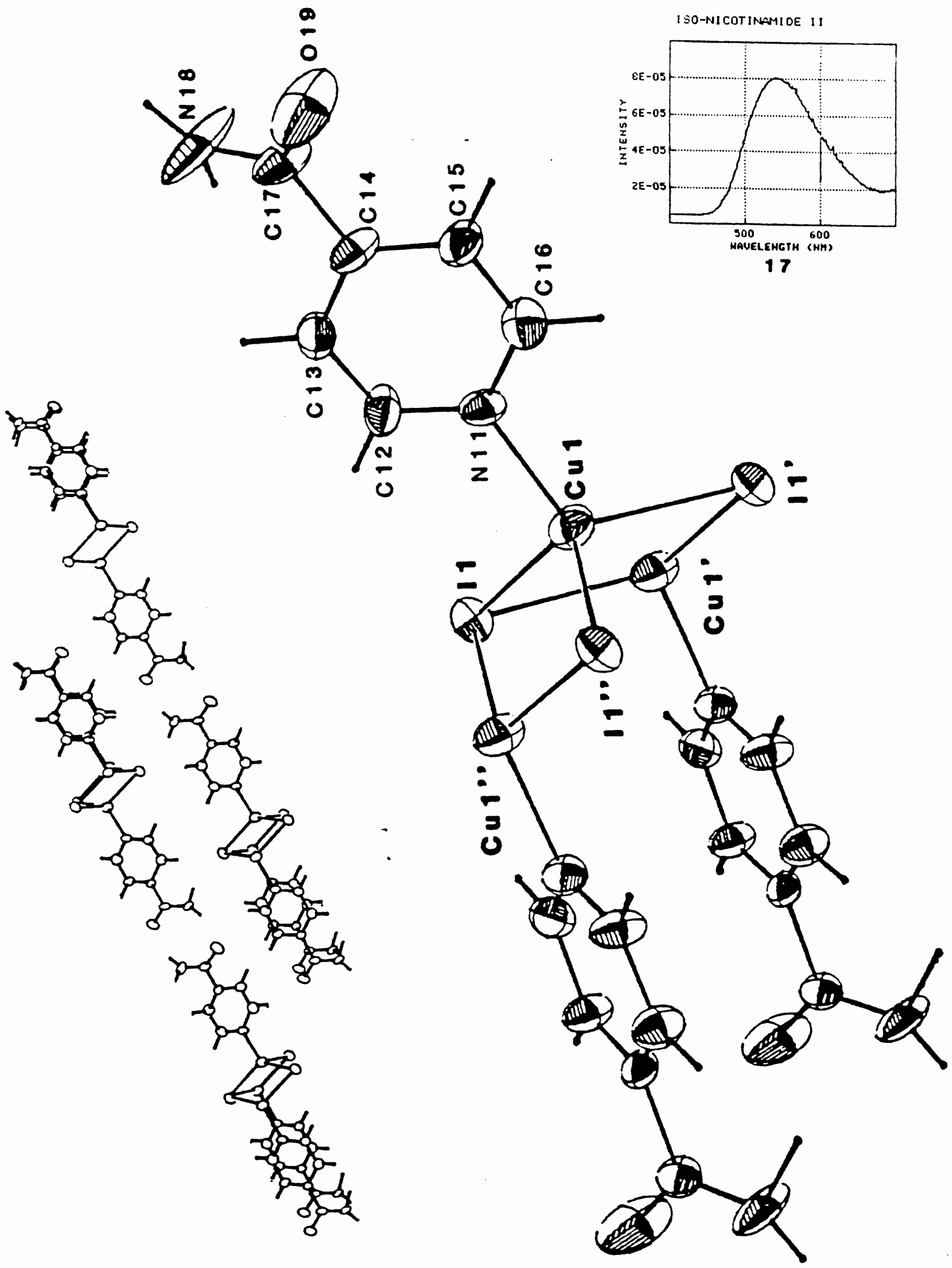


Figure 19. (CuI(isonicotinamide))$_x$ (Packing Diagram Inset)

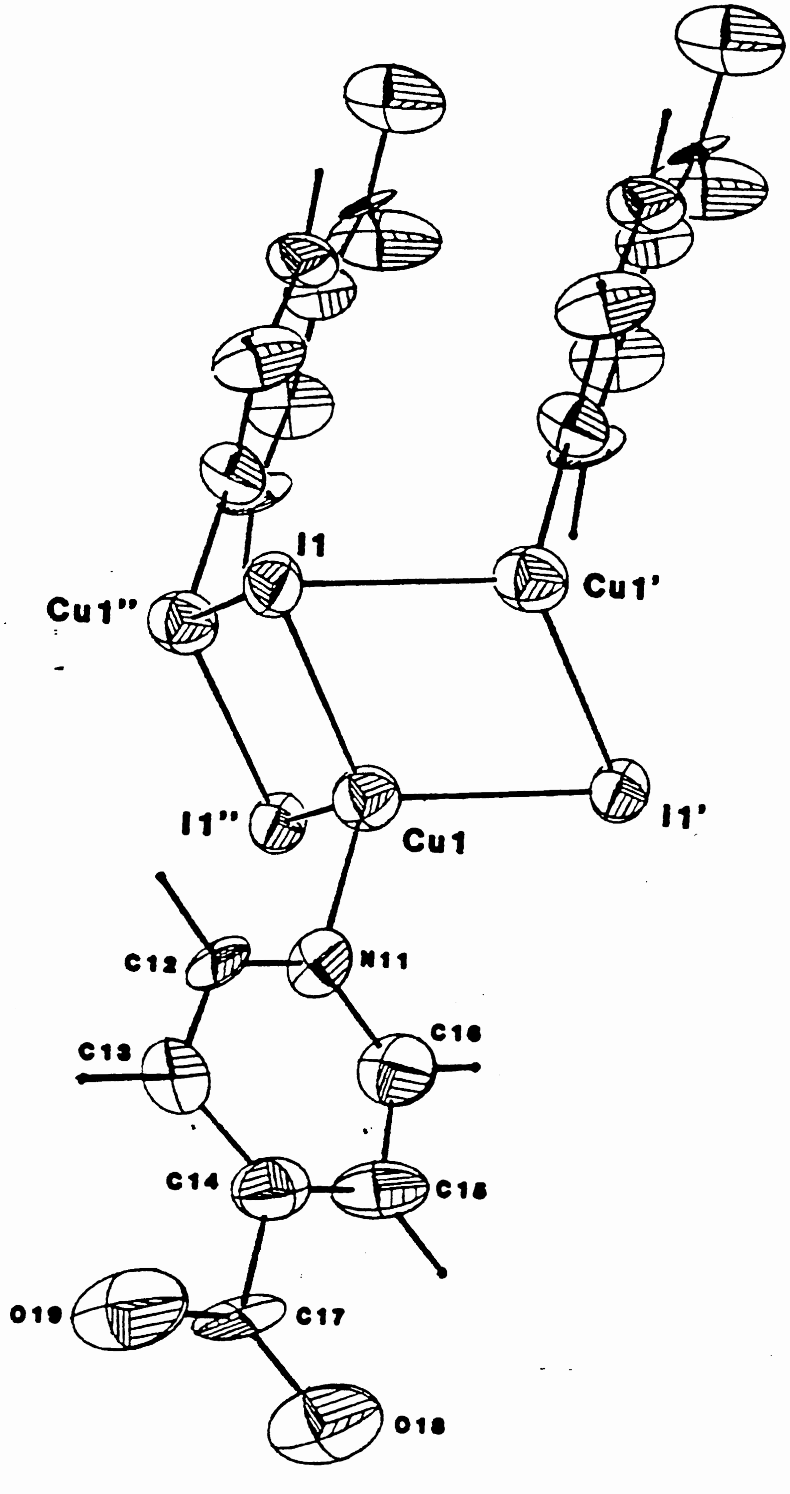
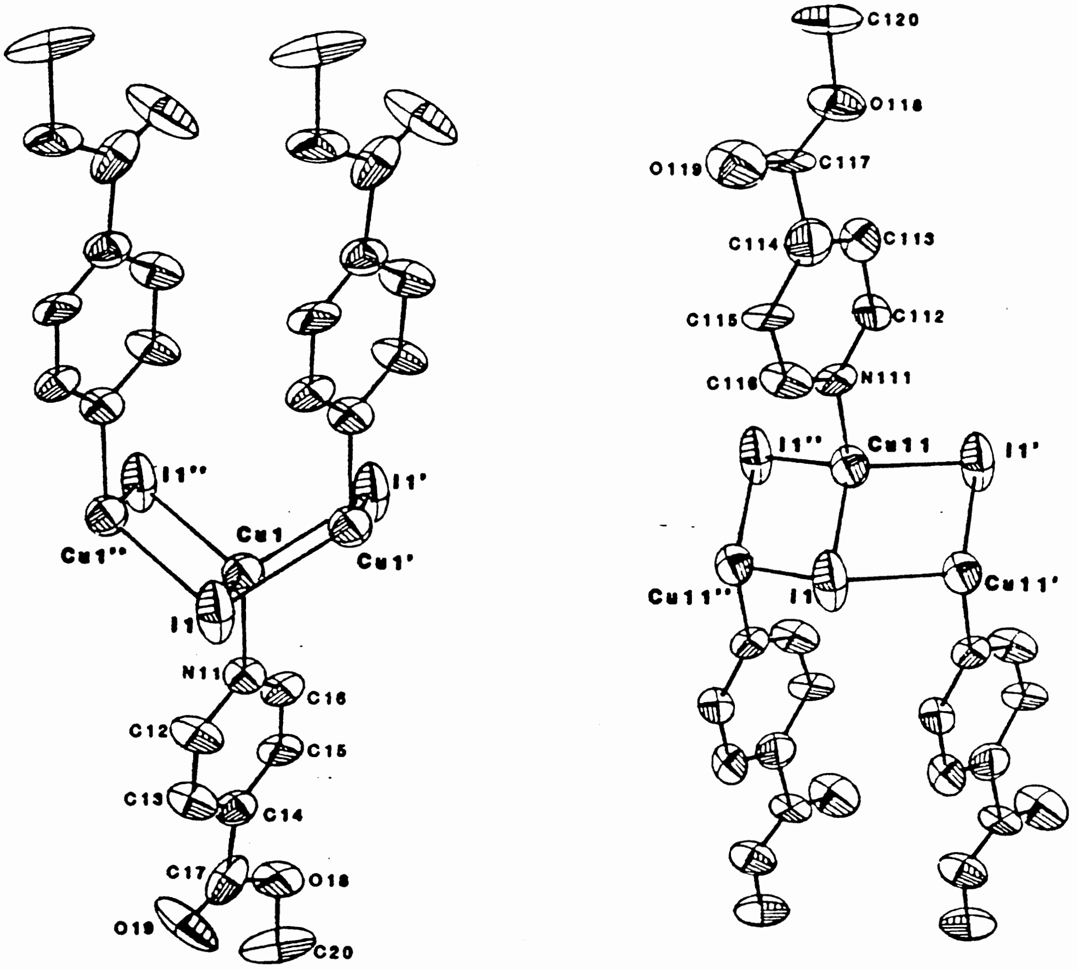


Figure 20. (CuI(isonicotinic acid))$_x$



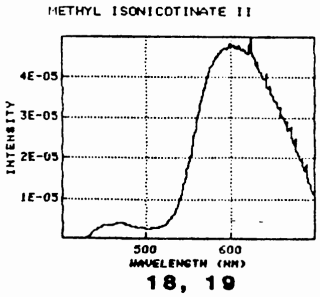


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Figure 21. (CuI(methylisonicotinate))$_x$ 2-Fold Disordered Structure.

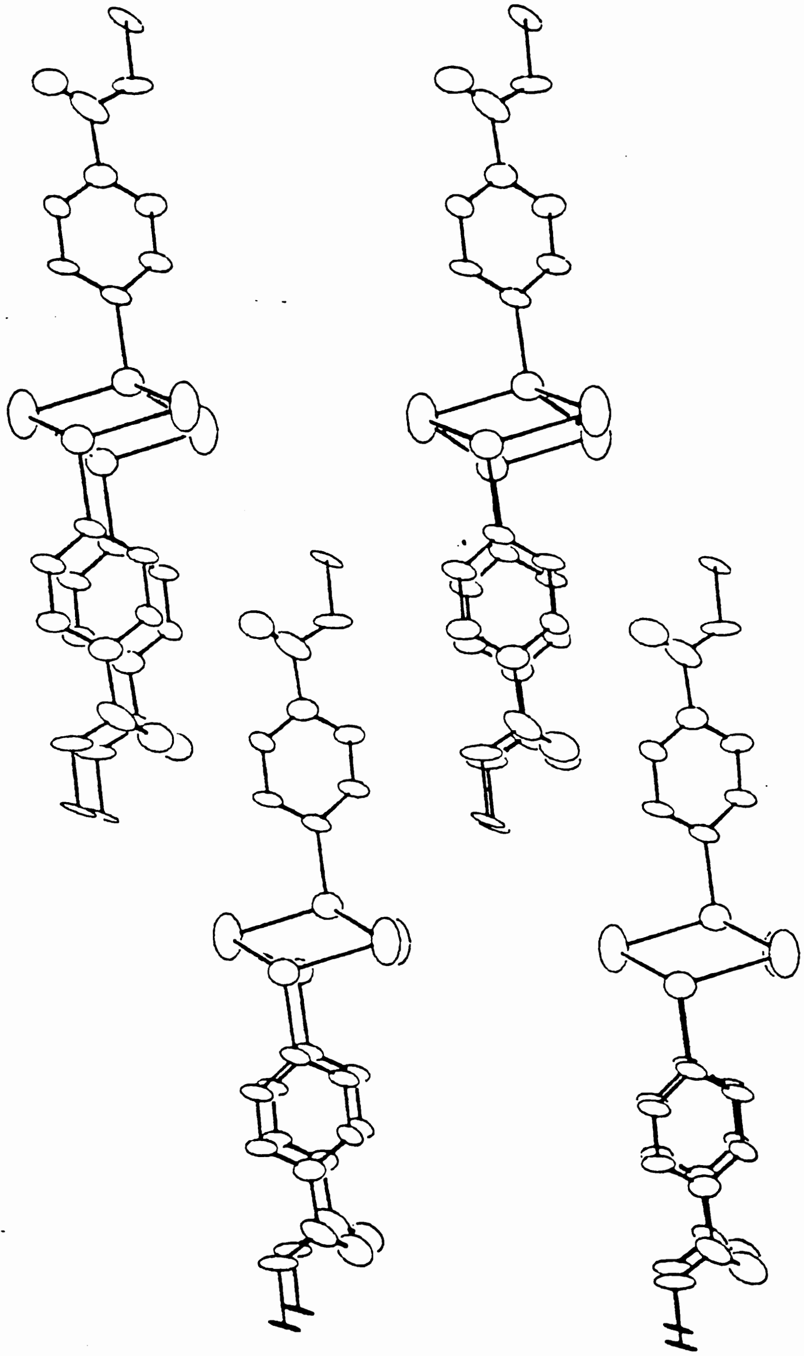


Figure 22. Packing Diagram for (CuI(methylisonicotinate))$_x$

Two new Cu(I) iodide cubes were prepared with benzylnicotinamide (Table CXXV - CXXXIII) and phenyl nicotinate (Table CXIII - CXVIII), as ligands. A third cube whose structure was previously determined (5) is included here because the structure at low temperature had not been solved. ((CuI(isopropylnicotinate))$_4$, Table CIX - CXIII) The benzylnicotinamide and isopropylnicotinate complexes are both thermochromic. The cubic motif of Cu_4I_4 involves copper atoms at alternate corners of a distorted cube in a roughly tetrahedral arrangement. Iodine atoms occupy the other corners of the three dimensional figure. Average Cu - I distances in the cube are 2.711 Å. Average angles at copper are 109.48^o. Ligands are bound through nitrogen to copper on pseudo diagonals of the cube, at typical Cu - N distances of 2.04 Å (Figures 23 - 25).

The complex with isopropyl nicotinate changes from yellow at room temperature to blue at 77K and the benzylnicotinamide changes from yellow at room temperature to orange at low temperature but the cube with phenyl nicotinate emits blue at both temperatures. The room temperature structural details do not differentiate the thermochromic cubes from the one non-thermochromic cube. Average Cu...Cu separations in thermochromic cubes are 2.667 and 2.680 Å respectively, whereas those in the non-thermochromic solid are 2.71 Å.

A comparison of the room temperature and low temperature single crystal X-ray structures of the Cu_4I_4isopropylnicotinate$_4$ and Cu_4I_4benzylnicotinamide$_4$ shows a contraction of the unit cell edges (maximum 0.9%) and a shrinkage of the volume of the unit cell.

A low temperature structure determination for Cu_4I_4-isopropylnicotinate$_4$ was not possible because of the severe disordering of the crystal. This is illustrated in Figure 28. Photograph 4 shows the diffraction pattern of a single crystal of CuI(isopropylnicotinate) at room temperature. Photographs 3 and 2 show the low temperature diffraction patterns and Photograph 1 shows the pattern when the temperature of the crystal was between 100K and room temperature. The room temperature (photograph 4) rotation photograph was actually taken after the crystal had been warmed from 100K and shows the same diffraction pattern as it did on the very first rotation photograph. Thus the crystal shows reversible disorder at low temperature.

The refinement of the benzylnicotinamide complex at low temperature showed an improvement from 7 to 4% with an improvement of the errors associated with details such as bond lengths and angles.

The internal symmetry (crystallographic) of the cubic motifs differ. Cu_4I_4isopropylnicotinate$_4$ crystallizes with a $\bar{4}$ symmetry element in the center of the tetramer; Cu_4I_4-benzylnicotinamide$_4$ has no symmetry element relating copper positions and Cu_4I_4phenylnicotinate$_4$ has a two-fold rotation axis relating one-half of the cube to the other. Thus the thermochromic materials show the highest and the lowest symmetry of the three. This confirms the recent finding

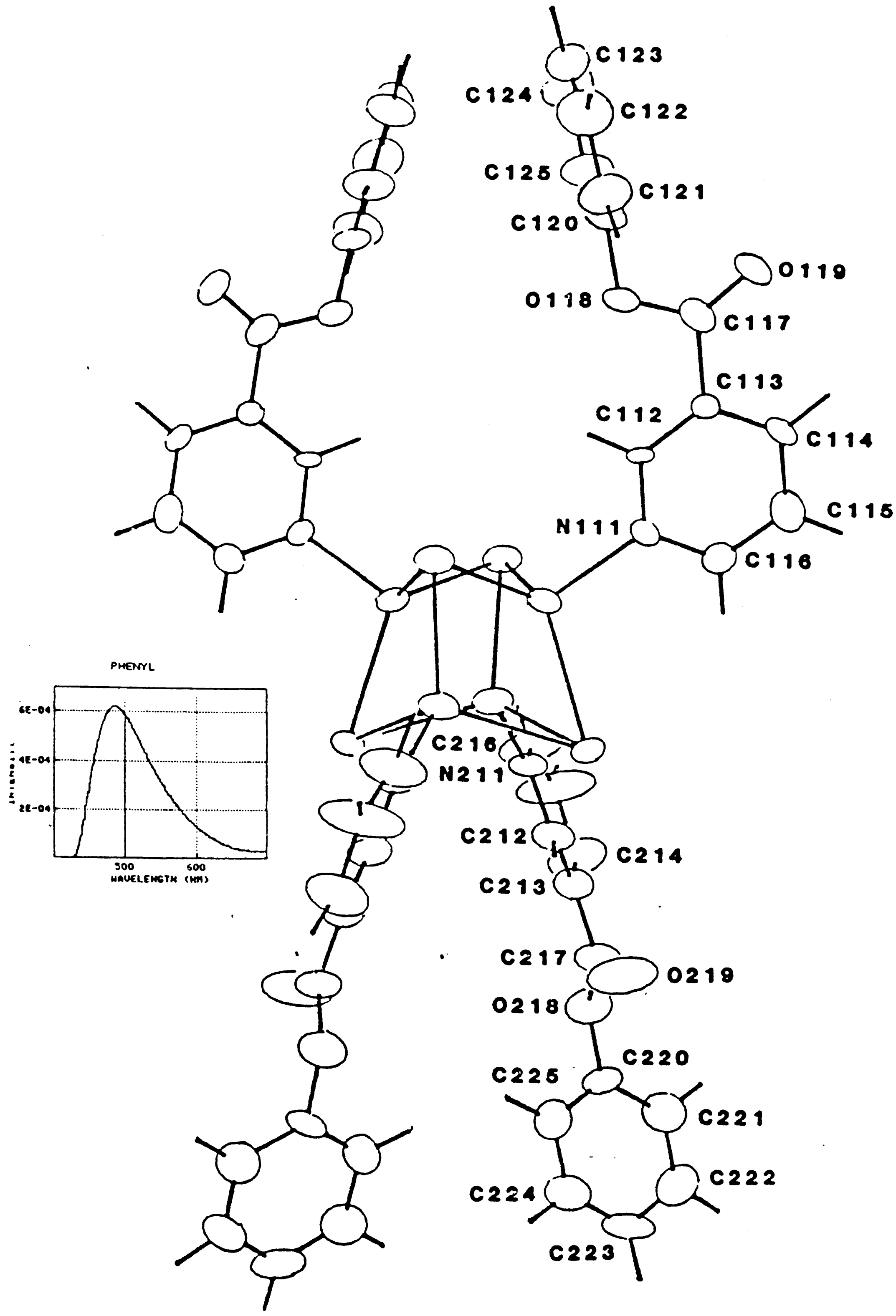


Figure 23. $((\mathrm{CuI(phenylnicotinate)})_2)_2$

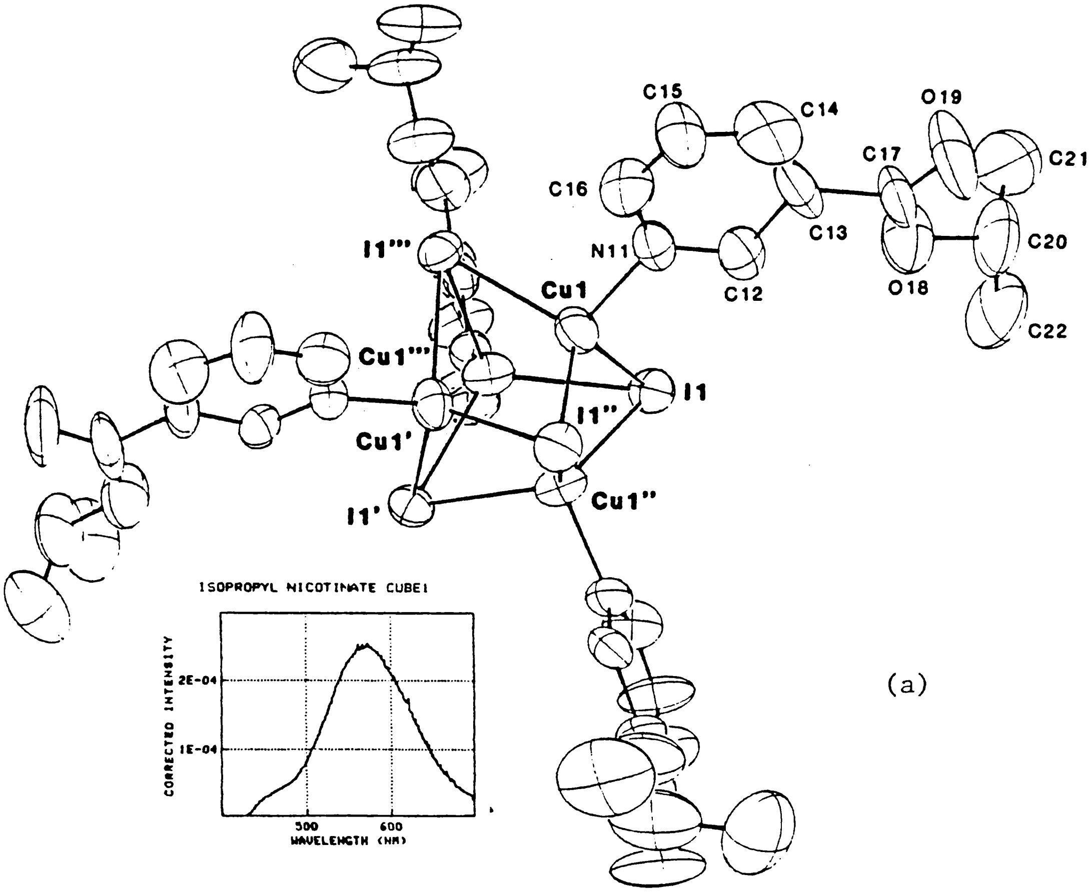


Figure 24a. Cu_4I_4(isopropylnicotinate)$_4$

(b)

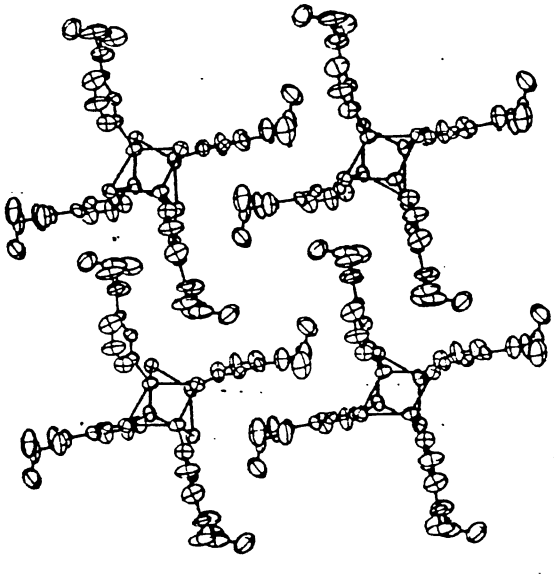
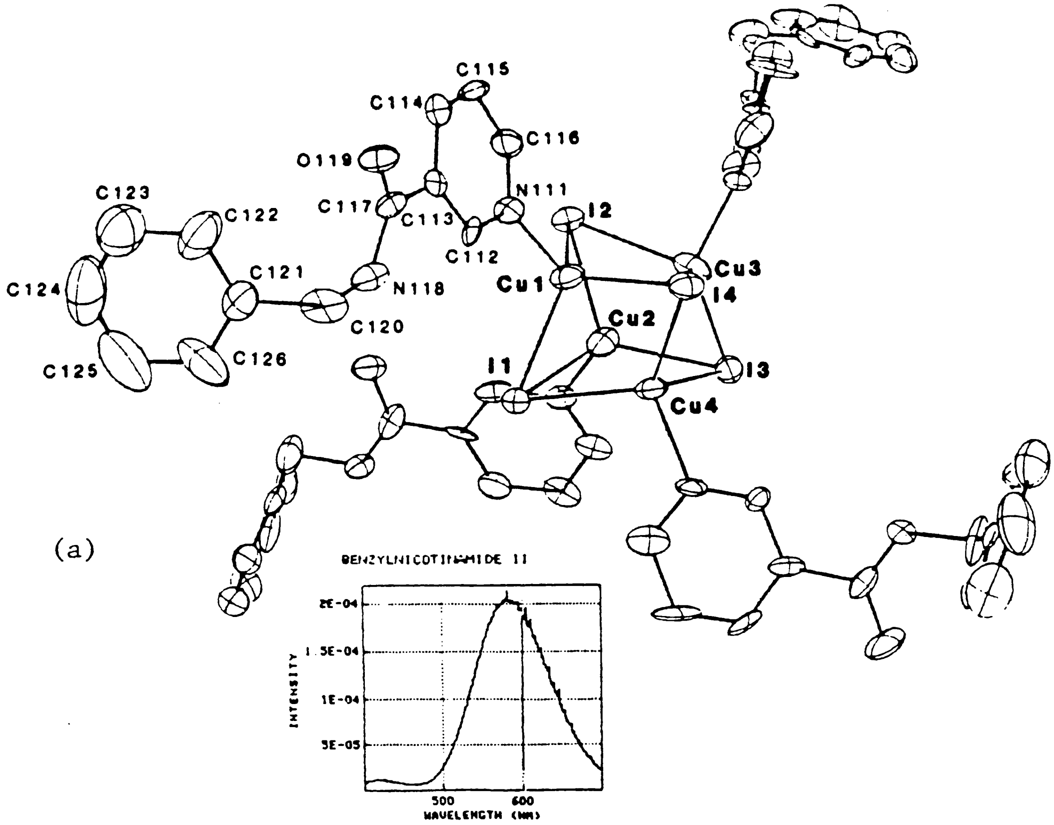


Figure 24b. Packing Diagram for Cu_4I_4(isopropylnicotinate)$_4$ View Down c Axis



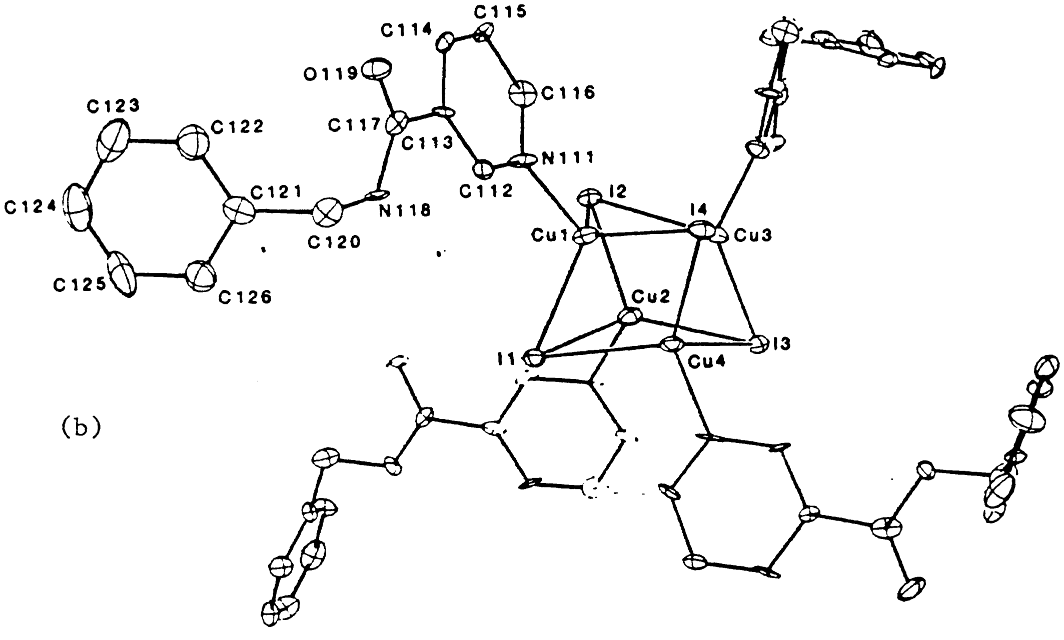
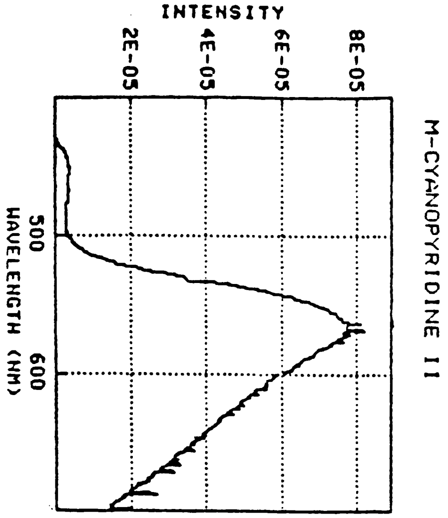


Figure 25a. Cu$_4$I$_4$(benzylnicotinamide)$_4$ Room Temperature.
Fugure 25b. Cu$_4$I$_4$(benzylnicotinamide)$_4$ Low Temperature.



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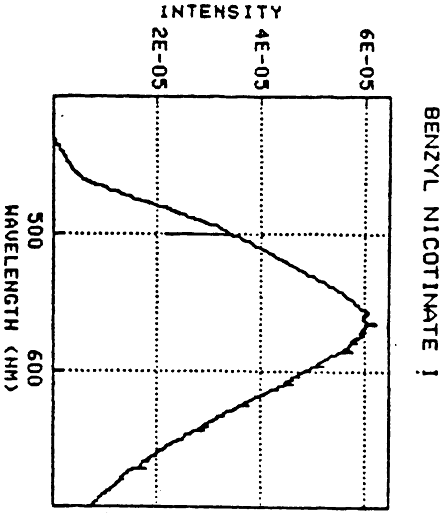

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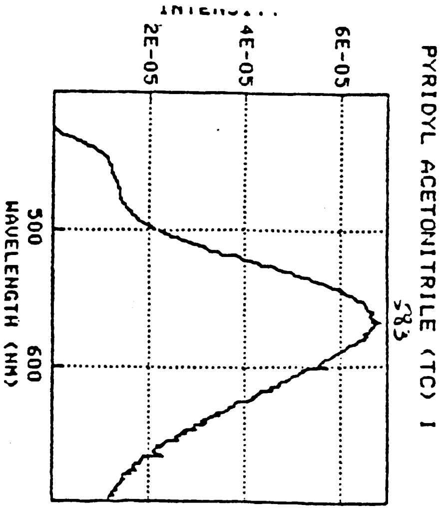

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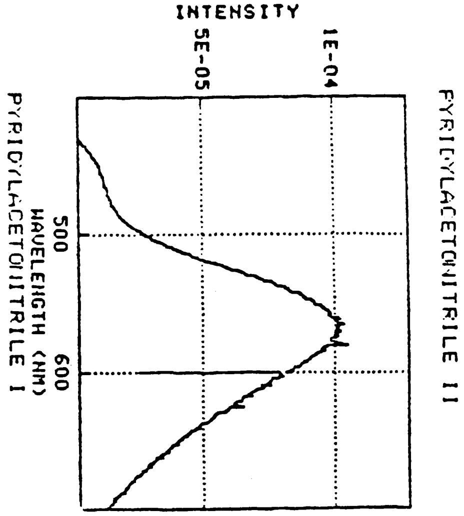

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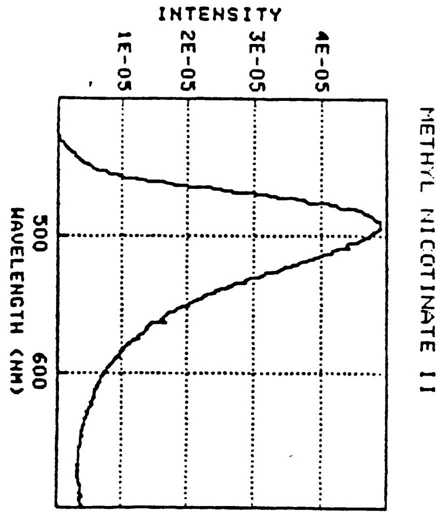

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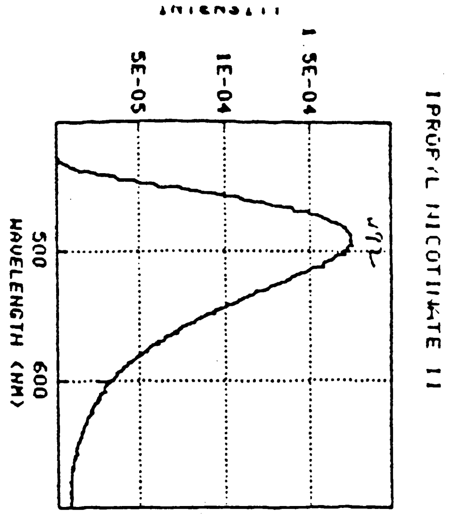
Figure 26. Emission Spectra for $(\mathrm{CuIL})_x$ Room Temperature (Structures were determined at RT and LT.)



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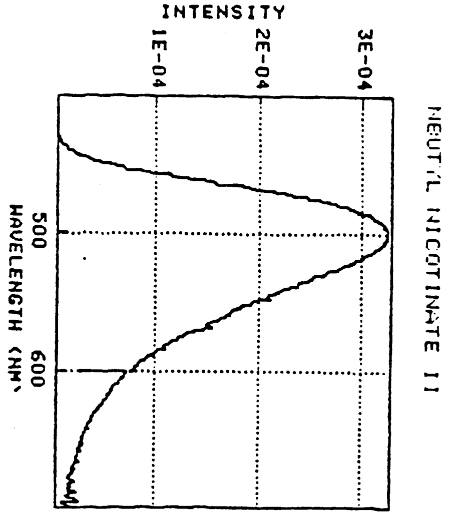

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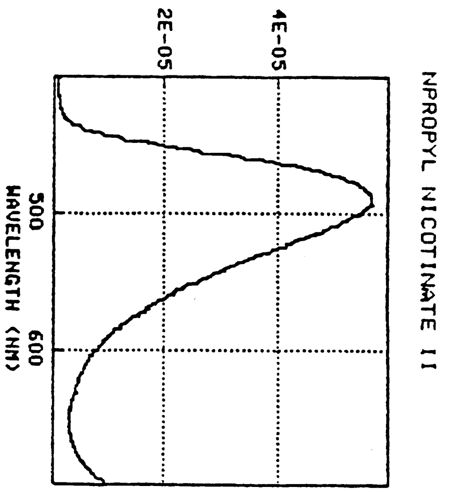

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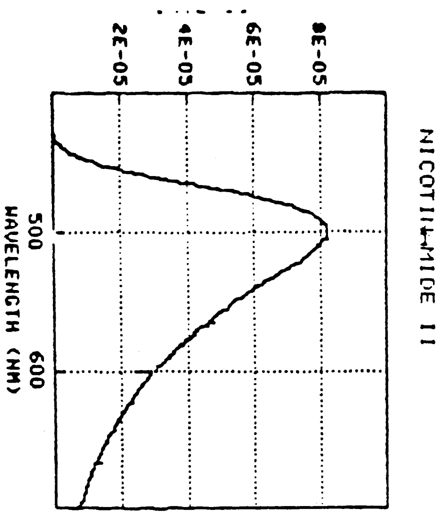

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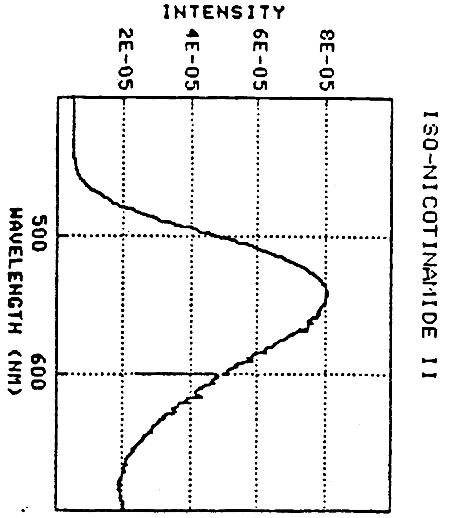

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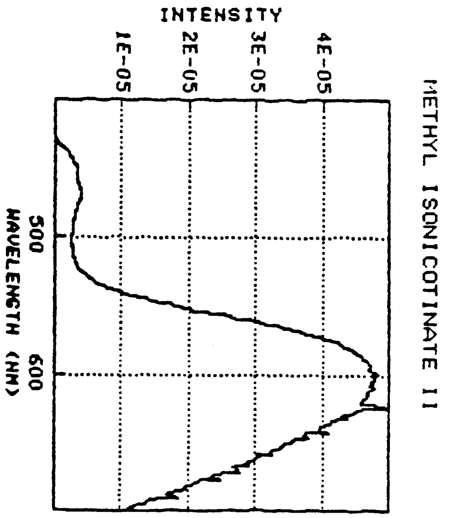

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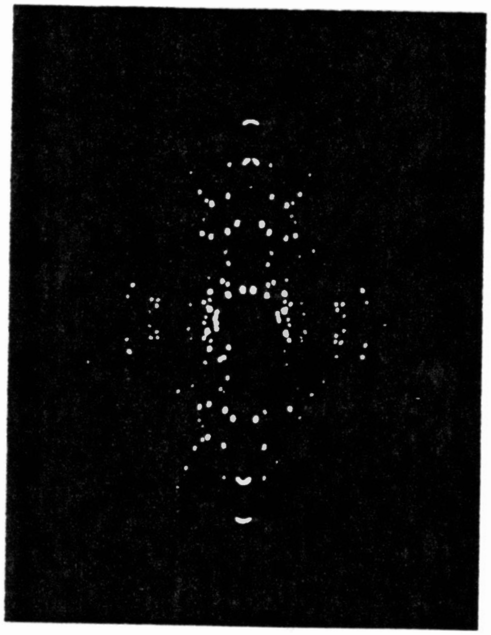
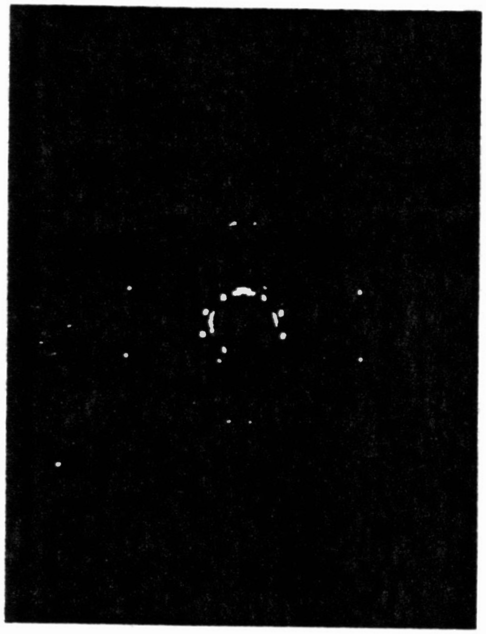
Figure 27. Emission Spectra for $(CuIL)_x$ Room Temperature.
(Entry 15 is $(CuI(nicotinamide)_2)_x$.)

④ R.T. yellow

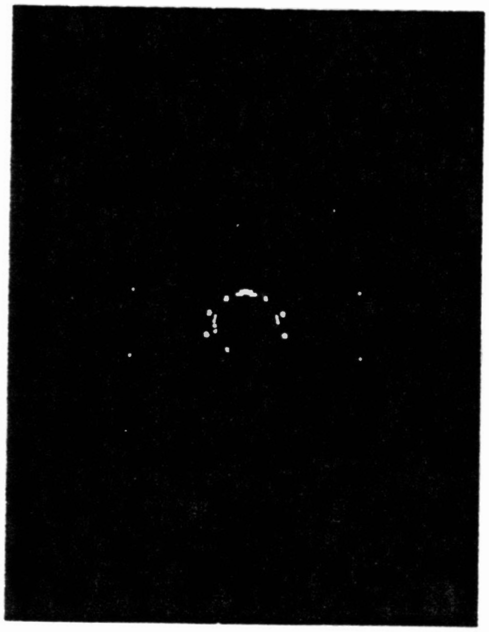


③ [illegible] blue

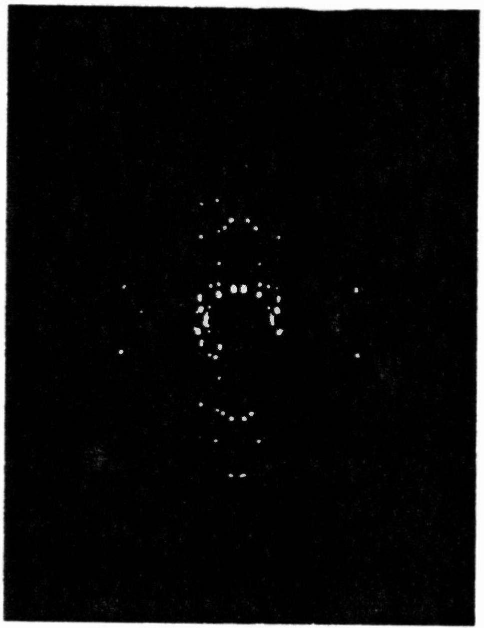


crystal was blue RATE of N_2 was 20 [illegible]

②



①



LOW TEMP 8' [illegible] crystal was yellow

Figure 28. Rotation Photographs at Room Temperature and Low Temperatures near 100K.

that symmetry cannot be generally correlated with thermochromism; because one of these materials with a two-fold axis (CuI(phenylnicotinate)$_2$)$_2$ is non-thermochromic.

The emission spectra of cubes (Figure 29) with isopropyl nicotinate and phenyl nicotinate show shoulders at 460 and 485 nm respectively consistent with the assignment of bands in this region to MLCT excitation for the polymeric pleated sheet structures of esters of nicotinic acid. The high energy shoulder at 420 nm seen for Cu$_4$I$_4$benzylnicotinamide$_4$ may be compared to the MLCT band observed at 484 nm for the (CuI(nicotinamide)$_2$)$_x$ solid but the increase in energy of the position of the MLCT band on replacement of H by benzyl is unexpected.

Room temperature emission spectra of the thermochromic species Cu$_4$I$_4$ also contain lower energy bands of greater intensity; 583 nm for isopropylnicotinate and for benzylnicotinamide. This band is absent in the room temperature spectrum of the phenylnicotinate complex. In these cubic materials, Cu...Cu distances across rhombs include shorter distances than those observed in polymeric pleated sheet structures: range 2.667(3) to 2.676(3)Å for L = isopropylnicotinate, and 2.637(8) to 2.706(7)Å for L = benzylnicotinamide. These bands may be assigned to metal - metal interactions consistent with observation of bands in the 570 - 626 nm region for other materials in which Cu...Cu separations are in a range from 2.6 - 2.7 Å. However Cu$_4$I$_4$-(phenylnicotinate)$_4$ shows a range of Cu...Cu separations of

2.640(3) - 2.820(4) which also includes short distances, but the room temperature emission spectrum shows no band in this area. The assignment of the low energy band to activity involving an additional chromophore also breaks down. Both polymeric pleated sheet, L = benzylnicotinate, and cube, L = benzylnicotinamide show low energy bands, 565 nm and 583 nm respectively. However Cu_4I_4isopropylnicotinate$_4$, with no additional aromatic system other than the heterocycle, shows this low energy band (583 nm). $((CuI(phenylnicotinate)_2)_2$ with an esterifying phenyl group shows only MLCT emission. Thus the assignment of the low energy band is not clear.

The preparation of both polymeric pleated sheet and cubic structures of isopropylnicotinate complexes with CuI provided the opportunity to make direct comparisons of emission data independent of the nature of the ligand. The polymeric pleated sheet (Figure 13) and the cubic motif (Figure 24a) both show MLCT phenomena at 460 - 492 nm. The polymeric pleated sheet with Cu...Cu separations of 2.842(3) and 2.855(3) Å shows no additional bands. The Cu_4I_4isopropylnicotinate$_4$ with copper ...copper separations which are considerably shorter (2.667(3) - 2.676(3) Å shows an additional band which appears to be metal to metal phenomena.

ORTEP drawings for the three cubic complexes are given in Figures 23 through 25. Emission spectra accompany the drawings and also appear in Figure 29.

Three other new Cu(I) iodide complexes were prepared, none of which is thermochromic. Cu_2I_2(methyl 2-pyridylacetate)$_4$ (Figure 30, Table LXXXV - XC) shows a rhombohedral arrangement of Cu_2I_2 with a Cu...Cu separation of 3.427(7) Å. The emission spectrum of this solid material shows only the MLCT band at 492 nm. The rhomb may then be compared to the non-emitting complex formed with methylquinaldate which crystallized as a single strand polymer of Cu - I - Cu - I - and methyl quinaldate molecules coordinated to copper in a bidentate fashion through nitrogen and the carbonyl of the ester group. The 2-pyridylacetate is like the quinaldate except for insertion of a CH_2 group between the heterocycle and the carbonyl at the 2- position. Both involve methyl esterification groups. The insertion of the CH_2 group thus removed the carbonyl from bonding position and emission of the solid was observed. Cu_2I_2(3-cyanopyridine)$_4$ with short Cu...Cu distance of 2.66(2)Å shows an asymmetric peak at 525 nm in the emission spectrum with a flatter slope on the high energy side.

A unique chair complex is observed for Cu_4I_4(4-cyanopyridine)$_5$ in which two Cu_2I_2 rhombohedra share a single edge (Figure 31, Table LXXIX - LXXXIV). The copper atoms not on the ends of this chair are bonded to two molecules of 4-cyanopyridine through the nitrogen of the heterocycle. The cyano- nitrogen atom of these ligands is not coordinated. However the two copper atoms of the seat of the chair are bound to a disordered 4-cyanopyridine molecule 50% through the cyano- nitrogen and 50% through the nitrogen of the heterocycle. Adjacent chair motifs are linked at these

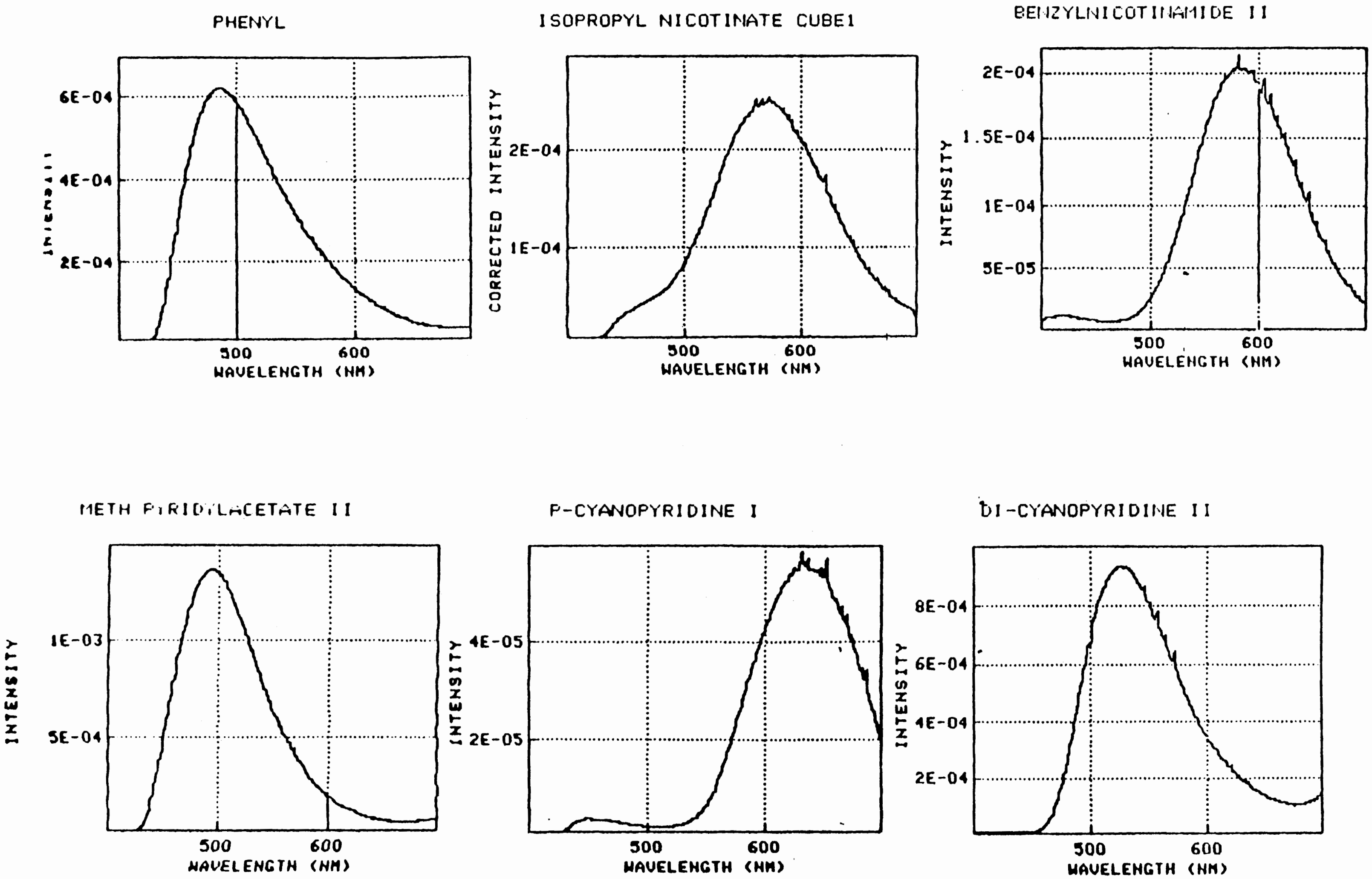


Figure 29. Emission Spectra for Cubes and Rhombs.

coppers by the bridging 4-cyanopyridines. The disorder was clearly evident from the crystallographic data. The emission spectrum of this nonthermochromic material shows a band at 625 nm (maximum). (A second peak shows at 450 nm but this emission is interference from the sample holder.) There are two possible MLCT mechanisms; Cu to ligand through the cyano- nitrogen and Cu to ligand through the heterocyclic nitrogen; the former having been previously observed for $(CuI(acetonitrile))_x$ (540 nm). Separations between copper atoms in this solid are long; 2.751(4) and 2.830(3) Å and thus metal to metal interactions are not suspected.

A second form of copper iodide 3-cyanopyridine which crystallized as a rhonb with stoichiometry of 1:1:2 (Figure 32, Table CXX - CXXIV) formed when an excess of ligand was present in the reaction and when the solvent (acetonitrile) was evaporated quickly, suggesting that this complex forms in solution first, followed by conversion to the more stable mono- complex $(CuI(3\text{-cyanopyridine})_x$. This complex showed a single emission maximum at 529 nm and was non-thermochromic. The pale green appearance of these crystals was attributed to its emission rather than absorption since Cu(I) is not colored. This property illustrates emission at a specific wavelength after excitation over a wide range of excitation wavelengths. The Cu...Cu separation of 2.660(2) Å is short but for a Cu_2 system is long enough to preclude the possibility of a Cu - Cu interaction and the assignment for this green emission is to MLCT. The emission spectrum for

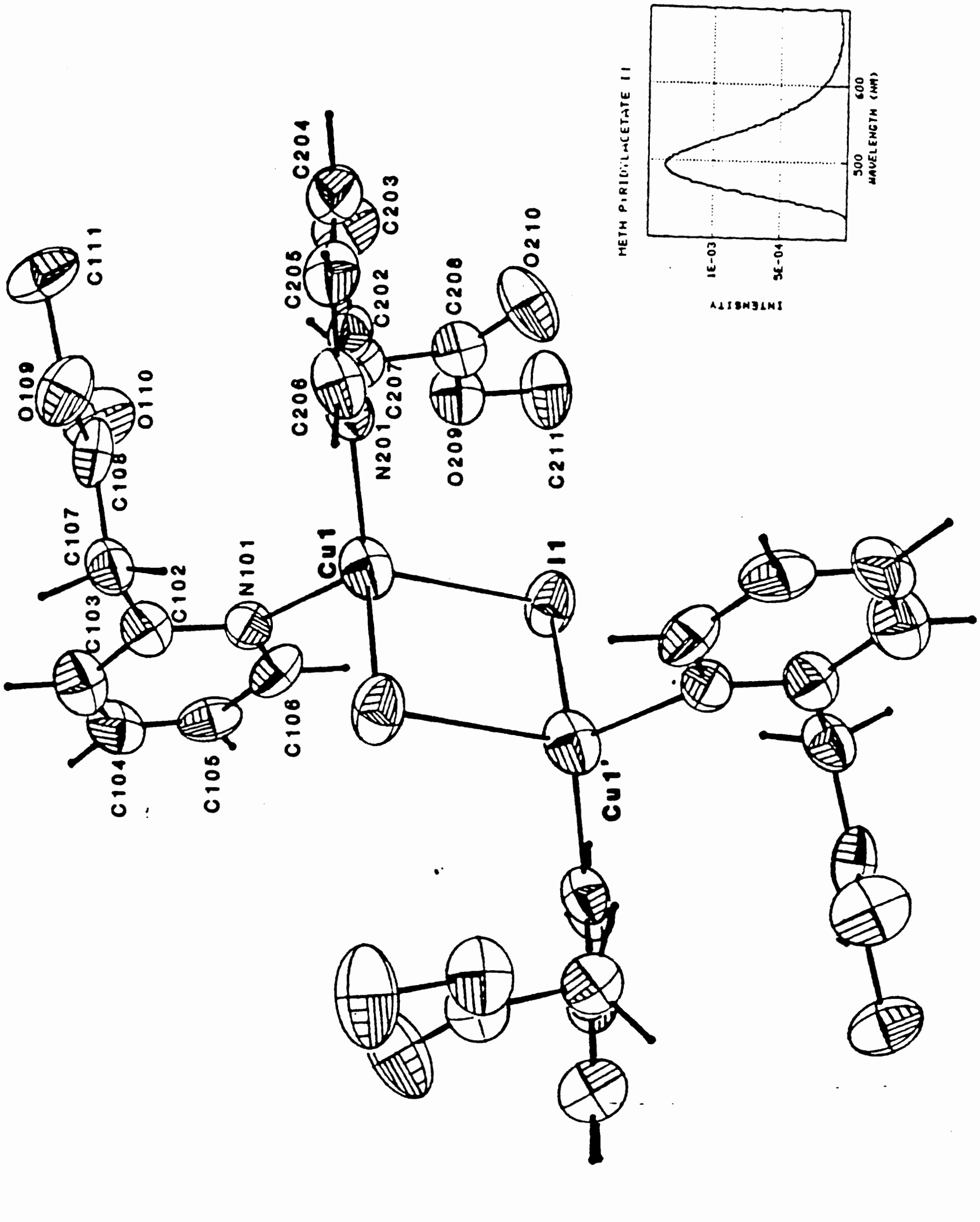


Figure 30. (CuI(methyl 2-pyridylacetate)$_2$)$_2$

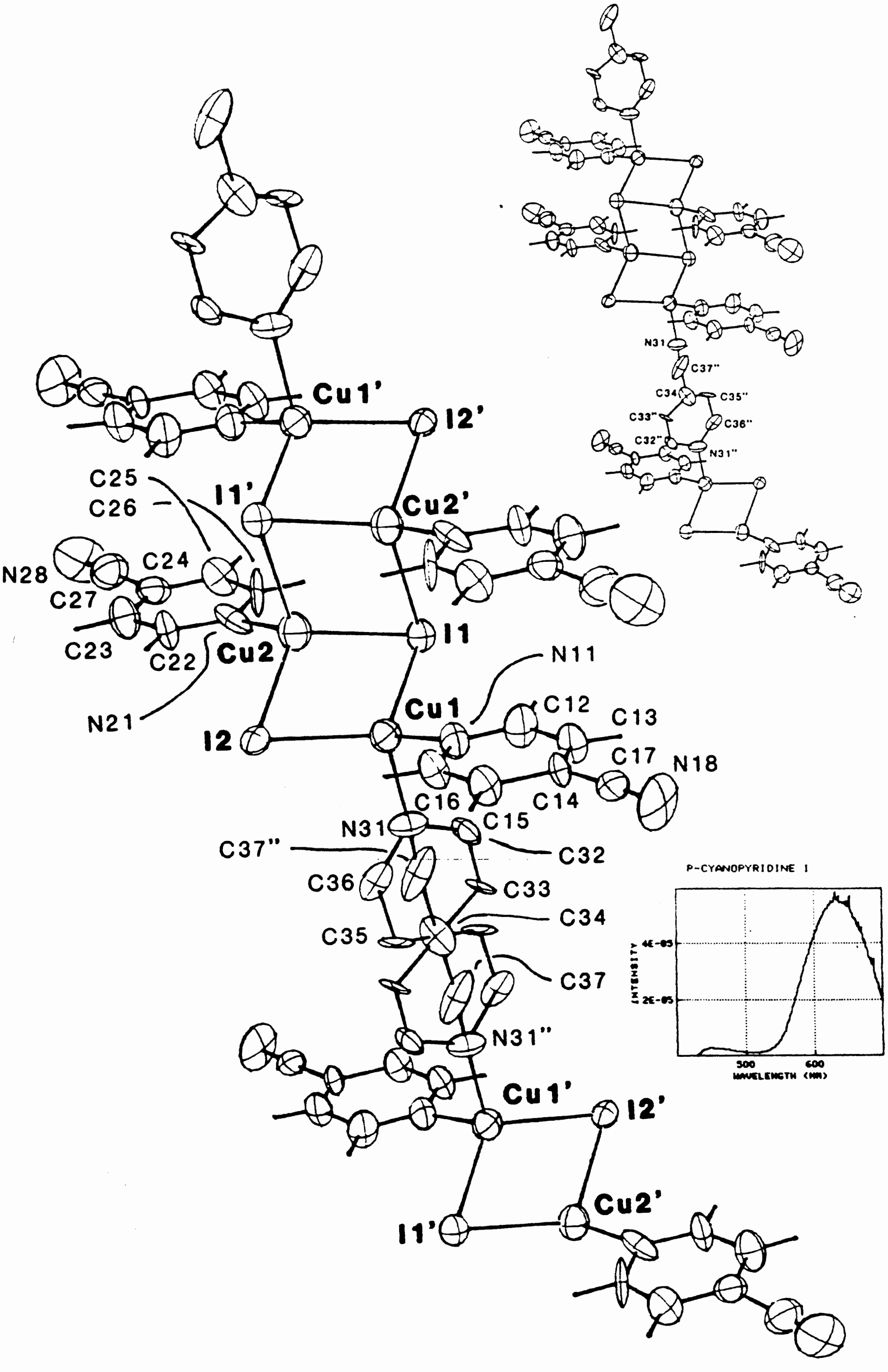


Figure 31. $(Cu_2I_2(4\text{-cyanopyridine})_{2.5})_2$ - inset, disorder about Cu3 partially resolved

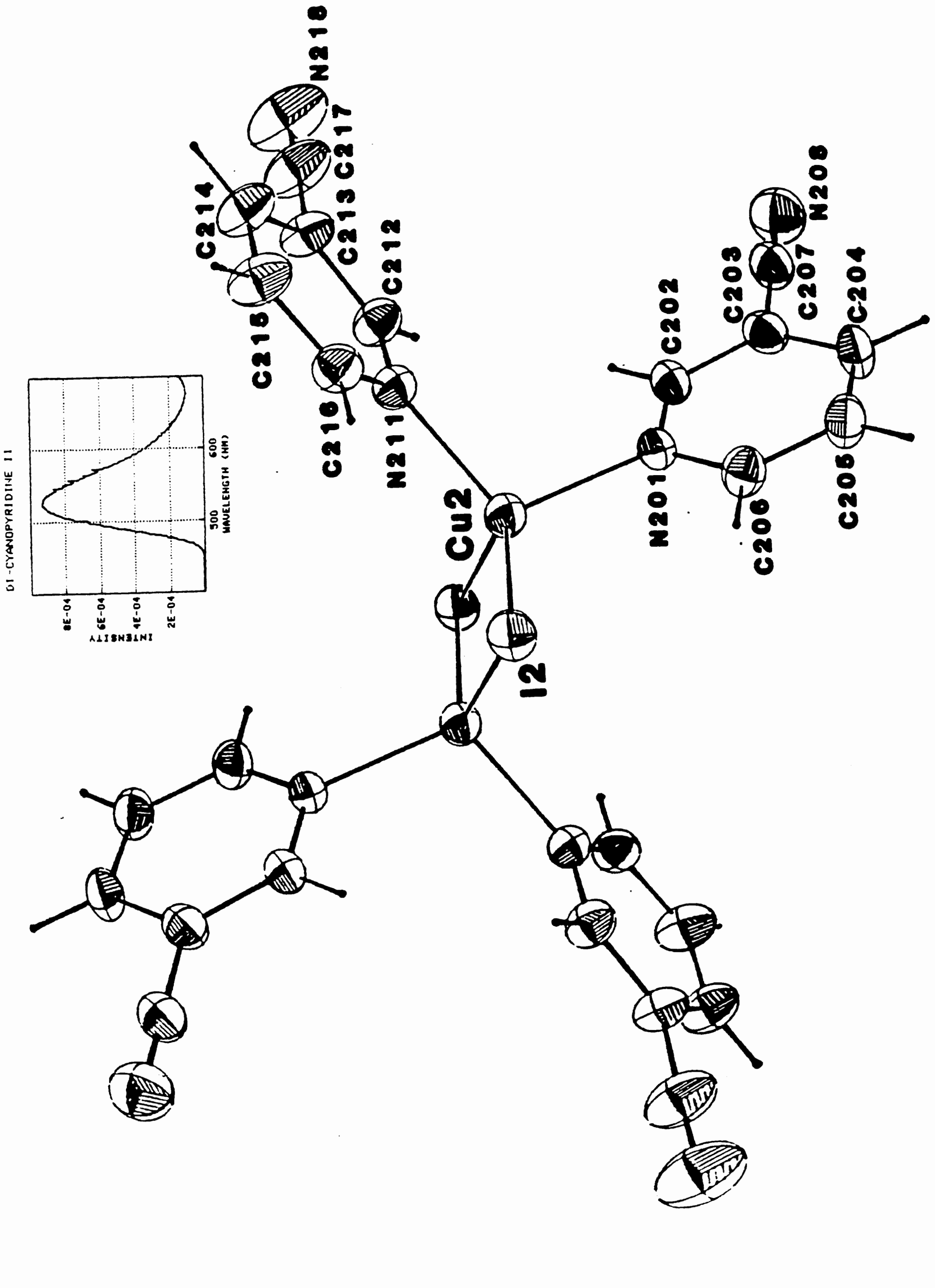


Figure 32. $(CuI(3\text{-cyanopyridine})_2)_2$

$(CuI(3\text{-cyanopyridine})_2)_2$ is shown in Figure 29.

The examination of room temperature data for polymeric pleated sheet and cube structures of copper(I) iodide complexed with Lewis base ligands (nitrogen heterocycles with donor pairs of electrons) does not permit prediction of the thermochromic behavior of the emission of these solids. A comparison of the changes in crystal structure on cooling these solid materials to 100K does not reveal interpretable changes in copper geometry or unit cell packing for thermochromic materials which are different from those seen for non-thermochromic materials. All unit cells contract in volume. All bond distances decrease. The 100K structures do not show more significant changes for thermochromic materials. However, a number of the thermochromic materials show distinct signs of onset of disorder at low temperatures. Those solids which showed onset of disorder also emitted blue at 100K and yellow at room temperature. No materials of temperature independent emission showed such disorder. The disorder appears reversible and does not involve crystal fracture or decomposition, suggesting a second order phase change, which does not involve loss of crystal component or significant unit cell reorganization, but rather one in which there is distortion of rhombohedra or angles at copper in reversible fashion. It was not possible to document such changes within the range of temperature of which the current diffractometer equipment is capable.

All thermochromic materials show a band in the 570 - 630 nm region in addition to the expected MLCT emission at lower wavelengths. The assignment of this band to metal - metal interactions is not entirely consistent in as much as this emission does not always appear in solids which display Cu...Cu interactive distances of 2.67 Å (as in $(Cu_2I_2(\text{phenylnicotinate})_2)_2$) yet does appear in thermochromic materials which do not display Cu...Cu interactive distances as in $(CuI(\text{benzylnicotinate}))_x$ and $(CuI(\text{3-pyridylacetonitrile}))_x$. Whether or not this band is present depends, in at least one instance, on the method of preparation.

Sample preparation is an important factor in the emission behavior of these solids. Thus samples of $(CuI(\text{3-pyridylacetonitrile}))_x$ crystallized from various solvent systems showed altered emission behavior (thermochromic or non-thermochromic). The interpretation of these data is complicated by the realities of the X-ray and emission experiments. The X-ray data arises from the bulk of the solid with the surface involving only a minor number of unit cells. The surface unit cells contribute relatively little to the diffraction of the solid. However, the luminescence measurements are made from the surface of the material only. The altered emission may arise because of impurities (excess ligand or solvent) which are included in the unit cells near the surface or throughout the crystal but in a disordered fashion. At low temperature, these thermochromically emitting substances behave like glasses in which ligand molecules of the complex may interact with included molecules. The increased R factors are further evidence of their glass-like nature at 100K and below. Thus it is possible that the solid as seen by the diffractometer has little or no solvent content, whereas the unit cells as seen by the emission phenomena do in reality include solvent. Further work in this area whould involve an evaluation of these effects at temperatures below that of liquid nitrogen.

The Cu_4I_4(benzylnicotinate)$_4$ complex behaved differently in both emission and crystallographic properties. For complexes such as this one, being approximately spherical in structure, there is the likelihood for first order phase changes which involves a change in internal symmetry. In the experiment reported in this work, the improvement of R factor at low temperature but a relatively poor R factor at room temperature indicates that the triclinic space group chosen does not fit the observered data very well at room temperature. This suggests that at some value above room temperature the space group may be of higher symmetry. The low temperature determination shows distortion of angles about copper and the emission changes from yellow at room temperature to orange at low temperature. Thus the thermochromism for this complex is associated with distortion about copper atoms which is not seen in any other structure determination in this work.

Eighteen new solid state materials of the composition CuI(L) have been prepared and characterized by single crystal X-ray diffraction and by emission techniques. Eleven of these are of the family; $(CuI(L)_x$. Comparison of the structural details has permitted the determination of 'standard' structural parameters for this motif on which further comparisons can be based. The three cubic motifs studied here display three different types of emission behavior. Future work on cubes should involve a compilation of all known cubic structures to determine their 'standard' parameters and a comparison of luminescent properties. A suggestion for future work on luminescent copper(I) complexes should involve syntheses and characterization of those in which substituted nicotinamides are used as ligands.

TABLE I

CRYSTAL DATA FOR COPPER IODIDE n-BUTYL NICOTINATE

Formula	$(CuIC_{10}H_{13}NO_2)_n$
Mwt	369.668
<u>a</u>	4.215(1) Å
<u>b</u>	8.971(4)
<u>c</u>	15.689(7)
α	71.53(3)°
β	89.93(3)
γ	102.13(3)
V	609.8(5) $Å^3$
F(OOO)	356
μMoK_{α}	42.8127 cm^{-1}
λMoK_{α}	0.71069 Å
D_{calc}	2.0129 g cm^{-3}
Z	2
Meas. Refl.	1611
Obs. Refl.	1439
R	3.9%
R_w	6.15%
Space Group	$P\bar{1}$
Octants Meas.	±h, k, ±l

TABLE II

POSITIONAL PARAMETERS FOR COPPER IODIDE n-BUTYL NICOTINATE

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.3476(1)	0.1953(1)	0.9080(0)
Cu1	0.7933(3)	0.0871(1)	1.0136(1)
O18	0.2399(24)	-0.0211(9)	1.3487(5)
O19	0.3994(101)	0.1805(75)	1.3874(43)
N11	0.8443(21)	0.1857(9)	1.1117(6)
C12	0.6325(51)	0.1245(9)	1.1877(13)
C13	0.5948(51)	0.1936(24)	1.2497(15)
C14	0.7574(63)	0.3372(24)	1.2302(16)
C15	0.9523(34)	0.3996(12)	1.1530(9)
C16	0.9877(97)	0.3196(68)	1.0991(41)
C17	0.3772(97)	0.1274(55)	1.3341(30)
C20	0.0639(58)	-0.1017(30)	1.4265(16)
C21	-0.0067(69)	-0.2575(30)	1.4320(18)
C22	-0.1412(63)	-0.2820(30)	1.3468(17)
C23	-0.2510(73)	-0.4387(31)	1.3548(18)
O119	1.2869(97)	0.1866(65)	1.3783(34)
C112	0.9911(53)	0.1231(22)	1.1888(14)
C113	1.1022(46)	0.1957(22)	1.2493(14)
C114	1.0794(66)	0.3386(23)	1.2293(16)
C116	0.8569(93)	0.3260(55)	1.0920(33)
C117	1.2409(84)	0.1183(64)	1.3315(40)

TABLE II (Continued)

C120	0.3350(73)	-0.0994(29)	1.4261(16)
C121	0.2566(75)	-0.2559(31)	1.4315(16)
C122	0.3594(65)	-0.2817(28)	1.3482(17)
C123	0.2985(74)	-0.4392(29)	1.3578(18)

TABLE III

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE n-BUTYL NICOTINATE

ATOM	X	Y	Z
H12	0.5003	0.0260	1.1980
H14	0.7364	0.3923	1.2691
H15	1.0668	0.5022	1.1366
H16	1.1316	0.3672	1.0413
H201	0.1914	-0.0883	1.4760
H202	-0.1372	-0.0724	1.4298
H211	0.2055	-0.2894	1.4406
H212	-0.1537	-0.3137	1.4808
H221	-0.3168	-0.2349	1.3300
H222	0.0355	-0.2378	1.2970
H231	-0.2372	-0.4988	1.4165
H232	-0.4625	-0.4603	1.3349
H233	-0.0951	-0.4632	1.3165
H112	1.0162	0.0225	1.2017
H114	1.1575	0.3923	1.2709
H115	0.9168	0.4979	1.1376
H116	0.7904	0.3801	1.0362
H1201	0.5638	-0.0685	1.4325
H1202	0.2122	-0.0901	1.4765
H1211	0.3669	-0.3113	1.4789
H1212	0.0215	-0.2949	1.4435

TABLE III (Continued)

H1221	0.2288	-0.2340	1.3003
H1222	0.5837	-0.2372	1.3321
H1231	0.3580	-0.5022	1.4137
H1232	0.0669	-0.4759	1.3499
H1233	0.4266	-0.4575	1.3100

TABLE IV

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE n-BUTYL NICOTINATE

ATOM	U11	U22	U33	U12	U13	U23
I1	33(0)	31(0)	47(0)	7(0)	0(0)	-7(0)
Cu1	55(0)	39(0)	47(0)	9(0)	-2(0)	-18(0)
O18	109(7)	50(5)	42(5)	10(5)	0(5)	-21(4)
O19	56(25)	75(17)	63(20)	12(19)	-33(17)	-32(15)
N11	49(5)	30(5)	42(5)	1(4)	3(4)	-14(4)
C12	49(12)	31(11)	34(11)	9(9)	-3(9)	-12(9)
C13	43(12)	48(13)	51(13)	24(10)	-24(10)	-19(11)
C14	69(17)	36(13)	62(16)	0(11)	5(13)	-29(12)
C15	87(9)	22(5)	74(9)	2(6)	-2(7)	-21(6)
C16	50(27)	53(23)	64(24)	7(22)	-13(22)	-9(18)
C17	48(26)	43(18)	23(15(	-3(23)	-14(20)	-12(12)
C20	38(13)	85(18)	47(14)	5(12)	1(11)	-40(14)
C21	58(17)	61(17)	58(16)	1(14)	0(14)	-6(13)
C22	61(16)	71(18)	62(16)	3(13)	-17(13)	-27(14)
C23	85(20)	61(17)	70(18)	1(15)	-13(15)	-17(15)
O119	65(27)	68(14)	38(14)	23(21)	-26(17)	-42(11)
C112	49(12)	34(11)	36(12)	0(9)	-4(10)	-8(10)
C113	30(10)	39(12)	43(12)	-6(9)	4(9)	-19(10)
C114	84(19)	29(12)	45(14)	0(12)	16(13)	-15(10)
C116	60(28)	28(14)	35(14)	26(21)	-26(20)	-12(11)
C117	31(22)	52(19)	66(25)	-9(21)	-20(20)	-31(16)

TABLE IV (Continued)

C120	85(21)	64(17)	42(14)	22(15)	-21(13)	-31(13)
C121	76(20)	76(19)	37(14)	23(16)	-16(14)	-13(13)
C122	72(17)	61(16)	59(16)	24(13)	-1(13)	-19(13)
C123	94(21)	51(15)	71(18)	19(14)	4(15)	-23(14)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C, N, and O.

TABLE V

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE n-BUTYL NICOTINATE

I1 - Cu1	2.693(2)	Cu1 - I1 - Cu1''	103.00(5)
I1 - Cu1''	2.693(2)	Cu1 - I1 - Cu1'''	64.20(5)
I1 - Cu1''''	2.629(2)	Cu1'' - I1 - Cu1''''	64.18(5)
Cu1 - Cu1'''	2.828(2)	I1 - Cu1 - I1'	103.01(4)
Cu1 - Cu1''''	2.928(2)	I1 - Cu1 - I1''''	115.80(5)
Cu1 - N11	2.09(1)	I1' - Cu1 - I1''''	115.82(7)
N11 - C12	1.39(2)	I1 - Cu1 - N11	107.0(3)
N11 - C16	1.30(6)	I1' - Cu1 - N11	106.6(2)
C12 - C13	1.40(4)	I1'''' - Cu1 - N11	107.9(2)
C13 - C14	1.39(3)	C12 - N11 - C16	113(3)
C13 - C17	1.51(5)	C16 - N11 - Cu1	125(3)
C14 - C15	1.37(3)	C12 - N11 - Cu1	119(1)
C15 - C16	1.37(8)	N11 - C12 - C13	125(2)
C17 - O18	1.41(5)	C12 - C13 - C14	118(2)
C17 - O19	1.1(1)	C13 - C14 - C15	118(2)
O18 - C20	1.36(2)	C14 - C15 - C16	120(2)
C20 - C21	1.49(4)	C12 - C13 - C17	125(3)
C21 - C22	1.55(4)	C14 - C15 - C16	120(2)
C22 - C23	1.50(4)	C15 - C16 - N11	111(4)
		C13 - C17 - O18	111(4)
N11 - C112	1.40(2)	C13 - C17 - O19	121(4)
N11 - C116	1.32(6)	O18 - C17 - O19	124(4)
C112 - C113	1.41(3)	C17 - O18 - C20	119(2)

TABLE V (Continued)

C113 - C114	1.38(3)	O18 - C20 - C21	109(2)
C113 - C117	1.49(6)	C20 - C21 - C22	113(2)
C114 - C15	1.35(3)	C21 - C22 - C23	114(2)
C15 - C116	1.41(6)		
C117 - O18	1.33(6)	C112 - N11 - C116	115(2)
C117 - O119	1.1(1)	C112 - N11 - Cul	119(1)
O18 - C120	1.35(3)	C116 - N11 - Cul	125(3)
C120 - C121	1.50(4)	N11 - C112 - C113	124(2)
C121 - C122	1.51(4)	C112 - C113 - C114	118(2)
C122 - C123	1.49(4)	C112 - C113 - C117	122(3)
C122 - C123	1.49(4)	C113 - C114 - C15	118(2)
		C114 - C15 - C116	123(2)
		C15 - C116 - N11	122(3)
		C113 - C117 - O18	119(5)
		C113 - C117 - O119	111(5)
		O18 - C117 - O119	129(5)
		C117 - O18 - C120	121(3)
		O18 - C120 - C121	108(2)
		C120 - C121 - C122	114(2)
		C121 - C122 - C123	113(2)

Symmetry operations:

' = x + 1, y, z

'' = x - 1, y, z

''' = 2 - x, -y, 2 - z

TABLE V (Continued)

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

TABLE VI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE n-BUTYL NICOTINATE

C12 - H12	0.98	N11 - C12 - H12	117
C14 - H14	0.97	C13 - C12 - H12	118
C15 - H15	0.98	C13 - C14 - H14	122
C16 - H16	1.02	C15 - C14 - H14	120
C20 - H201	0.99	C16 - C15 - H15	120
C20 - H202	0.96	C14 - C15 - H15	119
C21 - H211	1.00	N11 - C16 - H16	114
C21 - H212	0.94	C15 - C16 - H16	120
C22 - H221	0.96	O18 - C20 - H201	109
C22 - H222	1.01	O18 - C20 - H202	109
C23 - H231	0.99	H201 - C20 - C21	110
C23 - H232	0.95	H202 - C20 - C21	109
C23 - H233	1.01	H201 - C20 - H202	109
		C20 - C21 - H211	107
C112 - H112	0.99	C20 - C21 - H212	110
C114 - H114	1.00	H211 - C21 - H212	109
C15 - H115	0.98	H211 - C21 - C22	108
C116 - H116	0.96	H212 - C21 - C22	110
C120 - H1201	0.96	C21 - C22 - H221	110
C120 - H1202	1.00	C21 - C22 - H222	109
C121 - H1211	0.99	H221 - C22 - H222	108
C121 - H1212	0.98	H221 - C22 - C23	109
C122 - H1221	1.00	H222 - C22 - C23	107

TABLE VI (Continued)

C122 - H1222	0.95	C22 - C23 - H231	109
C123 - H1231	0.98	C22 - C23 - H232	112
C123 - H1232	0.99	C22 - C23 - H233	109
C123 - H1233	1.02	H231 - C23 - H232	112
		H231 - C23 - H233	107
		H232 - C23 - H233	107
		N11 - C112 - H112	118
		C113 - C112 - H112	118
		C113 - C114 - H114	120
		C15 - C114 - H114	123
		C114 - C15 - H115	121
		C116 - C15 - H115	116
		N11 - C116 - H116	121
		C15 - C116 - H116	118
		O18 - C120 - H1201	113
		O18 - C120 - H1202	110
		H1201 - C120 - H1202	107
		H1201 - C120 - C121	110
		H1202 - C120 - C121	108
		C120 - C121 - H1211	110
		C120 - C121 - H1212	110
		H1211 - C121 - C122	107
		H1212 - C121 - C122	108
		C121 - C122 - H122	107
		C121 - C122 - H1222	119

TABLE VI (Continued)

	H1211 - C122 - H1222	109
	H1222 - C122 - C123	110
	C122 - C123 - H1231	116
	C122 - C123 - H1232	110
	C122 - C123 - H1233	112
	H1231 - C123 - H1232	109
	H1231 - C123 - H1233	105
	H1232 - C123 - H1233	105

TABLE VII

CRYSTAL DATA FOR COPPER IODIDE ISOPROPYL NICOTINATE

Formula	$(CuIC_9H_{11}NO_2)_n$
Mwt	355.6414
a	17.605(8) Å
b	8.630(2)
c	4.317(2)
α	104.64(3)°
β	68.24(3)
γ	81.01(3)
V	566.3(4) $Å^3$
F(000)	340
μMoK_α	46.0593 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.0652 g cm^{-3}
Z	2
Meas. Refl.	3082
Obs. Refl.	1928
R	5.6%
R_w	7.0%
Space Group	$P\bar{1}$
Octants Meas.	±h, k, ±l

TABLE VIII

POSITIONAL PARAMETERS FOR COPPER IODIDE ISOPROPYL NICOTINATE

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.0681(0)	0.1601(1)	0.2279(2)
Cu1	-0.0214(1)	0.1154(2)	-0.1603(2)
O18	-0.3288(5)	0.2403(11)	0.8648(25)
O119	-0.3803(12)	0.5135(22)	1.2231(47)
N11	-0.1278(6)	0.3099(13)	0.0955(29)
C12	-0.1923(12)	0.2883(25)	0.4023(53)
C13	-0.2590(16)	0.4212(32)	0.6644(61)
C14	-0.2625(14)	0.5864(27)	0.6584(52)
C15	-0.1968(8)	0.6059(16)	0.3526(42)
C16	-0.1287(27)	0.4691(44)	0.1310(83)
C17	-0.3285(7)	0.3994(16)	0.9405(30)
C20	-0.3901(14)	0.2010(30)	1.1905(58)
C21	-0.4729(15)	0.2345(40)	1.1740(75)
C22	-0.3486(20)	0.0191(36)	1.1247(87)
O19	-0.3812(11)	0.5144(23)	0.9401(57)
C112	-0.1932(14)	0.2901(31)	-0.0335(59)
C113	-0.2603(12)	0.4234(27)	0.0347(50)
C114	-0.2601(15)	0.5835(29)	0.2094(68)
C116	-0.1345(24)	0.4636(54)	0.2399(87)
C120	-0.3884(14)	0.1967(33)	-0.3280(60)
C121	-0.4760(17)	0.2289(42)	-0.0292(73)

TABLE VIII (Continued)

C122	-0.3450(74)	0.0133(39)	-0.5742(105)

TABLE IX

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE ISOPROPYL NICOTINATE

ATOM	U11	U22	U33	U12	U13	U23
I1	47(0)	43(0)	32(0)	-23(0)	-21(0)	20(0)
Cu1	45(0)	45(0)	56(0)	-11(0)	-18(0)	16(0)
O18	42(4)	42(4)	73(6)	-10(3)	-15(4)	13(3)
O119	63(11)	47(10)	47(9)	4(8)	-16(9)	8(8)
N11	37(5)	43(6)	66(7)	-11(4)	-13(4)	10(5)
C12	27(9)	30(0)	34(9)	2(7)	-3(8)	12(8)
C13	60(15)	53(14)	41(12)	-25(12)	-28(11)	18(11)
C14	47(13)	36(11)	26(9)	1(9)	-11(9)	2(8)
C15	47(7)	37(6)	86(10)	-10(5)	-18(7)	20(6)
C16	66(9)	39(12)	18(16)	-27(11)	-20(15)	-27(12)
C17	39(6)	55(7)	39(5)	-8(5)	-16(4)	22(5)
C20	35(11)	51(13)	36(10)	3(9)	-1(9)	23(10)
C21	24(12)	97(22)	51(13)	-18(12)	-17(11)	29(15)
C22	69(19)	51(17)	79(21)	-11(14)	-9(16)	37(15)
O19	46(10)	57(11)	90(14)	0(8)	-41(10)	26(10)
C112	35(11)	65(15)	44(11)	-24(10)	-30(9)	18(11)
C113	27(10)	46(12)	31(9)	-14(8)	-14(8)	15(8)
C114	47(13)	40(12)	64(15)	-11(10)	-29(12)	27(12)
C116	52(14)	72(19)	21(17)	-34(12)	-15(13)	39(14)
C120	33(11)	65(16)	38(11)	-8(10)	-13(9)	20(11)
C121	44(15)	105(24)	46(14)	-31(15)	-26(12)	27(15)

TABLE IX (Continued)

C122	102(26)	48(17)	105(28)	-16(17)	-59(23)	5(18)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C, N, and O.

TABLE X

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE ISOPROPYL NICOTINATE

I1 - Cu1	2.695(2)	Cu1 - I1 - Cu1'	106.6(6)
I1 - Cu1'	2.688(2)	Cu1 - I1 - Cu1''	64.99(6)
I1 - Cu1'''	2.618(2)	Cu1' - I1 - Cu1'''	65.75(6)
Cu1 - Cu1'''	2.855(3)	I1 - Cu1 - I1''	106.62(8)
Cu1 - Cu1''''	2.842(3)	I1 - Cu1 - I1'''	115.01(8)
Cu1 - N11	2.023(9)	I1'' - Cu1 - I1'''	115.25(6)
N11 - C12	1.47(2)	I1 - Cu1 - N11	105.9(4)
N11 - C16	1.34(4)	I1' - Cu1 - N11	105.2(4)
C12 - C13	1.38(2)	I1''' - Cu1 - N11	108.1(3)
C13 - C14	1.42(4)	Cu1 - N11 - C12	113(1)
C13 - C17	1.43(3)	Cu1 - N11 - C16	125(2)
C14 - C15	1.47(3)	C12 - N11 - C16	114(2)
C15 - C16	1.37(3)	N11 - C12 - C13	122(2)
C17 - O18	1.33(2)	C12 - C13 - C14	120(2)
C17 - O19	1.25(3)	C12 - C13 - C17	122(2)
O18 - C20	1.58(3)	C14 - C13 - C17	117(2)
C20 - C21	1.47(4)	C13 - C14 - C15	117(1)
		C15 - C16 - N11	126(3)
N11 - C112	1.47(3)	C13 - C17 - O18	111(3)
N11 - C116	1.28(4)	C13 - C17 - O119	125(2)
C112 - C113	1.40(3)	O18 - C17 - O119	124(1)
C113 - C114	1.40(3)	C17 - O18 - C20	113(1)
C113 - C17	1.43(3)	O18 - C20 - C21	104(2)

TABLE X (Continued)

C114 - C15	1.48(4)	O18 - C20 - C22	104(2)
C15 - C116	1.35(4)	C21 - C20 - C22	116(3)
C17 - O119	1.26(2)	C112 - N111 - C116	112(2)
O18 - C120	1.60(3)	N11 - C112 - C113	123(2)
C120 - C121	1.53(3)	C112 - C113 - C114	118(2)
		C112 - C113 - C17	122(2)
		C114 - C113 - C17	120(2)
		C113 - C114 - C15	120(2)
		C114 - C15 - C116	113(2)
		C15 - C116 - N11	133(4)
		C113 - C17 - O18	111(1)
		O18 - C17 - O19	124(2)
		C17 - O18 - C120	113(1)
		O18 - C120 - C121	105(2)
		O18 - C120 - C122	105(2)
		C121 - C120 - O119	111(5)
		O18 - C117 - O119	129(5)
		C117 - O18 - C120	121(3)
		O18 - C120 - C121	108(2)
		C120 - C121 - C122	114(2)
		C121 - C120 - C122	115(3)

Symmetry operations:

' = x, y, z + 1

'' = x, y, z - 1

TABLE X (Continued)

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

'''' = -x, -y, -1 - z

TABLE XI

CRYSTAL DATA FOR COPPER IODIDE n-PROPYL NICOTINATE

Formula	$(CuIC_9H_{11}NO_2)_n$
Mwt	355.6414
<u>a</u>	4.261(1) Å
<u>b</u>	9.23(1)
<u>c</u>	15.64(1)
α	106.51(8)°
β	97.77(7)
γ	103.54(8)
V	559.7(9) $Å^3$
F(OOO)	340
μMoK_α	46.6024 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.1098 g cm^{-3}
Z	2
Meas. Refl.	2703
Obs. Refl.	1618
R	6.1%
R_w	8.0%
Space Group	$P\bar{1}$
Octants Meas.	±h, k, ±l

TABLE XII

POSITIONAL PARAMETERS FOR COPPER IODIDE n-PROPYL NICOTINATE

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.2715(2)	0.1262(1)	-0.0831(1)
Cu1	0.1857(5)	-0.1095(2)	-0.0188(1)
O18	0.4185(29)	-0.3089(13)	-0.3533(7)
O19	0.4184(62)	-0.5669(27)	-0.3931(16)
N11	0.0304(36)	-0.3138(14)	-0.1262(9)
C12	0.2075(65)	-0.3171(31)	-0.1978(16)
C13	0.2078(70)	-0.4546(38)	-0.2653(19)
C14	0.0468(79)	-0.4546(38)	0.2653(19)
C15	-0.1330(53)	-0.5978(20)	-0.1818(13)
C16	-0.0413(49)	-0.4552(20)	-0.1187(12)
C17	0.3509(34)	-0.4533(18)	-0.3429(10)
C20	0.5991(82)	-0.3003(39)	-0.4277(23)
C21	0.6082(93)	-0.1378(36)	-0.4400(24)
C22	0.8104(118)	-0.0013(41)	-0.3568(27)
O119	0.1369(64)	-0.5629(24)	-0.3917(15)
C112	-0.2232(66)	-0.3156(31)	-0.2005(21)
C113	-0.4163(70)	-0.4496(32)	-0.2623(19)
C114	-0.3998(90)	-0.5979(46)	-0.2570(23)
C120	0.1692(81)	-0.3031(43)	-0.4328(24)
C121	0.3093(91)	-0.1422(39)	-0.4411(25)
C122	0.3344(103)	0.0028(45)	-0.3552(28)

TABLE XIII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE n- PROPYL NICOTINATE

ATOM	U11	U22	U33	U12	U13	U23
I1	35(0)	48(0)	46(0)	14(0)	9(0)	24(0)
Cu1	66(1)	43(1)	43(1)	12(1)	5(1)	10(0)
O18	72(7)	45(6)	40(6)	16(5)	7(5)	13(5)
O19	67(15)	50(13)	60(15)	31(12)	9(12)	-3(11)
N11	74(9)	30(6)	40(7)	8(6)	2(6)	6(5)
C12	43(14)	31(14)	16(13)	6(11)	-4(10)	-13(10)
C13	45(15)	66(20)	38(17)	40(15)	1(12)	11(15)
C14	57(18)	28(15)	53(20)	13(13)	0(14)	4(13)
C15	98(14)	46(10)	60(12)	21(9)	13(10)	27(9)
C16	91(12)	41(9)	58(11)	12(8)	15(9)	27(8)
C17	40(7)	47(8)	31(7)	12(6)	1(5)	6(6)
C20	67(20)	61(20)	56(22)	18(16)	47(17)	35(17)
C21	74(23)	35(17)	62(23)	-1(16)	12(18)	21(16)
C22	123(37)	33(18)	59(24)	-28(20)	6(23)	-3(16)
O119	77(16)	31(11)	44(13)	-8(11)	3(11)	-6(10)
C112	37(13)	29(14)	56(19)	14(19)	41(18)	30(19)
C113	47(15)	31(14)	32(15)	8(12)	41(18)	30(19)
C114	69(22)	82(26)	50(22)	14(19)	41(18)	30(19)
C120	54(18)	70(23)	62(23)	14(16)	-20(16)	38(19)
C121	64(21)	44(19)	67(24)	18(16)	2(17)	15(17)
C122	79(26)	56(22)	76(26)	24(20)	12(20)	4(20)

TABLE XIII (Continued)

Anisotropic thermal parameters in the form:

$$\exp(-2\pi(U_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$$ for I, Cu; $\times 10^3$ for C, N, and O.

TABLE XIV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE n-PROPYL NICOTINATE

I1 - Cu1	2.616(4)	Cu1 - I1 - Cu1'	64.30(8)
I1 - Cu1'	2.686(3)	Cu1 - I1 - Cu1''	64.56(8)
I1 - Cu1''	2.682(3)	Cu1' - I1 - Cu1''	105.0(1)
Cu1 - Cu1'	2.823(4)	I1 - Cu1 - I1'	115.69(8)
Cu1 - Cu1''	2.830(4)	I1 - Cu1 - I1''	115.43(9)
Cu1 - N11	2.03(1)	I1' - Cu1 - I1''	105.0(1)
N11 - C12	1.42(3)	I1 - Cu1 - N11	108.2(4)
C12 - C13	1.40(4)	I1' - Cu1 - N11	105.6(4)
C13 - C14	1.43(5)	I1'' - Cu1 - N11	105.9(4)
C13 - C17	1.43(4)	C16 - N11 - Cu1	124(1)
C14 - C15	1.46(4)	C12 - N11 - Cu1	114(1)
C15 - C16	1.33(2)	C16 - N11 - C12	107(2)
C16 - N11	1.31(2)	C16 - N11 - C112	107(2)
C17 - O18	1.35(2)	C13 - C12 - N11	124(2)
C17 - O19	1.23(3)	C14 - C13 - C12	116(3)
C20 - C21	1.55(5)	C17 - C13 - C12	123(43
C21 - C22	1.50(4)	C17 - C13 - C14	119(3)
N11 - C112	1.46(3)	C15 - C14 - C13	118(2)
C112 - C113	1.33(3)	C16 - C15 - C14	111(2)
C114 - C15	1.52(4)	C16 - C15 - C114	107(2)
C17 - O119	1.17(2)	C15 - C16 - N11	131(2)
O18 - C120	1.54(4)	O19 - C17 - C13	124(2)
C120 - C121	1.51(5)	O119 - C17 - C13	111(2)

TABLE XIV (Continued)

C121 - C122	1.57(5)	O18 - C17 - C13	111(2)
		O19 - C17 - C113	91(2)
		O19 - C17 - O18	123(2)
		O119 - C17 - C113	126(2)
		O18 - C17 - C113	110(1)
		C20 - O18 - C17	112(2)
		C120 - O18 - C17	112(2)
		C21 - C20 - O18	105(3)
		C22 - C21 - C20	112(3)
		C113 - C112 - N11	121(3)
		C114 - C113 - C112	121(3)
		C112 - C113 - C17	122(3)
		C15 - C114 - C113	116(2)
		C121 - C120 - O18	104(2)
		C122 - C121 - C120	115(3)

Symmetry operations:

' = 1 - x, -y, -z

'' = -x, -y, -z

TABLE XV

CRYSTAL DATA FOR COPPER IODIDE METHYL NICOTINATE (LOW TEMPERATURE)

Formula	$(CuIC_7H_7NO_2)_n$
Mwt	295.5891
a	4.136(2) Å
b	12.191(3)
c	17.818(6)
α	90.0 °
β	92.32(3)
γ	90.0
V	897.6(6) $Å^3$
F(000)	552
μMoK_α	57.7403 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.1869 g cm^{-3}
Z	4
Meas. Refl.	1176
Obs. Refl.	1066
R	5.3%
R_w	7.7%
Space Group	$P2_1/c$
Octants Meas.	h, k, $+^1$

TABLE XVI

POSITIONAL PARAMETERS FOR COPPER IODIDE METHYL NICOTINATE (LOW TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.2612(2)	0.1269(1)	0.0717(0)
Cu1	-0.2501(4)	0.0740(1)	-0.0154(1)
O18	0.1566(24)	0.4815(8)	-0.0881(5)
O19	-0.0106(26)	0.5323(9)	-0.2050(6)
N11	-0.2714(24)	0.1795(9)	-0.1053(6)
C12	-0.1294(29)	0.2801(11)	-0.1017(8)
C13	-0.1543(32)	0.3561(11)	-0.1590(8)
C14	-0.3431(32)	0.3312(12)	-0.2245(8)
C15	-0.4991(28)	0.2297(12)	-0.2281(7)
C16	-0.4629(34)	0.1554(11)	-0.1582(8)
C17	0.0040(35)	0.4683(12)	-0.1536(9)
C20	0.3126(35)	0.5876(12)	-0.0788(8)

TABLE XVII

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE METHYL NICOTINATE (LOW TEMPERATURE)

ATOM	X	Y	Z
H12	-0.0034	0.3006	-0.0556
H14	-0.3652	0.3834	-0.2663
H15	-0.6328	0.2103	-0.2729
H16	-0.5759	0.0845	-0.1712
H20	0.4262	-0.5736	-0.0277
H21	0.4652	0.6028	-0.1181
H22	0.1582	0.6481	-0.0777

TABLE XVIII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE METHYL NICOTINATE (LOW TEMPERATURE)

ATOM	U11	U22	U33	U12	U13	U23
I1	22(0)	21(0)	21(0)	0(0)	3(0)	-3(0)
Cu1	25(0)	22(1)	21(1)	-1(0)	3(0)	1(0)
O18	40(6)	28(5)	24(6)	-8(4)	0(4)	-3(4)
O19	50(6)	34(6)	29(6)	-6(5)	1(5)	9(5)
N11	14(5)	27(7)	23(6)	2(5)	5(4)	-5(5)
C12	12(6)	30(8)	25(8)	14(6)	6(5)	-1(6)
C13	20(7)	19(7)	23(8)	15(6)	4(6)	-1(6)
C14	23(7)	25(7)	28(8)	0(6)	13(6)	0(6)
C15	4(5)	41(9)	20(8)	7(6)	3(5)	-5(6)
C16	32(8)	20(7)	28(9)	13(6)	2(6)	-10(6)
C17	30(8)	30(8)	27(9)	-2(6)	26(7)	0(7)
C20	29(7)	19(7)	36(9)	-10(6)	22(6)	2(6)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C, N, and O.

TABLE XIX

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE METHYL NICOTINATE (LOW TEMPERATURE)

I1 - Cu1	2.652(2)	Cu1 - I1 - Cu1'	101.84(6)
I1 - Cu1'	2.676(2)	Cu1 - I1 - Cu1''''	63.39(5)
I1 - Cu1'''	2.645(2)	Cu1' - I1 - Cu1''''	63.85(5)
Cu1 - Cu1'''	2.783(2)	I1 - Cu1 - I1''	101.83(7)
Cu1 - Cu1''''	2.814(2)	I1 - Cu1 - I1'''	116.61(7)
Cu1 - N11	2.05(1)	I1'' - Cu1 - I1'''	116.15(6)
N11 - C12	1.36(2)	I1 - Cu1 - N11	108.2(3)
C12 - C13	1.38(2)	I1'' - Cu1 - N11	107.0(3)
C13 - C14	1.41(2)	I1''' - Cu1 - N11	106.3(3)
C13 - C17	1.52(2)	Cu1 - N11 - C12	121.6(9)
C14 - C15	1.39(2)	Cu1 - N11 - C16	120.4(9)
C15 - C16	1.40(2)	C12 - N11 - C16	118(1)
C16 - N16	1.38(2)	N11 - C12 - C13	123(1)
C17 - O18	1.31(2)	C12 - C13 - C14	119(1)
C17 - O19	1.20(2)	C12 - C13 - C17	123(1)
O18 - C20	1.45(2)	C14 - C13 - C17	118(1)
		C13 - C14 - C15	118(1)
		C14 - C15 - C16	120(1)
		C15 - C16 - N11	121(1)
		C13 - C17 - O19	127(2)
		C13 - C17 - O18	111(1)
		O18 - C17 - O19	127(2)
		C17 - O18 - C20	114(1)

TABLE XIX (Continued)

Symmetry operations:

' = x + 1, y, z

'' = x - 1, y, z

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

'''' = -1 - x, -y, -z

TABLE XX

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE METHYL NICOTINATE, HYDROGEN ATOMS (LOW TEMPERATURE)

C12 - H12	0.99	N11 - C12 - H12	119
C14 - H14	0.98	C13 - C12 - H12	118
C15 - H15	0.98	C13 - C14 - H14	121
C16 - H16	0.98	C15 - C14 - H14	121
C20 - H20	1.02	C16 - C15 - H15	120
C20 - H21	0.98	C14 - C15 - H15	120
C21 - H22	0.98	N11 - C16 - H16	119
		C15 - C16 - H16	119
		018 - C20 - H20	98
		018 - C20 - H22	112
		H20 - C20 - H21	113
		H20 - C20 - H22	112
		H21 - C20 - H22	113
		H21 - C20 - H22	108

TABLE XXI

CRYSTAL DATA FOR COPPER IODIDE METHYL NICOTINATE (ROOM TEMPERATURE)

Formula	$(CuIC_7H_7NO_2)_n$
Mwt	295.5891
$\underline{a}$	4.172(1) Å
$\underline{b}$	12.224(4)
$\underline{c}$	18.021(5)
α	90.0°
β	92.95(3)
γ	90.0
V	918.0(5) Å^3
F(OOO)	552
μMoK_α	56.4572 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.1383 g cm^{-3}
Z	4
Meas. Refl.	1204
Obs. Refl.	1018
R	5.2%
R_w	7.5%
Space Group	$P2_1/c$
Octants Meas.	h, k, ±l

TABLE XXII

POSITIONAL PARAMETERS FOR COPPER IODIDE METHYL NICOTINATE (ROOM TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.2659(2)	0.1269(1)	0.0696(1)
Cu1	-0.2474(5)	0.0751(2)	-0.0164(1)
O18	0.1517(31)	0.4808(9)	-0.0889(7)
O19	-0.0082(31)	0.5300(10)	-0.2051(7)
N11	-0.2739(30)	0.1805(10)	-0.1063(8)
C12	-0.1310(36)	0.2786(12)	-0.1043(8)
C13	-0.1515(35)	0.3541(11)	-0.1602(8)
C14	-0.3405(42)	0.3268(13)	-0.2232(9)
C15	-0.4934(35)	0.2274(14)	-0.2275(8)
C16	-0.4520(37)	0.1577(13)	-0.1679(8)
C17	-0.0046(40)	0.4627(13)	-0.1553(10)
C20	0.3008(42)	0.5866(13)	-0.0807(10)

TABLE XXIII

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE METHYL NICOTINATE (ROOM TEMPERATURE)

ATOM	X	Y	Z
H12	0.0000	0.2993	-0.0583
H14	-0.3612	0.3787	-0.2651
H15	-0.6275	0.2069	-0.2724
H16	-0.5604	0.0856	-0.1711
H20	0.4562	0.5736	-0.0277
H21	0.4698	0.6041	-0.1241
H22	0.1433	0.6456	-0.0771

TABLE XXIV

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE METHYL NICOTINATE (ROOM TEMPERATURE)

ATOM	U11	U22	U33	U12	U13	U23
I1	43(0)	36(0)	42(0)	-1(0)	3(0)	-5(0)
Cu1	59(1)	40(1)	43(1)	-4(6)	3(0)	4(0)
O18	68(7)	38(6)	59(7)	-10(5)	0(5)	5(5)
O19	91(9)	50(7)	67(8)	-9(6)	3(6)	20(7)
N11	59(8)	39(7)	35(7)	-9(6)	8(6)	-6(6)
C12	51(8)	43(9)	32(8)	8(7)	9(7)	-7(7)
C13	44(8)	31(8)	36(8)	11(6)	17(6)	6(6)
C14	77(11)	30(8)	44(9)	21(8)	16(8)	7(7)
C15	49(9)	57(11)	37(9)	24(8)	-5(7)	-10(8)
C16	58(10)	42(9)	38(9)	11(8)	17(8)	-6(7)
C17	62(10)	38(9)	56(11)	20(8)	33(9)	9(9)
C20	66(10)	33(8)	73(12)	5(8)	27(9)	4(8)

Anisotropic thermal parameters in the form:

$$\exp(-2\pi(U_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$$ for I, Cu; $\times 10^3$ for C, N, and O.

TABLE XXV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE METHYL NICOTINATE (ROOM TEMPERATURE)

I1 - Cu1	2.654(2)	Cu1 - I1 - Cu1'	102.57(6)
I1 - Cu1'	2.692(2)	Cu1 - I1 - Cu1''''	63.83(6)
I1 - Cu1'''	2.649(2)	Cu1' - I1 - Cu1''''	65.24(6)
Cu1 - Cu1'''	2.804(3)	I1 - Cu1 - I1''	102.57(8)
Cu1 - Cu1''''	2.880(2)	I1 - Cu1 - I1'''	116.17(8)
Cu1 - N11	2.07(1)	I1'' - Cu1 - I1'''	114.75(7)
N11 - C12	1.34(2)	I1 - Cu1 - N11	108.5(4)
N11 - C16	1.33(2)	I1'' - Cu1 - N11	107.0(4)
C12 - C13	1.37(2)	I1''' - Cu1 - N11	107.3(4)
C13 - C14	1.39(2)	Cu1 - N11 - C12	122(1)
C13 - C17	1.46(2)	Cu1 - N11 - C16	122(1)
C14 - C15	1.37(2)	C12 - N11 - C16	116(1)
C15 - C16	1.37(2)	N11 - C12 - C13	125(1)
C17 - O18	1.35(2)	C12 - C13 - C14	117(1)
C17 - O19	1.22(2)	C12 - C13 - C17	124(1)
O18 - C20	1.44(2)	C14 - C13 - C17	119(1)
		C13 - C14 - C15	120(1)
		C14 - C15 - C16	118(1)
		C15 - C16 - N11	124(1)
		C13 - C17 - O19	126(2)
		C13 - C17 - O18	112(1)
		O18 - C17 - O19	122(1)
		C17 - O18 - C20	115(1)

TABLE XXV (Continued)

Symmetry operations:

' = x + 1, y, z

'' = x - 1, y, z

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

'''' = -1 - x, -y, -z

TABLE XXVI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE METHYL NICOTINATE (HYDROGEN ATOMS) (ROOM TEMPERATURE)

C12 - H12	1.00	N11 - C12 - H12	118
C14 - H14	0.99	C13 - C12 - H12	117
C15 - H15	0.99	C13 - C14 - H14	120
C16 - H16	0.99	C15 - C14 - H14	120
C20 - H20	1.14	C16 - C15 - H15	122
C20 - H21	1.00	C14 - C15 - H15	121
C21 - H22	0.98	N11 - C16 - H16	118
		C15 - C16 - H16	118
		O18 - C20 - H20	101
		O18 - C20 - H22	107
		H20 - C20 - H21	112
		H20 - C20 - H22	114
		H21 - C20 - H22	113
		H21 - C20 - H22	107

TABLE XXVII

CRYSYAL DATA FOR COPPER IODIDE BENZYL NICOTINATE (ROOM TEMPERATURE)

Formula	$(CuIC_{13}H_{11}NO_2)_n$
Mwt	403.685
a	4.3298(8) Å
b	14.475(4)
c	20.641(6)
α	90.0°
β	90.0
γ	90.0
V	1293.7(6) $Å^3$
F(000)	776
μMoK_α	40.4556 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.0722 g cm^{-1}
Z	4
Meas refl	1051
Obs refl	904
R	3.0%
R_w	3.8
Space Group	$P2_12_12_1$
Octants meas	h, k, l

TABLE XXVIII

POSITIONAL PARAMETERS FOR COPPER IODIDE BENZYL NICOTINATE (ROOM TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.4738(1)	0.2472(0)	1.0950(0)
Cu1	0.9707(4)	0.1980(1)	1.0274(1)
O18	1.4945(23)	-0.0831(4)	1.1530(3)
O19	1.3953(26)	-0.2207(5)	1.1112(4)
N11	0.9815(25)	0.0560(5)	1.0224(4)
C12	1.1431(25)	0.0067(7)	1.0664(5)
C13	1.1799(26)	-0.0876(6)	1.0633(5)
C14	1.0241(29)	-0.1344(6)	1.0143(5)
C15	0.8539(39)	-0.0854(8)	0.9693(6)
C16	0.8352(27)	0.0095(7)	0.9757(6)
C17	1.3613(28)	-0.1392(7)	1.1110(5)
C20	1.6761(30)	-0.1228(8)	1.2045(6)
C21	1.8329(28)	-0.0461(8)	1.2397(5)
C22	1.8213(33)	0.0439(8)	1.2211(6)
C23	1.9836(47)	0.1113(8)	1.2211(6)
C24	2.1465(38)	0.0899(10)	1.3104(7)
C25	2.1557(32)	-0.0005(11)	1.3283(6)
C26	2.0047(34)	-0.0693(8)	1.2947(6)

TABLE XXIX

POSITIONAL PARAMETERS FOR COPPER IODIDE BENZYL NICOTINATE (HYDROGEN ATOMS - ROOM TEMPERATURE)

ATOM	X	Y	Z
H12	1.2383	0.0399	1.1020
H14	1.0255	-0.2008	1.0130
H15	0.7529	-0.1165	0.9336
H16	0.7066	0.0436	0.9454
H201	1.8333	-0.1636	1.1863
H202	1.5481	-0.1564	1.2341
H22	1.7024	0.0608	1.1828
H23	1.9715	0.1746	1.2418
H24	2.2535	0.1388	1.3351
H25	2.2740	-0.0177	1.3668
H26	2.0145	-0.1325	1.3089

TABLE XXX

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE BENZYL NICOTINATE (ROOM TEMPERATURE)

ATOM	U11	U22	U33	U12	U13	U23
I1	34(0)	38(0)	37(0)	0(0)	-1(0)	-2(0)
Cu1	54(0)	33(0)	51(0)	3(0)	-4(0)	0(0)
O18	66(5)	35(3)	46(4)	12(4)	-23(5)	0(3)
O19	102(7)	24(4)	94(6)	16(5)	-20(6)	-2(4)
N11	52(5)	28(3)	35(4)	-6(5)	1(6)	-3(3)
C12	38(6)	33(5)	34(6)	-6(5)	0(5)	1(5)
C13	34(5)	18(5)	47(6)	2(5)	7(5)	-3(5)
C14	46(6)	24(4)	53(7)	-10(6)	17(7)	-10(4)
C15	46(7)	50(7)	32(6)	-7(6)	-6(6)	-16(6)
C16	37(6)	41(6)	47(6)	-9(6)	9(6)	4(6)
C17	51(7)	34(6)	41(7)	-3(6)	8(6)	-3(5)
C20	47(7)	48(6)	46(7)	6(6)	13(6)	12(6)
C21	36(6)	44(6)	38(7)	10(6)	4(5)	1(5)
C22	51(7)	45(7)	49(7)	6(6)	-17(9)	-7(6)
C23	85(10)	48(6)	62(8)	7(9)	-18(9)	0(6)
C24	73(10)	78(10)	60(10)	-25(9)	6(8)	-23(8)
C25	43(8)	108(12)	51(8)	4(9)	-11(7)	12(9)
C26	47(7)	57(7)	62(8)	2(8)	5(8)	12(6)

Anisotropic thermal parameters in the form:

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

TABLE XXX (Continued)

$+ 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C, N, and O.

TABLE XXXI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
COPPER IODIDE BENZYL NICOTINATE
(ROOM TEMPERATURE)

I1 - Cu1	2.662(2)	Cu1 - I1 - Cu1''	108.17(4)
I1 - Cu1''	2.684(2)	Cu1 - I1 - Cu1''''	65.41(4)
I1 - Cu1''''	2.648(2)	Cu1'' - I1 - Cu1''''	65.11(4)
Cu1 - Cu1'''	2.869(2)	I1 - Cu1 - I1'	108.17(3)
Cu1 - Cu1''''	2.869(2)	I1 - Cu1 - I1'''	115.10(6)
Cu1 - N11	2.058(7)	I1' - Cu1 - I1'''	114.37(5)
N11 - C12	1.35(1)	I1 - Cu1 - N11	108.2(3)
N11 - C16	1.34(1)	I1' - Cu1 - N11	105.8(3)
C12 - C13	1.38(1)	I1''' - Cu1 - N11	104.6(2)
C13 - C14	1.39(1)	Cu1 - N11 - C12	120.4(7)
C13 - C17	1.46(2)	Cu1 - N11 - C16	121.9(7)
C14 - C15	1.38(2)	C12 - N11 - C16	117.7(8)
C15 - C16	1.38(2)	N11 - C12 - C13	123.6(9)
C17 - O18	1.32(1)	C12 - C13 - C14	117.4(9)
C17 - O19	1.19(1)	C12 - C13 - C17	122.5(9)
O18 - C20	1.44(1)	C14 - C13 - C17	120.0(8)
C20 - C21	1.49(2)	C13 - C14 - C15	119.9(9)
C21 - C22	1.36(2)	C14 - C15 - C16	118(1)
C22 - C23	1.40(2)	C15 - C16 - N11	123(1)
C23 - C24	1.36(2)	C13 - C17 - O18	111.2(8)
C24 - C25	1.36(2)	C13 - C17 - O19	125(1)
C25 - C26	1.38(2)	O18 - C17 - O19	124(1)
C26 - C21	1.39(2)	C17 - O18 - C20	118.5(8)

TABLE XXXI (Continued)

O18 - C20 - C21	108.1(9)
C20 - C21 - C22	124(1)
C20 - C21 - C26	117(1)
C22 - C21 - C26	119(1)
C21 - C22 - C23	120(1)
C22 - C23 - C24	122(1)
C23 - C24 - C25	117(1)
C24 - C25 - C26	123(1)
C25 - C26 - C21	119(1)

Symmetry Operations

' = 1 + x, y, z

'' = -1 + x, y, z

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

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

TABLE XXXII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE BENZYL NICOTINATE ROOM TEMPERATURE, HYDROGEN ATOMS

C12 - H12	0.97	N11 - C12 - H12	118
C14 - H14	0.96	C13 - C12 - H12	119
C15 - H15	0.97	C13 - C14 - H14	120
C16 - H16	0.98	C15 - C14 - H14	120
C20 - H201	0.96	C14 - C15 - H15	121
C20 - H202	0.96	C16 - C15 - H15	120
C22 - H22	0.97	C15 - C16 - H16	118
C23 - H23	0.96	N11 - C16 - H16	119
C24 - H24	0.99	O18 - C20 - H201	110
C25 - H25	0.98	O18 - C20 - H202	111
C26 - H26	0.96	H201 - C20 - H202	110
		H201 - C20 - C21	109
		H202 - C20 - C21	109
		C21 - C22 - H22	119
		C23 - C22 - H22	120
		C22 - C23 - H23	118
		C24 - C23 - H23	120
		C23 - C24 - H24	120
		C25 - C24 - H24	122
		C24 - C25 - H25	119
		C26 - C25 - H25	118
		C25 - C26 - H26	121
		C21 - C26 - H26	120

TABLE XXXIII

CRYSYAL DATA FOR COPPER IODIDE BENZYL NICOTINATE (LOW TEMPERATURE)

Formula	$(CuIC_{13}H_{11}NO_2)_n$
Mwt	403.685
<u>a</u>	4.306(1) Å
<u>b</u>	14.387(5)
<u>c</u>	20.327(8)
α	90.0°
β	90.0
γ	90.0
V	1259.7(8) $Å^3$
F(000)	776
μMoK_α	41.5475 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.1281 g cm^{-1}
Z	4
Meas refl	1026
Obs refl	938
R	6.0%
R_w	8.4
Space Group	$P2_12_12_1$
Octants meas	h, k, l

TABLE XXXIV

POSITIONAL PARAMETERS FOR COPPER IODIDE BENZYL NICOTINATE (LOW TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.4575(3)	0.2483(1)	1.0965(1)
Cu1	0.9547(8)	0.1997(2)	1.0277(1)
O18	1.4908(45)	-0.0816(9)	1.1540(6)
O19	1.3933(48)	-0.2220(10)	1.1104(7)
N11	0.9657(47)	0.0572(11)	1.0232(8)
C12	1.1390(64)	0.0068(15)	1.0652(10)
C13	1.1615(57)	-0.0878(14)	1.0620(11)
C14	1.0157(66)	-0.1351(14)	1.0127(10)
C15	0.8329(67)	-0.0853(14)	0.9691(12)
C16	0.8210(59)	0.0098(14)	0.9756(11)
C17	1.3601(63)	-0.1395(14)	1.1101(10)
C20	1.6868(78)	-0.1230(13)	1.2045(11)
C21	1.8404(72)	-0.0465(16)	1.2402(10)
C22	1.8255(87)	0.0475(16)	1.2209(12)
C23	1.9694(89)	0.1151(14)	1.2574(11)
C24	2.1601(61)	0.0912(16)	1.3103(12)
C25	2.1763(99)	-0.0012(18)	1.3291(12)
C26	2.0223(63)	-0.0684(16)	1.2939(10)

TABLE XXXVI

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE BENZYL NICOTINATE (LOW TEMPERATURE)

ATOM	U11	U22	U33	U12	U13	U23
I1	41(0)	20(0)	15(0)	0(0)	0(0)	-1(0)
Cu1	46(1)	20(1)	20(1)	2(1)	0(1)	0(1)
O18	51(11)	22(7)	17(7)	3(8)	-9(8)	4(6)
O19	74(13)	25(9)	23(8)	-3(9)	-6(9)	-2(6)
N11	32(10)	17(8)	17(8)	-9(9)	-8(10)	0(7)
C12	52(17)	22(12)	20(12)	-3(13)	-12(12)	-11(10)
C13	30(13)	16(11)	33(13)	-15(11)	26(12)	-5(10)
C14	54(17)	19(11)	23(12)	3(13)	14(14)	-9(9)
C15	49(15)	16(10)	25(12)	-13(12)	6(14)	-13(10)
C16	37(14)	24(11)	21(11)	0(12)	-5(13)	1(11)
C17	54(17)	18(12)	18(12)	0(13)	18(12)	-7(9)
C20	84(21)	13(11)	18(12)	-10(14)	0(15)	0(9)
C21	58(18)	33(13)	17(12)	0(14)	13(13)	1(10)
C22	80(22)	23(12)	29(14)	-4(15)	0(16)	3(10)
C23	90(23)	21(12)	26(12)	16(16)	-18(16)	-6(10)
C24	26(13)	39(14)	39(15)	-2(13)	0(12)	-16(12)
C25	125(34)	48(16)	26(14)	3(23)	-6(20)	-11(13)
C26	32(14)	40(14)	22(12)	0(13)	-9(13)	11(10)

Anisotropic thermal parameters in the form:

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

TABLE XXXV

POSITIONAL PARAMETERS FOR COPPER IODIDE BENZYL NICOTINATE, HYDROGEN ATOMS (LOW TEMPERATURE)

ATOM	X	Y	Z
H12	1.2504	0.0392	1.0993
H14	1.0543	-0.1999	1.0081
H15	0.7139	-0.1171	0.9351
H16	0.6987	0.0444	0.9440
H201	1.8430	-0.1624	1.1839
H202	1.5634	-0.1594	1.2344
H22	1.7092	0.0643	1.1817
H23	1.9437	0.1802	1.2457
H24	2.2760	0.1371	1.3347
H25	2.2995	-0.0180	1.3675
H26	2.0416	-0.1325	1.3071

TABLE XXXVI (Continued)

+ $2U_{13}hla^*c^*$ + $2U_{23}klb^*c^*$)) x 10^4 for I, Cu; x 10^3 for C, N, and O.

TABLE XXXVII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE BENZYL NICOTINATE (LOW TEMPERATURE)

I1 - Cu1	2.651(3)	Cu1 - I1 - Cu1''	108.07(8)
I1 - Cu1''	2.671(3)	Cu1 - I1 - Cu1''''	64.73(9)
I1 - Cu1''''	2.634(3)	Cu1'' - I1 - Cu1''''	64.46(9)
Cu1 - Cu1'''	2.829(2)	I1 - Cu1 - I1'	108.07(8)
Cu1 - Cu1''''	2.829(2)	I1 - Cu1 - I1'''	115.7(1)
Cu1 - N11	2.05(2)	I1' - Cu1 - I1'''	115.1(1)
N11 - C12	1.35(3)	I1 - Cu1 - N11	107.8(5)
N11 - C16	1.34(3)	I1' - Cu1 - N11	105.4(5)
C12 - C13	1.37(3)	I1''' - Cu1 - N11	103.9(4)
C13 - C14	1.36(3)	Cu1 - N11 - C12	121(1)
C13 - C17	1.48(3)	Cu1 - N11 - C16	122(1)
C14 - C15	1.38(3)	C12 - N11 - C16	116(2)
C15 - C16	1.38(3)	N11 - C12 - C13	123(2)
C17 - O18	1.34(3)	C12 - C13 - C14	120(2)
C17 - O19	1.20(3)	C12 - C13 - C17	120(2)
O18 - C20	1.46(3)	C14 - C13 - C17	120(2)
C20 - C21	1.47(3)	C13 - C14 - C15	118(2)
C21 - C22	1.41(3)	C14 - C15 - C16	118(2)
C22 - C23	1.37(4)	C15 - C16 - N11	124(2)
C23 - C24	1.40(4)	C13 - C17 - O18	111(2)
C24 - C25	1.39(4)	C13 - C17 - O19	124(2)
C25 - C26	1.37(4)	O18 - C17 - O19	124(2)
C26 - C21	1.38(3)	C17 - O18 - C20	117(1)

TABLE XXXVII (Continued)

O18 - C20 - C21	108(2)
C20 - C21 - C22	124(2)
C20 - C21 - C26	118(2)
C22 - C21 - C26	118(2)
C21 - C22 - C23	120(2)
C22 - C23 - C24	121(2)
C23 - C24 - C25	119(2)
C24 - C25 - C26	120(3)
C25 - C26 - C21	122(2)

Symmetry Operations

' = 1 + x, y, z

'' = -1 + x, y, z

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

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

TABLE XXXVIII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE BENZYL NICOTINATE, HYDROGEN ATOMS (LOW TEMPERATURE)

C12 - H12	0.96	N11 - C12 - H12	118
C14 - H14	0.96	C13 - C12 - H12	119
C15 - H15	0.97	C13 - C14 - H14	119
C16 - H16	0.97	C15 - C14 - H14	123
C20 - H201	0.97	C14 - C15 - H15	121
C20 - H202	0.96	C16 - C15 - H15	121
C22 - H22	0.97	C15 - C16 - H16	118
C23 - H23	0.98	N11 - C16 - H16	118
C24 - H24	0.96	O18 - C20 - H201	110
C25 - H25	0.98	O18 - C20 - H202	110
C26 - H26	0.96	H201 - C20 - H202	110
		H201 - C20 - C21	110
		H202 - C20 - C21	110
		C21 - C22 - H22	119
		C23 - C22 - H22	120
		C22 - C23 - H23	120
		C24 - C23 - H23	119
		C23 - C24 - H24	122
		C25 - C24 - H24	119
		C24 - C25 - H25	120
		C26 - C25 - H25	120
		C25 - C26 - H26	119
		C21 - C26 - H26	119

TABLE XXXIX

CRYSYAL DATA FOR COPPER IODIDE 3-CYANOPYRIDINE (ROOM TEMPERATURE)

Formula	$(CuIC_6H_4N_2)_n$
Mwt	294.561
$\underline{a}$	4.161(1) Å
$\underline{b}$	7.614(2)
$\underline{c}$	12.833(2)
α	80.98(2)°
β	102.64(2)
γ	98.13(2)
V	389.4(2) $Å^3$
F(000)	272
μMoK_α	66.5781 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.51 g cm^{-1}
Z	2
Meas refl	1099
Obs refl	1011
R	3.9%
R_w	5.5
Space Group	$P\bar{1}$
Octants meas	±h, k, ±l

TABLE XL

POSITIONAL PARAMETERS FOR COPPER IODIDE 3-CYANOPYRIDINE (ROOM TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.2768(1)	0.2577(0)	0.9385(1)
Cu1	-0.1885(3)	0.0968(2)	1.0396(1)
N11	-0.1049(20)	0.1640(11)	1.1937(7)
N18	0.4142(34)	0.6647(18)	1.3792(9)
C12	0.0527(26)	0.3220(15)	1.2211(8)
C13	0.0772(25)	0.3712(14)	1.3216(8)
C14	-0.0645(31)	0.2563(15)	1.3982(8)
C15	-0.2319(30)	0.0993(15)	1.3694(8)
C16	-0.2514(28)	0.0588(14)	1.2682(8)
C17	0.2635(33)	0.5390(17)	1.3507(9)

TABLE XLI

POSITIONAL PARAMETERS FOR COPPER IODIDE 3-CYANOPYRIDINE, HYDROGEN ATOMS (ROOM TEMPERATURE)

ATOM	X	Y	Z
H12	0.1192	0.3813	1.1568
H14	-0.0182	0.2794	1.4761
H15	-0.3158	0.0000	1.4279
H16	-0.4030	-0.0400	1.2440

TABLE XLII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 3- CYANOPYRIDINE (ROOM TEMPERATURE)

ATOM	U11	U22	U33	U12	U13	U23
I1	30(0)	22(0)	52(0)	0(0)	12(0)	-1(0)
Cu1	42(0)	32(0)	42(0)	0(0)	11(0)	-7(0)
N11	35(4)	24(4)	43(4)	-3(3)	8(3)	-2(3)
N18	125(10)	61(7)	67(7)	-55(8)	26(7)	-18(6)
C12	43(5)	31(6)	40(6)	0(5)	10(4)	-2(4)
C13	42(5)	33(6)	32(5)	1(5)	3(4)	-10(4)
C14	73(7)	36(6)	33(5)	-1(6)	16(5)	-2(5)
C15	68(7)	39(7)	38(6)	-5(6)	26(5)	-6(5)
C16	53(6)	27(6)	43(6)	-8(5)	15(5)	-7(5)
C17	73(8)	43(7)	35(6)	-4(6)	11(5)	-3(5)

Anisotropic thermal parameters in the form:

$$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$$ for I, Cu; $\times 10^3$ for C and N.

TABLE XLIII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 3-CYANOPYRIDINE (ROOM TEMPERATURE)

I1 - Cu1	2.619(2)	Cu1 - I1 - Cu1'	103.67(5)
I1 - Cu1'	2.673(2)	Cu1 - I1 - Cu1'''	62.55(5)
I1 - Cu1'''	2.651(2)	Cu1' - I1 - Cu1'''	64.90(4)
Cu1 - Cu1'''	2.736(2)	I1 - Cu1 - I1''	103.67(5)
Cu1 - Cu1''''	2.856(2)	I1 - Cu1 - I1'''	117.45(6)
Cu1 - N11	2.064(9)	I1'' - Cu1 - I1'''	115.10(5)
N11 - C12	1.34(1)	I1 - Cu1 - N11	110.9(2)
N11 - C16	1.34(1)	I1'' - Cu1 - N11	103.3(2)
C12 - C13	1.38(2)	I1''' - Cu1 - N11	105.6(2)
C13 - C14	1.38(1)	Cu1 - N11 - C12	123.3(6)
C13 - C17	1.45(2)	Cu1 - N11 - C16	119.6(2)
C14 - C15	1.36(2)	C12 - N11 - C16	116.4(9)
C15 - C16	1.36(2)	N11 - C12 - C13	122.3(9)
C17 - N18	1.13(2)	C12 - C13 - C14	120(1)
		C12 - C13 - C17	121.0(9)
		C14 - C13 - C17	119.1(9)
		C13 - C14 - C15	118(1)
		C14 - C15 - C16	120(1)
		C15 - C16 - N11	124(1)
		C13 - C17 - N18	176(1)

Symmetry Operations

' = 1 + x, y, z

TABLE XLIII (Continued)

'' = -1 + x, y, z

''' = -x, -y, 2 - z

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

TABLE XLIV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 3-CYANOPYRIDINE, HYDROGEN (ROOM TEMPERATURE)

C12 - H12	0.95	N11 - C12 - H12	104
C14 - H14	1.01	C13 - C12 - H12	135
C15 - H15	1.06	C13 - C14 - H14	121
C16 - H16	0.96	C15 - C14 - H14	120
		C14 - C15 - H15	120
		C16 - C15 - H15	119
		C15 - C16 - H16	119
		N11 - C16 - H16	116

TABLE XLV

CRYSYAL DATA FOR COPPER IODIDE 3-CYANOPYRIDINE (LOW TEMPERATURE)

Formula	$(CuIC_6H_4N_2)_n$
Mwt	294.561
<u>a</u>	4.131(2) Å
<u>b</u>	7.579(3)
<u>c</u>	12.732(7)
α	80.84(4)^{o}
β	103.19(2)
γ	97.96(3)
V	381.9(2) Å^3
F(000)	272
μ MoK$_\alpha$	68.0460 cm^{-1}
λ MoK$_\alpha$	0.71069 Å
D_{calc}	2.5671 g cm^{-1}
Z	2
Meas refl	1023
Obs refl	969
R	4.7%
R_w	6.6
Space Group	$P\bar{1}$
Octants meas	±h, k, ±l

TABLE XLVI

POSITIONAL PARAMETERS FOR COPPER IODIDE 3-CYANOPYRIDINE (LOW TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.2724(2)	0.2604(1)	0.9375(1)
Cu1	-0.1908(3)	0.0948(2)	1.0388(1)
N11	-0.1062(23)	0.1618(12)	1.1933(7)
N18	0.4140(33)	0.6704(18)	1.3795(9)
C12	0.0587(30)	0.3173(15)	1.2224(9)
C13	0.0861(29)	0.3679(15)	1.3249(9)
C14	-0.0681(34)	-0.2547(16)	1.4001(10)
C15	-0.2308(35)	0.0944(18)	1.3711(10)
C16	-0.2509(28)	0.0528(16)	1.2689(10)
C17	0.2679(37)	0.5387(20)	1.3520(10)

TABLE XLVII

POSITIONAL PARAMETERS FOR COPPER IODIDE 3-CYANOPYRIDINE, HYDROGEN ATOMS (LOW TEMPERATURE)

ATOM	X	Y	Z
H12	0.1753(356)	0.3813(204)	1.1812(112)
H14	0.0289(335)	0.2841(187)	1.4789(113)
H15	-0.3343(361)	0.0333(208)	1.4083(117)
H16	-0.3471(370)	-0.0445(211)	1.2432(115)

TABLE XLVIII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 3-CYANOPYRIDINE (LOW TEMPERATURE)

ATOM	U11	U22	U33	U12	U13	U23
I1	16(0)	9(0)	29(0)	-3(0)	7(0)	1(0)
Cu1	19(0)	13(0)	22(0)	-4(0)	6(0)	-1(0)
N11	15(5)	12(5)	20(5)	-3(4)	0(4)	2(4)
N18	58(7)	12(6)	36(6)	-22(5)	7(5)	-3(5)
C12	24(6)	11(6)	12(6)	0(5)	5(5)	11(4)
C13	21(6)	11(6)	29(6)	-10(5)	11(5)	-11(5)
C14	40(7)	17(6)	16(6)	-9(5)	5(5)	-1(5)
C15	37(7)	26(7)	18(6)	-9(6)	16(5)	-2(5)
C16	29(7)	8(6)	28(7)	-1(5)	8(5)	-2(5)
C17	42(8)	37(9)	20(7)	-8(7)	14(6)	0(6)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C and N.

TABLE XLIX

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 3-CYANOPYRIDINE (LOW TEMPERATURE)

I1 - Cu1	2.616(2)	Cu1 - I1 - Cu1'	102.89(6)
I1 - Cu1'	2.666(2)	Cu1 - I1 - Cu1'''	61.89(5)
I1 - Cu1'''	2.644(2)	Cu1' - I1 - Cu1'''	63.70(5)
Cu1 - Cu1'''	2.705(2)	I1 - Cu1 - I1''	102.89(6)
Cu1 - Cu1''''	2.802(2)	I1 - Cu1 - I1'''	118.11(7)
Cu1 - N11	2.050(9)	I1'' - Cu1 - I1'''	116.30(7)
N11 - C12	1.34(1)	I1 - Cu1 - N11	110.7(3)
N11 - C16	1.36(2)	I1'' - Cu1 - N11	102.6(3)
C12 - C13	1.40(2)	I1''' - Cu1 - N11	105.3(2)
C13 - C14	1.39(2)	Cu1 - N11 - C12	123.7(7)
C13 - C17	1.44(2)	Cu1 - N11 - C16	119.2(7)
C14 - C15	1.37(2)	C12 - N11 - C16	117(1)
C15 - C16	1.37(2)	N11 - C12 - C13	123(1)
C17 - N18	1.15(2)	C12 - C13 - C14	118(1)
		C12 - C13 - C17	121(1)
		C14 - C13 - C17	121(1)
		C13 - C14 - C15	118(1)
		C14 - C15 - C16	120(1)
		C15 - C16 - N11	123(1)
		C13 - C17 - N18	176(2)

Symmetry Operations

' = 1 + x, y, z

TABLE XLIX (Continued)

'' = -1 + x, y, z

''' = -x, -y, 2 - z

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

TABLE L

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 3-CYANOPYRIDINE HYDROGEN (LOW TEMPERATURE)

C12 - H12	0.84(1)	N11 - C12 - H12	119(1)
C14 - H14	1.04(1)	C13 - C12 - H12	117(1)
C15 - H15	0.77(1)	C13 - C14 - H14	111(1)
C16 - H16	0.86(1)	C15 - C14 - H14	126(1)
		C14 - C15 - H15	120(1)
		C16 - C15 - H15	119(1)
		C15 - C16 - H16	127(1)
		N11 - C16 - H16	109(1)

TABLE LI

CRYSYAL DATA FOR COPPER IODIDE 3-PYRIDYL-ACETONITRILE (ROOM TEMPERATURE)

Formula	$(CuIC_7H_6N_2)_n$
Mwt	308.5879
<u>a</u>	4.2595(8) Å
<u>b</u>	7.926(3)
<u>c</u>	13.978(7)
α	97.71(3)°
β	70.59(3)
γ	78.91(2)
V	426.7(3) $Å^3$
F(000)	288
μMoK_α	60.8141 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.4013 g cm^{-1}
Z	2
Meas refl	1127
Obs refl	981
R	3.0%
R_w	4.3
Space Group	$P\bar{1}$
Octants meas	±h, k, ±l

TABLE LII

POSITIONAL PARAMETERS FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (ROOM TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	-0.1103(1)	0.2459(1)	-0.0616(0)
Cu1	0.2343(3)	0.4097(2)	0.0384(1)
N11	0.0529(18)	0.3500(9)	0.1813(5)
N19	-0.1195(24)	-0.1900(12)	0.4216(7)
C12	0.1975(20)	0.2021(11)	0.2027(6)
C13	0.0709(21)	0.1494(11)	0.2965(6)
C14	-0.2245(24)	0.2603(13)	0.3714(7)
C15	-0.3815(24)	0.4134(12)	0.3518(7)
C16	-0.2340(23)	0.4530(12)	0.2551(7)
C17	0.2651(23)	-0.0188(13)	0.3121(8)
C18	0.0466(25)	-0.1166(12)	0.3728(7)

TABLE LIII

POSITIONAL PARAMETERS FOR COPPER IODIDE 3-PYRIDYLACETONITRILE, HYDROGEN ATOMS (ROOM TEMPERATURE)

ATOM	X	Y	Z
H12	0.4047	0.1263	0.1506
H14	-0.3205	0.2279	0.4365
H15	-0.5878	0.4926	0.4044
H16	-0.3437	0.5590	0.2416
H171	0.4197	0.0078	0.3452
H172	0.3999	-0.0958	0.2431

TABLE LIV

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (ROOM TEMPERATURE)

ATOM	U11	U22	U33	U12	U13	U23
I1	28(0)	35(0)	44(0)	-9(0)	-10(0)	8(0)
Cu1	44(0)	48(0)	38(0)	-9(0)	-9(0)	20(0)
N11	36(4)	39(4)	33(4)	-11(3)	-10(3)	12(3)
N19	66(6)	61(5)	70(6)	-20(5)	-6(5)	37(5)
C12	26(4)	33(4)	32(4)	-4(3)	-6(3)	15(3)
C13	37(4)	33(4)	31(4)	-13(3)	-15(4)	7(3)
C14	47(5)	56(6)	32(5)	-20(4)	-13(4)	23(4)
C15	47(5)	36(5)	39(5)	-3(4)	0(4)	10(4)
C16	43(5)	36(5)	39(5)	-4(4)	-7(4)	10(4)
C17	35(5)	58(6)	57(6)	-9(4)	-13(4)	35(5)
C18	49(5)	41(5)	39(5)	2(4)	-17(4)	10(4)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$ x 10^4 for I, Cu; x 10^3 for C and N.

TABLE LV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (ROOM TEMPERATURE)

I1 - Cu1	2.721(2)	Cu1 - I1 - Cu1'	105.27(5)
I1 - Cu1''	2.638(1)	Cu1 - I1 - Cu1''	63.40(5)
I1 - Cu1''''	2.632(2)	Cu1' - I1 - Cu1''''	66.57(4)
Cu1 - Cu1'''	2.892(2)	I1 - Cu1 - I1'	105.27(4)
Cu1 - Cu1''''	2.814(2)	I1 - Cu1 - I1''''	116.60(5)
Cu1 - N11	2.045(7)	I1' - Cu1 - I1''''	113.44(6)
N11 - C12	1.33(1)	I1 - Cu1 - N11	101.2(2)
N11 - C16	1.333(9)	I1' - Cu1 - N11	110.9(2)
C12 - C13	1.40(1)	I1'''' - Cu1 - N11	108.8(2)
C13 - C14	1.38(1)	Cu1 - N11 - C12	122.3(4)
C13 - C17	1.51(1)	Cu1 - N11 - C16	120.4(6)
C14 - C15	1.38(1)	C12 - N11 - C16	117.1(7)
C15 - C16	1.39(1)	N11 - C12 - C13	124.6(6)
C17 - C18	1.45(1)	C12 - C13 - C14	116.6(6)
C18 - N19	1.12(1)	C12 - C13 - C17	119.4(6)
		C14 - C13 - C17	123.9(8)
		C13 - C14 - C15	120.3(8)
		C14 - C15 - C16	118.4(7)
		C15 - C16 - N11	123.0(9)
		C13 - C17 - C18	114.3(8)
		C17 - C18 - N19	178(1)

Symmetry Operations

TABLE LV (Continued)

' = 1 + x, y, z

'' = -1 + x, y, z

''' = 1 - x, 1 - y, -z

'''' = -x, 1 - y, -z

TABLE LVI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 3-PYRIDYLACETONITRILE, HYDROGEN (ROOM TEMPERATURE)

C12 - H12	0.96	N11 - C12 - H12	118
C14 - H14	0.96	C13 - C12 - H12	117
C15 - H15	0.97	C13 - C14 - H14	119
C16 - H16	0.97	C15 - C14 - H14	121
C17 - H171	0.96	C14 - C15 - H15	121
C17 - H172	0.99	C16 - C15 - H15	121
		C15 - C16 - H16	118
		N11 - C16 - H16	119
		C13 - C17 - H171	109
		C13 - C17 - H172	108
		H171 - C17 - H172	109
		H171 - C17 - C18	109
		H172 - C17 - C18	107

TABLE LVII

CRYSTAL DATA FOR COPPER IODIDE 3-PYRIDYL-ACETONITRILE (LOW TEMPERATURE)

Formula	$(CuIC_7H_6N_2)_n$
Mwt	308.5879
<u>a</u>	4.235(1) Å
<u>b</u>	7.876(4)
<u>c</u>	13.756(9)
α	98.41(4)°
β	71.24(4)
γ	78.93(3)
V	415.6(4) $Å^3$
F(000)	288
μMoK_α	62.4383 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.4654 g cm^{-1}
Z	2
Meas refl	1099
Obs refl	996
R	2.7%
R_w	3.8
Space Group	$P\bar{1}$
Octants meas	±h, k, ±l

TABLE LVIII

POSITIONAL PARAMETERS FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (LOW TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	-0.1120(1)	0.2430(1)	-0.0638(0)
Cu1	0.2349(3)	0.4106(2)	0.0368(1)
N11	0.0517(15)	0.3532(8)	0.1815(5)
N19	-0.1231(18)	-0.1894(9)	0.4217(6)
C12	0.1985(17)	0.2039(9)	0.2026(6)
C13	0.0687(18)	0.1539(9)	0.2986(6)
C14	-0.2312(19)	0.2638(10)	0.3722(5)
C15	-0.3868(19)	0.4178(10)	0.3515(6)
C16	-0.2378(21)	0.4561(10)	0.2558(6)
C17	0.2684(20)	-0.0130(10)	0.3147(6)
C18	0.0521(19)	-0.1127(10)	0.3747(6)

TABLE LIX

POSITIONAL PARAMETERS FOR COPPER IODIDE 3-PYRIDYLACETONITRILE, HYDROGEN ATOMS (ROOM TEMPERATURE)

ATOM	X	Y	Z
H12	0.4062	0.1249	0.1479
H14	-0.3332	0.2322	0.4394
H15	-0.5969	0.4989	0.4044
H16	-0.3498	0.5651	0.2409
H171	0.4129	-0.0898	0.2457
H172	0.4193	0.0187	0.3512

TABLE LX

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (LOW TEMPERATURE)

ATOM	U11	U22	U33	U12	U13	U23
I1	15(0)	18(0)	22(0)	-5(0)	-4(0)	4(0)
Cu1	20(0)	24(0)	18(0)	-4(0)	-3(0)	9(0)
N11	19(3)	21(3)	14(3)	-8(2)	-3(2)	5(2)
N19	33(4)	30(4)	40(4)	-8(3)	-11(3)	11(3)
C12	13(3)	14(3)	23(4)	-6(3)	-4(3)	6(3)
C13	17(3)	22(4)	21(4)	-10(3)	-7(3)	4(3)
C14	24(4)	25(4)	9(3)	-7(3)	-4(3)	3(3)
C15	23(4)	19(4)	25(4)	-5(3)	-4(3)	4(3)
C16	32(4)	17(4)	27(4)	-7(3)	-5(3)	4(3)
C17	28(4)	30(4)	18(4)	-4(3)	-3(3)	11(3)
C18	21(4)	22(4)	14(5)	-1(3)	-2(3)	8(3)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C, and N.

TABLE LXI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (LOW TEMPERATURE)

I1 - Cu1	2.708(1)	Cu1 - I1 - Cu1'	105.05(5)
I1 - Cu1''	2.628(1)	Cu1 - I1 - Cu1''	63.25(4)
I1 - Cu1''''	2.624(2)	Cu1' - I1 - Cu1''''	66.16(8)
Cu1 - Cu1'''	2.867(2)	I1 - Cu1 - I1'	105.05(4)
Cu1 - Cu1''''	2.757(2)	I1 - Cu1 - I1''''	117.85(5)
Cu1 - N11	2.042(6)	I1' - Cu1 - I1''''	113.84(4)
N11 - C12	1.34(1)	I1 - Cu1 - N11	100.4(2)
N11 - C16	1.332(8)	I1' - Cu1 - N11	111.1(2)
C12 - C13	1.40(1)	I1'''' - Cu1 - N11	107.9(2)
C13 - C14	1.371(8)	Cu1 - N11 - C12	121.8(4)
C13 - C17	1.51(1)	Cu1 - N11 - C16	120.9(6)
C14 - C15	1.38(1)	C12 - N11 - C16	117.1(6)
C15 - C16	1.37(1)	N11 - C12 - C13	123.6(5)
C17 - C18	1.46(1)	C12 - C13 - C14	116.9(7)
C18 - N19	1.14(1)	C12 - C13 - C17	118.4(5)
		C14 - C13 - C17	124.7(7)
		C13 - C14 - C15	120.3(7)
		C14 - C15 - C16	118.4(6)
		C15 - C16 - N11	123.6(7)
		C13 - C17 - C18	113.9(6)
		C17 - C18 - N19	179(1)

Symmetry Operations

TABLE LXI (Continued)

' = 1 + x, y, z

'' = -1 + x, y, z

''' = 1 - x, 1 - y, -z

'''' = -x, 1 - y, -z

TABLE LXII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 3-PYRIDYLACETONITRILE, HYDROGEN (LOW TEMPERATURE)

C12 - H12	0.98	N11 - C12 - H12	118
C14 - H14	0.98	C13 - C12 - H12	118
C15 - H15	0.98	C13 - C14 - H14	119
C16 - H16	0.98	C15 - C14 - H14	120
C17 - H171	0.98	C14 - C15 - H15	121
C17 - H172	0.98	C16 - C15 - H15	121
		C15 - C16 - H16	118
		N11 - C16 - H16	118
		C13 - C17 - H171	109
		C13 - C17 - H172	109
		H171 - C17 - H172	108
		H171 - C17 - C18	108
		H172 - C17 - C18	109

TABLE LXIII

CRYSTAL DATA FOR COPPER IODIDE ISO-NICOTINIC ACID

Formula	$(CuIC_6H_6NO_2)_n$
Mwt	313.5610
a	14.621(6) Å
b	4.120(2)
c	14.372(7)
α	90.0 °
β	105.24(3)
γ	90.0
V	835.4(6) $Å^3$
F(000)	292
μMoK_α	62.2719 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.4925 g cm^{-1}
Z	4
Meas refl	1268
Obs refl	637
R	5.9%
R_w	8.2
Space group	$P2_1/c$
Octants meas	±h, k, ±l

TABLE LXIV

POSITIONAL PARAMETERS FOR COPPER IODIDE ISO-NICOTINIC ACID

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.0793(1)	0.1848(5)	0.8837(1)
Cu1	-0.0711(2)	0.1858(11)	0.7321(2)
O18	-0.4828(16)	-0.0744(75)	0.8867(14)
O19	-0.3928(15)	0.1862(78)	1.0142(14)
N11	-0.1862(17)	0.1876(65)	0.7908(14)
C12	-0.1792(18)	0.2971(80)	0.8773(20)
C13	-0.2520(21)	0.2964(89)	0.9242(17)
C14	-0.3321(21)	0.1199(85)	0.8777(21)
C15	-0.3436(20)	-0.0050(93)	0.7873(22)
C16	-0.2655(22)	0.0354(95)	0.7482(19)
C17	-0.4085(18)	0.0807(79)	0.9297(21)

TABLE LXV

POSITIONAL PARAMETERS FOR COPPER IODIDE ISO-NICOTINIC ACID (HYDROGEN ATOMS)

ATOM	X	Y	Z
H12	-0.1173	0.3911	0.9123
H13	-0.2467	0.4105	0.9859
H15	-0.4032	-0.1171	0.7513
H16	-0.2698	-0.0611	0.6829

TABLE LXVI

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE ISO-NICOTINIC ACID

ATOM	U11	U22	U33	U12	U13	U23
I1	44(1)	38(1)	40(1)	1(1)	4(0)	-2(0)
Cu1	45(2)	57(2)	46(2)	-2(2)	15(1)	0(2)
O18	60(15)	163(28)	44(12)	-27(17)	30(11)	-7(15)
O19	53(14)	189(31)	43(12)	-22(18)	14(11)	-40(17)
N11	47(14)	58(16)	28(12)	-11(14)	14(10)	-3(13)
C12	24(16)	55(20)	52(18)	1(16)	-25(14)	-17(17)
C13	53(20)	97(28)	24(14)	1(20)	22(14)	-36(17)
C14	34(18)	70(26)	55(19)	1(18)	5(15)	-6(18)
C15	32(18)	93(28)	55(20)	-6(18)	22(15)	18(19)
C16	50(22)	105(30)	30(16)	4(21)	-1(15)	-22(18)
C17	11(15)	61(26)	53(19)	3(14)	-18(13)	19(16)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*$ $+ 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C, N, and O.

TABLE LXVII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE ISO-NICOTINIC ACID

I1 - Cu1	2.658(4)	Cu1 - I1 - Cu1'	65.8(1)
I1 - Cu1'	2.634(5)	Cu1 - I1 - Cu1''	65.9(1)
I1 - Cu1''	2.628(5)	Cu1' - I1 - Cu1''	103.1(1)
Cu1 - Cu1'	2.876(6)	I1 - Cu1 - I1'	114.1(1)
Cu1 - Cu1''	2.876(6)	I1 - Cu1 - I1''	114.0(2)
Cu1 - N11	2.07(3)	I1' - Cu1 - I1''	103.1(1)
N11 - C12	1.30(4)	I1 - Cu1 - N11	104.6(5)
N11 - C16	1.32(4)	I1' - Cu1 - N11	110.4(7)
C12 - C13	1.40(4)	I1'' - Cu1 - N11	110.7(7)
C13 - C14	1.39(4)	C12 - N11 - C16	125(2)
C14 - C15	1.37(4)	C12 - N11 - Cu1	121(2)
C14 - C17	1.51(5)	C16 - N11 - Cu1	121(2)
C15 - C16	1.41(5)	N11 - C12 - C13	125(2)
C17 - O18	1.27(4)	C12 - C13 - C14	115(3)
C17 - O19	1.25(4)	C13 - C14 - C15	122(3)
		C13 - C14 - C17	117(3)
		C15 - C14 - C17	122(3)
		C14 - C15 - C16	115(3)
		C15 - C16 - N11	125(3)
		C14 - C17 - O18	118(3)
		C14 - C17 - O19	118(2)
		O19 - C17 - O18	124(3)

TABLE LVII (Continued)

Symmetry Operations:

' = -x, 0.5 + y, 1.5 - z

'' = -x, -0.5 + y, 1.5 - z

TABLE LXVIII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE ISO NICOTINIC ACID - HYDROGEN ATOMS

C12 - H12	0.99	N11 - C12 - H12	117
C13 - H13	0.99	C13 - C12 - H12	118
C15 - H15	1.00	C12 - C13 - H13	123
C16 - H16	1.01	C14 - C13 - H13	122
		C14 - C15 - H15	122
		C16 - C15 - H15	122
		C15 - C16 - H16	118
		N11 - C16 - H16	117
		C17 - N18 - H18	139
		C17 - N18 - H18	110

TABLE LXIX

CRYSTAL DATA FOR COPPER IODIDE ISO-NICOTINAMIDE

Formula	$(CuIC_6H_6N_2O)_n$
Mwt	312.5762
<u>a</u>	13.482(5) Å
<u>b</u>	4.117(2)
<u>c</u>	16.718(7)
α	90.0 °
β	109.60(2)
γ	90.0
V	847.2(6) $Å^3$
F(000)	292
μMoK_α	61.3526 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.4501 g cm^{-1}
Z	4
Meas refl	2061
Obs refl	1311
R	6.0%
R_w	7.7
Space group	$P2_1/c$
Octants meas	±h, k, ±l

TABLE LXX

POSITIONAL PARAMETERS FOR COPPER IODIDE ISO-NICOTINAMIDE

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.8848(1)	0.0803(2)	0.6401(1)
Cu1	1.0766(1)	0.0629(5)	0.7535(1)
O19	1.4944(9)	0.4185(47)	0.6094(7)
N18	1.3698(11)	0.3737(56)	0.4852(8)
N11	1.1822(8)	0.1321(29)	0.6907(7)
C12	1.2850(11)	0.0416(36)	0.7264(9)
C13	1.3587(11)	0.1181(40)	0.6875(9)
C14	1.3249(10)	0.2782(40)	0.6108(8)
C15	1.2201(11)	0.3580(37)	0.5736(9)
C16	1.1529(10)	0.2813(40)	0.6163(8)
C17	1.4043(11)	0.3653(42)	0.5666(9)

TABLE LXXI

POSITIONAL PARAMETERS FOR COPPER IODIDE ISO-NICOTINAMIDE (HYDROGEN ATOMS)

ATOM	X	Y	Z
H12	1.3075	-0.0781	0.7804
H13	1.4329	0.0605	0.7140
H15	1.1947	0.4693	0.5188
H16	1.0790	0.3417	0.5909
H18	1.2962	0.2395	0.4651
H19	1.3923	0.3956	0.4453

TABLE LXXII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE ISO-NICOTINAMIDE

ATOM	U11	U22	U33	U12	U13	U23
I1	30(0)	31(0)	36(0)	-2(0)	4(0)	0(0)
Cu1	35(1)	54(1)	42(1)	0(0)	20(0)	5(0)
O19	27(6)	202(18)	50(6)	-30(8)	6(4)	21(9)
N18	43(8)	197(21)	32(6)	-56(10)	23(5)	-13(10)
N11	20(5)	43(6)	39(6)	0(4)	13(4)	-2(5)
C12	37(7)	39(7)	40(7)	-6(6)	11(5)	2(6)
C13	28(7)	57(9)	38(7)	-2(6)	16(5)	9(7)
C14	26(6)	56(8)	27(6)	-13(6)	13(5)	-10(6)
C15	34(7)	48(8)	37(7)	3(6)	12(5)	13(6)
C16	27(6)	56(9)	36(7)	-2(6)	9(5)	19(7)
C17	24(7)	72(11)	43(7)	-19(6)	19(5)	-13(8)

Anisotropic thermal parameters in the form:

$$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$$ for I, Cu; $\times 10^3$ for C, N, and O.

TABLE LXXIII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE ISO-NICOTINAMIDE

I1 - Cu1	2.645(2)	Cu1 - I1 - Cu1'	66.88(6)
I1 - Cu1'	2.600(2)	Cu1 - I1 - Cu1''	65.30(6)
I1 - Cu1''	2.711(2)	Cu1' - I1 - Cu1''	101.62(7)
Cu1 - Cu1'	2.891(3)	I1 - Cu1 - I1'	112.03(7)
Cu1 - Cu1''	2.891(3)	I1 - Cu1 - I1''	115.73(8)
Cu1 - N11	2.05(1)	I1' - Cu1 - I1''	101.62(7)
N11 - C12	1.36(2)	I1 - Cu1 - N11	108.0(3)
N11 - C16	1.32(2)	I1' - Cu1 - N11	102.3(3)
C12 - C13	1.39(2)	I1'' - Cu1 - N11	116.2(3)
C13 - C14	1.37(2)	C12 - N11 - C16	118(1)
C14 - C15	1.38(2)	C12 - N11 - Cu1	122(1)
C14 - C17	1.52(2)	C16 - N11 - Cu1	120.4(9)
C15 - C16	1.37(2)	N11 - C12 - C13	121(1)
C17 - N18	1.28(2)	C12 - C13 - C14	118(1)
C17 - O19	1.21(2)	C13 - C14 - C15	120(1)
		C13 - C14 - C17	120(1)
		C15 - C14 - C17	120(1)
		C14 - C15 - C16	124(1)
		C15 - C16 - N11	124(1)
		C14 - C17 - N18	117(1)
		C14 - C17 - O19	119(1)
		O19 - C17 - N18	124(2)

TABLE LXXIII (Continued)

Symmetry Operations:

' = 2 - x, 0.5 + y, 1.5 - z

'' = 2 - x, -0.5 + y, 1.5 - z

TABLE LXXIV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE ISO-NICOTINAMIDE, HYDROGEN ATOMS

C12 - H12	0.98	N11 - C12 - H12	120
C13 - H13	0.98	C13 - C12 - H12	120
C15 - H15	0.98	C12 - C13 - H13	121
C16 - H16	0.97	C14 - C13 - H13	121
N18 - H18	1.09	C14 - C15 - H15	121
N18 - H19	0.82	C16 - C15 - H15	121
		C15 - C16 - H16	118
		N11 - C16 - H16	118
		C17 - N18 - H18	139
		C17 - N18 - H18	110

TABLE LXXV

CRYSTAL DATA FOR COPPER IODIDE METHYL ISO-NICOTINATE

Formula	$(CuIC_7H_7NO_2)_n$
Mwt	327.5879
<u>a</u>	4.169(1) Å
<u>b</u>	9.473(4)
<u>c</u>	13.422(5)
α	72.11(3) °
β	105.07(3)
γ	81.69(3)
V	472.4(3) $Å^3$
F(000)	318
μMoK_α	55.1138 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.3025 g cm^{-1}
Z	2
Meas refl	1242
Obs refl	861
R	4.9%
R_w	6.3
Space group	$P\bar{1}$
Octants meas	±h, k, ±l

TABLE LXXVI

POSITIONAL PARAMETERS FOR COPPER IODIDE METHYL ISO-NICOTINATE

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.1780	0.2122	-0.0001
Cu1	0.2009	-0.0108	-0.0680
Cu11	0.3375	-0.0785	0.0677
O18	-0.3095(53)	0.2800(22)	-0.6446(15)
O118	0.9799	-0.3612	0.6433
O19	-0.6784(63)	0.4531(28)	-0.6231(17)
O119	0.5587	-0.1670	0.6219
N11	0.0142(50)	0.1040(22)	-0.2305(15)
N111	0.4856	-0.1275	0.2330
C12	-0.2256(76)	0.2436(29)	-0.2805(22)
C112	0.7103	-0.2554	0.3066
C13	-0.3825(73)	0.3172(31)	0.3883(20)
C113	0.7929	-0.2957	0.4148
C14	-0.2788(74)	0.2593(34)	0.4637(24)
C114	0.6377	-0.2009	0.4596
C15	-0.0382(66)	0.1172(29)	0.4194(24)
C115	0.3992	-0.0690	0.3898
C16	0.1070(63)	0.0530(27)	-0.3026(21)
C116	0.3221	-0.0297	0.2763
C17	-0.4484(76)	0.3410(36)	-0.5921(21)
C117	0.7061	-0.2365	0.5864

TABLE LXXVI (Continued)

C20	-0.4418(98)	0.3581(42)	-0.7688(25)
C120	1.0865	-0.4043	0.7677

TABLE LXXVII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE METHYL ISO-NICOTINATE

ATOM	U11	U22	U33	U12	U13	U23
I1	50	57	138	-15	44	-42
Cu1	51	55	49	-5	16	-10
Cu11	53	56	43	-6	10	-13
O18	92(15)	61(12)	24(12)	-2(11)	16(11)	-6(10)
O118	90	88	12	-9	6	-4
O19	96(18)	96(17)	38(15)	38(15)	-1(12)	-4(13)
O119	160	72	53	34	62	-5
N11	49(12)	45(12)	10(13)	-6(10)	-2(10)	5(10)
N111	55	43	18	1	3	5
C12	82(20)	39(15)	12(19)	14(14)	4(14)	11(13)
C112	52	51	17	-3	-6	3
C13	74(19)	57(17)	0(18)	-3(14)	-1(14)	2(14)
C113	56	60	19	14	-16	-7
C14	64(19)	69(21)	90(28)	-28(17)	24(19)	-53(21)
C114	58	57	30	-18	9	-9
C15	47(15)	39(15)	40(22)	12(12)	7(13)	0(14)
C115	79	34	24	17	6	3
C16	51(14)	40(14)	20(19)	-11(12)	17(13)	5(13)
C116	90	47	16	3	18	4
C17	64(18)	76(21)	0(16)	17(16)	-6(13)	-4(14)
C117	49	53	44	-18	-7	14

TABLE LXXVII (Continued)

C20	124(30)	101(27)	20(22)	-26(23)	13(19)	-21(19)
C120	177	43	9	-15	-27	15

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C, N, and O.

TABLE LXXVIII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE METHYL ISO-NICOTINATE

I1 - Cu11	2.544(4)	Cu1 - I1 - Cu1'	62.9(1)
I1 - Cu11	2.725(5)	Cu1 - I1 - Cu1''	64.1(1)
I1 - Cu11'	2.743(4)	Cu1' - I1 - Cu1''	99.2(1)
I1 - Cu1	2.544(5)	I1' - Cu1 - I1	117.1(1)
I1 - Cu1'	2.729(4)	I1' - Cu1 - I1''	99.2(1)
I1 - Cu1''	2.743(4)	I1'' - Cu1 - I1	115.0(2)
Cu1 - Cu1'	2.758(6)	N11 - Cu1 - I1	99.7(7)
Cu1 - Cu1''	2.811(7)	N11 - Cu1 - I1'	114.2(7)
Cu11 - Cu11'	2.748(6)	N11 - Cu1 - I1''	120.6(6)
Cu11 - Cu11''	2.811(7)	C16 - N11 - C12	113(2)
Cu1 - N11	1.99(2)	N11 - C12 - C13	127(3)
Cu11 - N111	2.02(2)	C12 - C13 - C14	119(3)
N11 - C12	1.38(3)	C13 - C14 - C15	118(3)
C12 - C13	1.33(3)	N13 - C14 - C17	122(2)
C13 - C14	1.42(5)	C15 - C14 - C17	120(3)
C14 - C15	1.41(4)	C14 - C15 - C16	116(3)
C14 - C17	1.57(4)	C15 - C16 - N11	127(2)
C15 - C16	1.42(4)	C14 - C17 - O18	113(2)
C16 - N11	1.32(4)	C14 - C17 - O19	116(3)
C17 - O18	1.23(4)	O18 - C17 - O19	131(3)
C17 - O19	1.20(4)	C17 - O18 - C20	116(3)
O18 - C20	1.51(3)	Cu11 - I1 - Cu11'	62.8(1)
N111 - C112	1.33(3)	Cu11 - I1 - Cu11''	64.1(1)

TABLE LXXVIII (Continued)

C112 - C113	1.32(5)	Cu11' - I1 - Cu11''	99.3(1)
C113- C114	1.40(3)	I1' - Cu11 - I1	117(2)
C114 - C115	1.37(4)	I1' - Cu11 - I1''	99.3(2)
C114 - C117	1.57(5)	I1'' - Cu11 - I1	115.9(1)
C115 - C116	1.39(5)	N111 - Cu11 - I1	99.8(7)
C116 - N111	1.42(5)	N111 - Cu11 - I1'	113.3(7)
C117 - O118	1.37(4)	N111 - Cu11 - I1''	111.9(7)
C117 - O119	1.12(8)	C116 - N111 - C112	116(3)
O118 - C120	1.51(4)	N111 - C112 - C113	125(4)
		C112 - C113 - C114	120(3)
		C113 - C114 - C115	119(3)
		C113 - C114 - C117	125(2)
		C115 - C114 - C117	116(3)
		C114 - C115 - C116	120(3)
		C115 - C116 - N111	120(2)
		C114 - C117 - O118	108(3)
		C114 - C117 - O119	125(3)
		O118 - C117 - O119	127(3)
		C117 - O118 - C120	114(3)

Symmetry Operations:

' = 1 - x, -y, -z

'' = -x, -y, -z

TABLE LXXIX

CRYSTAL DATA FOR Copper Iodide 4-Cyanopyridine

Formula	$(Cu_2I_2(C_6H_4N_2)_3)_n$
Mwt	549.1016
a	10.159(2) Å
b	12.215(3)
c	15.139(4)
α	90.0 °
β	99.93(5)
γ	90.0
V	1850.6(8) $Å^3$
F(000)	1016
μMoK_α	55.9835 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.9704 g cm^{-1}
Z	4
Meas refl	2428
Obs refl	1494
R	5.3%
R_w	6.9
Space group	$P2_1/C$
Octants meas	h, k, ±l

TABLE LXXX

POSITIONAL PARAMETERS FOR COPPER IODIDE 4-CYANOPYRIDINE

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.1048(1)	0.0905(1)	0.9006(1)
I2	-0.2007(1)	-0.1724(1)	0.8255(1)
Cu1	0.0265(2)	-0.0859(2)	0.8052(2)
Cu2	-0.1143(3)	-0.0091(2)	0.9322(2)
N11	0.1841(15)	-0.1928(14)	0.8216(9)
N21	-0.2624(17)	0.1101(14)	0.9263(10)
N31	0.0137(17)	-0.0466(13)	0.6723(10)
N18	0.5860(21)	-0.4744(18)	0.8030(16)
N28	-0.6292(23)	0.4144(18)	0.9537(15)
C12	0.3088(22)	-0.1578(18)	0.8298(17)
C13	0.4119(19)	-0.2294(16)	0.8221(15)
C14	0.3968(16)	-0.3366(19)	0.8139(13)
C15	0.2613(20)	-0.3773(16)	0.8070(15)
C16	0.1568(19)	-0.2998(18)	0.8110(14)
C17	0.5026(21)	-0.4182(18)	0.8114(13)
C22	-0.3884(19)	0.0807(21)	0.9205(15)
C23	-0.4899(21)	0.1589(18)	0.9227(16)
C24	-0.4534(20)	0.2701(19)	0.9360(13)
C25	-0.3222(22)	0.2978(18)	0.9469(15)
C26	-0.2313(18)	0.2157(20)	0.9408(16)
C27	-0.5569(24)	0.3495(20)	0.9485(25)

TABLE LXXX (Continued)

C32	0.1054(36)	0.0346(33)	0.6385(25)
C33	0.0954(36)	0.0691(32)	0.5492(29)
C34	0.0	0.0	0.5
C35	-0.0674(45)	-0.0758(37)	0.5149(31)
C36	-0.0674(49)	-0.0967(36)	0.6075(35)
C37	-0.0040	0.0356(43)	0.4005(40)

TABLE LXXXI

POSITIONAL PARAMETERS FOR COPPER IODIDE 4-CYANOPYRIDINE (HYDROGEN ATOMS)

ATOM	X	Y	Z
H12	0.3302	-0.0805	0.8428
H13	0.5002	-0.1991	0.8216
H15	0.2409	-0.4535	0.7956
H16	0.0663	-0.3252	0.8097
H22	-0.4126	-0.0001	0.9131
H23	-0.5825	0.1388	0.9137
H25	-0.2927	0.3753	0.9584
H26	-0.1386	0.2364	0.9487

TABLE LXXXII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 4-CYANOPYRIDINE

ATOM	U11	U22	U33	U12	U13	U23
I1	40(0)	47(0)	43(0)	-5(0)	8(0)	0(0)
I2	39(0)	54(0)	56(0)	-8(0)	10(0)	-5(0)
Cu1	39(1)	51(1)	41(1)	7(1)	5(1)	4(1)
Cu2	44(1)	48(1)	57(1)	3(1)	9(1)	1(1)
N11	34(10)	38(11)	28(9)	6(8)	7(7)	8(7)
N21	53(11)	38(11)	34(10)	-16(9)	-20(8)	10(8)
N31	67(11)	41(10)	24(9)	9(9)	6(8)	2(8)
N18	56(13)	115(20)	111(19)	60(14)	23(13)	7(15)
N28	100(17)	63(15)	111(19)	37(13)	1(14)	-25(13)
C12	48(14)	41(14)	96(19)	0(12)	24(12)	-30(13)
C13	36(12)	27(13)	78(16)	-4(9)	10(10)	-21(11)
C14	15(10)	66(17)	44(12)	3(10)	0(8)	-3(11)
C15	37(12)	34(12)	65(15)	10(10)	1(10)	-2(10)
C16	34(11)	33(14)	66(15)	2(10)	-1(10)	-6(11)
C17	40(13)	75(16)	42(13)	8(12)	6(10)	-18(12)
C22	22(12)	84(18)	66(16)	-13(12)	4(10)	-2(14)
C23	43(13)	40(15)	76(16)	-9(11)	8(11)	8(12)
C24	43(13)	58(16)	36(12)	13(11)	1(9)	-10(11)
C25	48(14)	38(13)	67(16)	9(11)	-1(11)	1(11)
C26	9(10)	71(18)	96(19)	0(10)	16(10)	15(14)
C27	68(16)	60(16)	61(15)	-3(13)	22(12)	-11(13)

TABLE LXXXII (Continued)

C32	5(0)	35(21)	42(24)	33(25)	-17(19)	-5(17)
C33	5(0)	36(23)	38(26)	24(25)	-11(19)	-7(19)
C34	53(20)	27(18)	64(25)	-5(17)	-9(17)	13(17)
C35	5(0)	58(28)	42(29)	18(24)	-12(24)	4(22)
C36	5(0)	80(36)	34(27)	98(41)	-41(26)	64(32)
C37	5(0)	78(39)	49(33)	122(54)	14(32)	73(38)

Anisotropic thermal parameters in the form:

$$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$$

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

TABLE LXXXIII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 4-CYANOPYRIDINE

I1 - Cu1	2.640(3)	Cu2 - I1 - Cu1	62.66(9)
I1 - Cu2	2.706(3)	Cu2 - I1 - Cu2'	63.77(8)
I2 - Cu2	2.621(3)	Cu1 - I1 - Cu2'	99.81(9)
I2 - Cu1'	2.604(3)	Cu2 - I2 - Cu1	63.56(9)
Cu1 - Cu2	2.751(4)	I2 - Cu1 - I1	117.2(1)
Cu2 - Cu2'	2.830(3)	I1 - Cu2 - I1'	116.2(1)
Cu1 - N11	2.05(2)	I2 - Cu2 - I1'	104.5(1)
Cu1 - N31	2.05(2)	I2 - Cu2 - I1	116.1(1)
Cu2 - N21	2.08(2)	N11 - Cu1 - I1	107.4(4)
N11 - C12	1.32(3)	N11 - Cu1 - I2	114.7(5)
N11 - C16	1.34(3)	N31 - Cu1 - I1	107.9(5)
C12 - C13	1.38(3)	N31 - Cu1 - I2	114.7(5)
C13 - C14	1.32(3)	N31 - Cu1 - N11	100.6(6)
C14 - C15	1.45(3)	N21 - Cu2 - I1	107.1(5)
C14 - C17	1.47(3)	N21 - Cu2 - I1'	101.9(4)
C15 - C16	1.43(3)	N21 - Cu2 - I2	110.0(4)
C17 - N18	1.11(3)	C12 - N11 - C16	120(2)
N21 - C22	1.32(3)	C12 - N11 - Cu1	121(1)
N21 - C26	1.34(3)	C16 - N11 - Cu1	118(1)
C22 - C23	1.41(3)	N11 - C12 - C13	121(2)
C23 - C24	1.41(3)	C12 - C13 - C14	124(2)
C24 - C25	1.36(3)	C13 - C14 - C15	116(2)
C24 - C27	1.47(3)	C13 - C14 - C17	127(2)

TABLE LXXXIII (Continued)

C25 - C26	1.38(3)	C15 - C14 - C17	117(2)
C27 - N28	1.09(3)	C14 - C15 - C16	118(2)
N31 - C32	1.51(4)	C15 - C16 - N11	121(2)
N31 - C36	1.32(5)	C14 - C17 - N18	173(2)
C32 - C33	1.40(6)	C22 - N21 - C26	118(2)
C33 - C34	1.4(1)	C22 - N21 - Cu2	120(2)
C34 - C35	1.2(1)	C26 - N21 - Cu2	121(1)
C34 - C37	1.6(1)	N21 - C22 - C23	121(2)
C35 - C36	1.42(7)	C22 - C23 - C24	119(2)
C37 - N31''	1.10(6)	C23 - C24 - C25	119(2)
		C23 - C24 - C27	119(2)
		C25 - C24 - C27	122(2)
		C24 - C25 - C26	118(2)
		C25 - C26 - N21	125(2)
		C24 - C27 - N28	174(3)
		C32 - N31 - C36	113(3)
		C32 - N31 - Cul	123(3)
		C36 - N31 - Cul	123(3)
		N31 - C32 - C33	125(3)
		C32 - C33 - C34	105(5)
		C33 - C34 - C35	137(8)
		C33 - C34 - C37	104(7)
		C35 - C34 - C37	118(7)
		C34 - C35 - C36	114(6)
		C35 - C36 - N31	123(4)

TABLE LXXXIII (Continued)

C34 - C37 - N31''	170(6)

Symmetry Operations:

' = -x, -y, 2 - z

'' = -x, -y, 1 - z

TABLE LXXXIV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 4-CYANOPYRIDINE - HYDROGEN ATOMS

C12 - H12	0.98	N11 - C12 - H12	120
C13 - H13	0.97	C13 - C12 - H12	119
C15 - H15	0.96	C12 - C13 - H13	118
C16 - H16	0.97	C14 - C13 - H13	118
C22 - H22	1.02	C14 - C15 - H15	121
C23 - H23	0.96	C16 - C15 - H15	121
C25 - H25	1.00	C15 - C16 - H16	120
C26 - H26	0.96	N11 - C16 - H16	120
C212 - H212	0.98	N21 - C22 - H22	119
		C23 - C22 - H22	120
		C22 - C23 - H23	122
		C24 - C23 - H23	120
		C24 - C25 - H25	121
		C26 - C25 - H25	121
		C25 - C26 - H26	117
		N21 - C26 - H26	118

TABLE LXXXV

CRYSTAL DATA FOR COPPER IODIDE METHYL 2-PYRIDYLACETATE

Formula	$Cu_2I_2(C_8H_9NO_2)_4$
Mwt	985.559
a	9.697(3) Å
b	10.771(4)
c	11.459(2)
α	51.91(2) °
β	98.33(2)
γ	93.70(3)
V	923.4(4) $Å^3$
F(000)	484
μMoK_α	28.5900 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.7720 g cm^{-1}
Z	1
Meas refl	3178
Obs refl	1778
R	4.8%
R_w	6.4
Space group	$P\bar{1}$
Octants meas	±h, k, ±l

TABLE LXXXVI

POSITIONAL PARAMETERS FOR COPPER IODIDE METHYL 2-PYRIDYLACETATE

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	-0.0128(1)	-0.2366(1)	0.0920(1)
Cu1	-0.1114(2)	0.0473(2)	-0.1547(2)
O109	-0.4005(9)	0.4078(9)	-0.5574(9)
O110	-0.3243(9)	0.2261(11)	-0.5695(11)
O209	-0.2606(9)	-0.3892(9)	-0.0913(9)
O210	-0.4021(11)	-0.3692(9)	-0.0313(11)
N101	-0.0273(9)	0.1075(10)	-0.3402(10)
N210	-0.3241(10)	0.0672(10)	-0.4771(13)
C102	-0.0470(12)	0.2516(13)	-0.4771(13)
C103	0.0301(15)	0.2964(15)	-0.5883(15)
C104	0.1253(13)	0.1904(17)	-0.5643(15)
C105	0.1407(11)	0.0460(16)	-0.4327(16)
C106	0.0651(12)	0.0067(14)	-0.3209(13)
C107	-0.1591(12)	0.3582(13)	-0.5036(13)
C108	-0.3003(14)	0.3188(13)	-0.5453(12)
C111	-0.5450(13)	0.3845(16)	-0.6010(16)
C202	-0.4119(13)	-0.0231(14)	-0.1988(12)
C203	-0.5547(14)	-0.0130(15)	-0.2042(15)
C204	-0.6106(14)	0.0939(17)	-0.1957(14)
C205	-0.5250(13)	0.1882(14)	-0.1775(13)
C206	-0.3834(14)	0.1712(13)	-0.1708(13)

TABLE LXXXVI (Continued)

C207	-0.3504(12)	-0.1368(14)	-0.2133(13)
C208	-0.3436(13)	-0.3057(14)	-0.0739(14)
C211	-0.2419(17)	-0.5587(15)	0.0348(15)

TABLE LXXXVII

POSITIONAL PARAMETERS FOR COPPER IODIDE METHYL 2-PYRIDYLACETATE (HYDROGEN ATOMS)

ATOM	X	Y	Z
H103	0.0161	0.4014	-0.6847
H104	0.1813	0.2216	-0.6422
H105	0.2047	-0.0311	-0.4151
H106	0.0786	-0.0980	-0.2244
H107	-0.1598	0.3468	-0.4115
H117	-0.1396	0.4669	-0.5842
H203	-0.6154	-0.0819	-0.2140
H204	-0.7105	0.1028	-0.2026
H205	-0.5607	0.2643	-0.1691
H206	-0.3222	0.2398	-0.1601
H207	-0.4065	-0.1301	-0.2952
H217	-0.2561	-0.1054	-0.2378

TABLE LXXXVIII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE METHYL 2-PYRIDYLACETATE

ATOM	U11	U22	U33	U12	U13	U23
I1	79(0)	34(0)	44(0)	2(0)	-4(0)	-20(0)
Cu1	61(1)	47(0)	51(0)	4(0)	15(0)	-26(0)
O109	70(6)	53(5)	53(5)	24(4)	-8(4)	-34(4)
O110	64(6)	74(6)	91(7)	12(4)	2(5)	-64(6)
O209	68(5)	56(5)	57(5)	9(4)	13(4)	-37(4)
O210	105(7)	53(5)	70(6)	-9(5)	50(6)	-35(5)
N101	38(5)	41(5)	39(5)	0(4)	5(4)	-24(4)
N201	48(6)	38(5)	39(5)	1(4)	13(4)	-19(4)
C102	52(7)	47(7)	45(7)	-2(5)	10(5)	-32(6)
C103	80(10)	51(7)	55(8)	-8(7)	16(7)	-31(6)
C104	55(8)	83(9)	55(8)	-13(7)	28(6)	-51(8)
C105	30(6)	72(8)	76(9)	7(6)	2(6)	-56(8)
C106	44(7)	57(7)	51(7)	18(6)	-12(5)	-34(6)
C107	48(7)	38(6)	45(6)	2(5)	14(5)	-17(5)
C108	75(9)	37(6)	29(6)	14(6)	-2(5)	-13(5)
C111	41(8)	70(8)	84(10)	22(6)	-16(7)	-47(8)
C202	50(8)	53(7)	31(6)	6(6)	2(5)	-23(5)
C203	59(9)	60(8)	72(9)	7(6)	0(6)	-47(7)
C204	48(8)	69(9)	46(7)	11(6)	3(6)	-25(7)
C205	54(8)	48(7)	46(7)	24(6)	5(5)	-22(6)
C206	75(9)	38(6)	44(7)	0(6)	22(6)	-25(5)

TABLE LXXXVIII (Continued)

C207	51(7)	51(7)	52(7)	0(5)	5(6)	-36(6)
C208	59(8)	47(7)	55(8)	-1(6)	9(6)	-36(6)
C211	120(13)	40(7)	56(8)	21(7)	12(8)	-20(6)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C, N, and O.

TABLE LXXXIX

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE METHYL 2-PYRIDYLACETATE

I1 - Cu1	2.673(4)	Cu1' - I1 - Cu1	79.01(7)
I1 - Cu1'	2.710(3)	Cu1 - I1 - Cu1'	79.01(7)
Cu1 - Cu1'	3.427(7)	I1 - Cu1 - I1'	100.99(8)
Cu1 - N101	2.06(1)	I1 - Cu1 - N201	111.9(2)
Cu1 - N201	2.04(1)	I1' - Cu1 - N201	110.6(4)
N101 - C102	1.35(1)	I1 - Cu1 - N101	110.4(2)
N101 - C106	1.34(2)	I1' - Cu1 - N101	104.8(3)
C102 - C103	1.36(2)	N101 - Cu1 - N201	116.5(4)
C102 - C107	1.49(2)	C102 - N101 - C106	117(1)
C103 - C104	1.38(2)	C102 - N101 - Cu1	123(1)
C104 - C105	1.33(2)	C106 - N101 - Cu1	118.6(7)
C105 - C106	1.37(2)	N101 - C102 - C103	121(1)
C107 - C108	1.50(1)	N101 - C102 - C107	117(1)
C108 - O109	1.34(2)	C103 - C102 - C107	121.0(9)
C108 - C110	1.18(2)	C102 - C103 - C104	119(1)
C109 - C111	1.47(2)	C103 - C104 - C105	119(2)
N201 - C202	1.35(2)	C104 - C105 - C106	119(2)
N201 - C206	1.34(2)	C105 - C106 - N101	122.5(9)
C202 - C203	1.38(2)	C102 - C107 - C108	111(1)
C202 - C207	1.50(2)	C107 - C108 - O109	111(1)
C203 - C204	1.36(3)	C107 - C108 - O110	126(1)
C204 - C205	1.36(2)	O109 - C108 - O110	122(1)
C205 - C206	1.38(2)	C108 - O109 - C111	116(1)

TABLE LXXXIX (Continued)

C207 - C208	1.50(1)	C202 - N201 - C206	116(1)
C208 - O209	1.36(2)	C202 - N201 - Cu1	122(1)
C208 - O210	1.17(2)	C206 - N201 - Cu1	120.4(9)
O209 - C211	1.46(1)	N201 - C202 - C203	121(1)
		N201 - C202 - C207	118(1)
		C203 - C202 - C207	120(1)
		C202 - C203 - C204	120(1)
		C203 - C204 - C205	119(1)
		C204 - C205 - C206	117(2)
		C205 - C206 - N201	124(1)
		C202 - C207 - C208	114(10
		C207 - C208 - O209	108(1)
		C207 - C208 - O210	127(2)
		O209 - C208 - O210	124(1)
		C208 - O209 - C211	115(1)

Symmetry Operations:

' = -x, -y, -z

TABLE XC

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE METHYL 2-PYRIDYLACETATE - HYDROGEN ATOMS

C103 - H103	0.97	C102 - C103 - H103	120
C104 - H104	0.96	C104 - C103 - H103	120
C105 - H105	0.97	C103 - C104 - H104	120
C106 - H106	0.97	C105 - C104 - H104	120
C107 - H107	0.98	C104 - C105 - H105	120
C107 - H117	0.97	C106 - C105 - H105	120
C203 - H203	0.97	C105 - C106 - H106	118
C204 - H204	0.97	N101 - C106 - H106	118
C205 - H205	0.97	C102 - C107 - H107	109
C206 - H206	0.97	C102 - C107 - H117	108
C207 - H207	0.97	H107 - C107 - H117	108
C207 - H117	0.97	H107 - C107 - C108	108
C215 - H215	0.97	H117 - C107 - C108	109
C216 - H216	0.98	C202 - C203 - H203	120
		C204 - C203 - H203	119
		C203 - C204 - H204	120
		C205 - C204 - H204	120
		C204 - C205 - H205	122
		C206 - C205 - H205	120
		C205 - C206 - H206	117
		N201 - C206 - H206	117
		C202 - C207 - H207	108
		C202 - C207 - H217	108

TABLE XC (Continued)

	H207 - C207 - H217	109
	H207 - C207 - C208	108
	H217 - C207 - C208	108

TABLE XCI

CRYSTAL DATA FOR COPPER IODIDE NICOTINAMIDE

Formula	$(CuI(C_6H_6N_2O)_2)_n$
Mwt	434.7024
<u>a</u>	9.511(3) Å
<u>b</u>	37.58(1)
<u>c</u>	4.045(1)
α	90.0 °
β	98.60(2)
γ	90.0
V	1429.9(8) $Å^3$
F(000)	840
μMoK_α	36.7286 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.0189 g cm^{-1}
Z	4
Meas refl	1898
Obs refl	1283
R	7.9%
R_w	12.6
Space group	$P2_1/n$
Octants meas	±h, k, ±l

TABLE XCII

POSITIONAL PARAMETERS FOR COPPER IODIDE NICOTINAMIDE

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.3922(2)	0.4538(1)	0.7169(5)
Cu1	0.4484(4)	0.5228(1)	0.7210(10)
O19	0.2265(24)	0.6516(5)	0.2826(53)
O29	0.4914(19)	0.7660(5)	0.6614(52)
N11	0.2593(25)	0.5499(7)	0.6665(59)
N18	0.0007(24)	0.6587(6)	0.3812(68)
N21	0.7392(26)	0.6564(6)	0.6895(63)
N28	0.7269(27)	0.7683(6)	0.8147(64)
C12	0.2459(28)	0.5858(8)	0.5516(72)
C13	0.1224(26)	0.6027(6)	0.5265(55)
C14	0.0063(32)	0.5860(10)	0.6440(98)
C15	0.0127(34)	0.5514(8)	0.7446(95)
C16	0.1392(33)	0.5351(8)	0.7505(90)
C17	0.1184(30)	0.6405(8)	0.3845(66)
C22	0.7290(26)	0.6921(6)	0.6912(69)
C23	0.6148(27)	0.7118(8)	0.7681(65)
C24	0.5087(33)	0.6923(9)	0.8742(70)
C25	0.5129(30)	0.6555(8)	0.8965(66)
C26	0.6331(36)	0.6394(7)	0.7997(78)
C27	0.6060(30)	0.7522(7)	0.7457(69)

TABLE XCIII

POSITIONAL PARAMETERS FOR COPPER IODIDE NICOTINAMIDE (HYDROGEN ATOMS)

ATOM	X	Y	Z
H12	0.3273	0.5986	0.4922
H14	-0.0831	0.5996	0.6235
H15	-0.0653	0.5407	0.8371
H16	0.1451	0.5123	0.8083
H22	0.8100	0.7055	0.6171
H24	0.4241	0.7051	0.9305
H25	0.4363	0.6419	0.9769
H26	0.6371	0.6128	0.8051

TABLE XCIV

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE NICOTINAMIDE

ATOM	U11	U22	U33	U12	U13	U23
I1	40(1)	32(1)	31(1)	-2(1)	5(0)	0(0)
Cu1	34(2)	28(2)	50(2)	7(1)	6(1)	0(1)
O19	52(14)	17(10)	64(14)	8(10)	20(11)	16(10)
O29	16(11)	36(12)	66(14)	1(9)	-6(10)	-9(10)
N11	31(14)	60(18)	36(14)	17(13)	-1(11)	29(13)
N18	17(13)	27(14)	81(19)	17(11)	11(12)	1(13)
N21	31(15)	25(14)	58(17)	5(11)	9(12)	-12(12)
C28	40(16)	17(13)	61(17)	9(11)	14(13)	-5(12)
C12	15(15)	46(19)	44(18)	-1(14)	1(13)	4(15)
C13	25(15)	0(11)	17(12)	0(10)	6(11)	-2(9)
C14	19(17)	75(17)	91(28)	-1(18)	1(17)	-39(23)
C15	41(21)	31(19)	91(27)	0(16)	33(19)	26(19)
C16	36(21)	30(18)	84(26)	-10(14)	23(19)	-8(17)
C17	23(17)	54(10)	23(15)	-13(16)	-4(13)	-3(14)
C22	14(14)	16(15)	50(18)	4(11)	2(13)	-26(13)
C23	15(14)	48(18)	29(14)	0(14)	7(11)	-3(15)
C24	41(20)	71(26)	24(16)	13(18)	14(14)	-10(16)
C25	30(17)	46(20)	27(16)	-2(14)	18(13)	13(14)
C26	72(26)	5(14)	52(20)	11(15)	11(18)	9(14)
C27	18(15)	24(14)	39(16)	10(14)	8(12)	-7(13)

TABLE XCIV (Continued)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C, N and O.

TABLE XCV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE NICOTINAMIDE

I1 - Cu1	2.650(4)	Cu1 - I1 - Cu1'	65.5(1)
I1 - Cu1'	2.686(4)	Cu1 - I1 - Cu1''	62.8(1)
I1 - Cu1''	2.649(5)	Cu1' - I1 - Cu1''	98.6(1)
Cu1 - Cu1'	2.888(5)	I1 - Cu1 - I1'	114.5(1)
Cu1 - Cu1''	2.762(6)	I1 - Cu1 - I1''	117.2(1)
Cu1 - N11	2.05(2)	I1' - Cu1 - I1''	98.6(1)
N11 - C12	1.36(4)	I1 - Cu1 - N11	108.2(6)
N11 - C16	1.36(4)	I1' - Cu1 - N11	107.7(7)
C12 - C13	1.32(4)	I1'' - Cu1 - N11	110.1(7)
C13 - C14	1.41(4)	Cu1 - N11 - C12	123(2)
C13 - C17	1.53(4)	Cu1 - N11 - C16	122(2)
C14 - C15	1.36(5)	C12 - N11 - C16	115(2)
C15 - C16	1.35(4)	N11 - C12 - C13	121(3)
C17 - N18	1.31(4)	C12 - C13 - C14	119(2)
C17 - O19	1.24(4)	C12 - C13 - C17	116(2)
N21 - C22	1.34(3)	C14 - C13 - C17	124(2)
N21 - C26	1.33(4)	C13 - C14 - C15	122(3)
C22 - C23	1.39(4)	C14 - C15 - C16	116(3)
C23 - C24	1.37(4)	C15 - C16 - N11	126(3)
C25 - C26	1.40(4)	C13 - C17 - N18	118(3)
C27 - N28	1.29(4)	C13 - C17 - O19	118(2)
C27 - O29	1.21(3)	N18 - C17 - O19	125(3)
		C22 - N21 - C26	115(2)

TABLE XCV (Continued)

N21 - C22 - C23	126(3)
C22 - C23 - C24	115(3)
C22 - C23 - C27	124(2)
C24 - C23 - C27	121(2)
C23 - C24 - C25	123(3)
C24 - C25 - C26	115(3)
C25 - C26 - N21	125(3)
C23 - C27 - N28	114(2)
C23 - C27 - O29	119(2)
N28 - C27 - O29	126(3)

Symmetry Operations:

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

'' = 1 - x, 1 - y, 1 - z

TABLE XCVI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE NICOTINAMIDE- HYDROGEN ATOMS

C12 - H12	0.97	N11 - C12 - H12	121
C14 - H14	0.99	C13 - C12 - H12	118
C15 - H15	0.97	C13 - C14 - H14	117
C16 - H16	0.89	C15 - C14 - H14	121
C22 - H22	1.00	C14 - C15 - H15	121
C24 - H24	0.99	C16 - C15 - H15	123
C25 - H25	0.98	N21 - C22 - H22	116
C26 - H26	1.00	C23 - C22 - H22	117
		C23 - C24 - H24	118
		C25 - C24 - H24	119
		C25 - C26 - H26	117
		N21 - C26 - H26	118

TABLE XCVII

CRYSYAL DATA FOR COPPER IODIDE 3-PYRIDYL-ACETONITRILE (LOW TEMPERATURE)

Formula	$(CuIC_7H_6N_2)_n$
Mwt	308.5879
a	7.869(3) Å
b	12.983(5)
c	4.232(2)
α	90.65(3)°
β	101.16(3)
γ	102.63(3)
V	413.3(3) $Å^3$
F(000)	288
μMoK_α	62.7918 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.4794 g cm^{-1}
Z	2
Meas refl	1110
Obs refl	1014
R	12.6%
R_w	17.0
Space Group	$P\bar{1}$
Octants meas	±h, k, ±l

TABLE XCVIII

POSITIONAL PARAMETERS FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (LOW TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.2582(7)	0.0748(5)	0.8078(14)
I11	0.2571(7)	0.0539(5)	0.8394(13)
Cu1	-0.0898(5)	0.0359(3)	0.7280(9)
N11	-0.1460(33)	0.1825(20)	0.7674(60)
N19	-0.6895(36)	0.4233(23)	0.7067(63)
C12	-0.2984(42)	0.2052(25)	0.6043(74)
C13	-0.3452(38)	0.2967(23)	0.6424(68)
C14	-0.2357(30)	0.3745(25)	0.8515(72)
C15	-0.0797(44)	0.3515(26)	1.0452(78)
C16	-0.0410(41)	0.2546(25)	0.9863(74)
C17	-0.5107(42)	0.3153(25)	0.4150(75)
C18	-0.6141(43)	0.3737(27)	0.5845(77)

TABLE XCIX

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (LOW TEMPERATURE)

ATOM	U11	U22	U33	U12	U13	U23
I1	5(0)					
I11	5(0)					
Cu1	3(2)	24(2)	11(2)	7(1)	-4(1)	-8(1)
N11	10(5)					
N19	10(14)	32(18)	12(14)	7(12)	4(11)	-7(13)
C12	12(7)					
C13	6(6)					
C14	10(6)					
C15	16(7)					
C16	11(5)					
C17	13(7)					
C18	15(7)					

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C and N.

TABLE C

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (LOW TEMPERATURE)

I1 - Cu1	2.627(7)	Cu1 - I1 - Cu1'	60.5(2)
I1 - Cu1'	2.814(7)	Cu1 - I1 - Cu1''	66.0(2)
I1 - Cu1''	2.626(6)	Cu1' - I1 - Cu1''	102.1(2)
Cu1 - Cu1'	2.744(5)	I1 - Cu1 - I1'	119.5(2)
Cu1 - Cu1''	2.860(6)	I1 - Cu1 - I1''	114(2)
Cu1 - N11	2.06(3)	I1' - Cu1 - I1''	102.1(2)
N11 - C12	1.36(4)	I1 - Cu1 - N11	104.5(7)
N11 - C16	1.33(4)	I1' - Cu1 - N11	102.4(8)
C12 - C13	1.34(5)	I1'' - Cu1 - N11	114.2(7)
C13 - C14	1.36(4)	Cu1 - N11 - C12	122(2)
C13 - C17	1.53(4)	Cu1 - N11 - C16	120(2)
C14 - C15	1.43(4)	C12 - N11 - C16	118(2)
C15 - C16	1.39(5)	N11 - C12 - C13	124(3)
C17 - C18	1.49(5)	C12 - C13 - C14	120(3)
C18 - N19	1.15(5)	C12 - C13 - C17	118(2)
I11 - Cu1	2.636(7)	C14 - C13 - C17	122(3)
I11 - Cu1'	2.599(7)	C13 - C14 - C15	118(3)
I11 - Cu1''	2.627(6)	C14 - C15 - C16	118(3)
I_{ave} - Cu1	2.631(7)	C15 - C16 - N11	123(3)
I_{ave} - Cu1'	2.706(7)	C13 - C17 - C18	112(3)
I_{ave} - Cu1''	2.626(7)	C17 - C18 - N19	176(3)
		Cu1 - I11 - Cu1'	63.2(2)
		Cu1 - I11 - Cu1''	65.8(2)

TABLE C (Continued)

Cu1' - I11 - Cu1''	108.2(2)
I11 - Cu1 - I11'	116.8(2)
I11 - Cu1 - I11''	114.2(2)
I11' - Cu1 - I11''	108.1(2)
I11 - Cu1 - N11	110.0(7)
I11' - Cu1 - N11	97.9(8)
I11'' - Cu1 - N11	108.4(7)
Cu1 - I_{ave} - Cu1'	61.8(2)
Cu1 - I_{ave} - Cu1''	66.4(2)
Cu1' - I_{ave} - Cu1''	105.2(2)
I_{ave} - Cu1 - I'_{ave}	118.1(2)
I_{ave} - Cu1 - I''_{ave}	114.1(5)
I'_{ave} - Cu1 - I''_{ave}	105.1(2)
I_{ave} - Cu1 - N11	107.2(7)
I'_{ave} - Cu1 - N11	100.1(8)
I''_{ave} - Cu1 - N11	111.3(8)

Symmetry Operations

' = -x, -y, 2 - z

'' = -x, -y, 1 - z

TABLE CI

CRYSYAL DATA FOR COPPER IODIDE 3-PYRIDYL-ACETONITRILE (ROOM TEMPERATURE)

Formula	$(CuIC_7H_6N_2)_n$
Mwt	308.5879
<u>a</u>	7.895(2) Å
<u>b</u>	13.144(5)
<u>c</u>	4.255(1)
α	91.51(3)°
β	101.16(2)
γ	101.88(2)
V	423.0(2) $Å^3$
F(000)	288
μMoK_α	61.3489 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.4224 g cm^{-1}
Z	2
Meas refl	1118
Obs refl	1040
R	8.5%
R_w	12.4
Space Group	$P\bar{1}$
Octants meas	±h, k, ±l

TABLE CII

POSITIONAL PARAMETERS FOR COPPER IODIDE 3-PYRIDYL-ACETONITRILE (ROOM TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.2547(2)	0.0617(1)	0.8281(3)
Cu1	-0.0904(4)	0.0384(2)	0.7291(1)
N11	-0.1505(23)	0.1819(13)	0.7668(42)
N19	-0.6873(29)	0.4214(19)	0.6999(57)
C12	-0.3003(29)	0.2018(16)	0.6007(47)
C13	-0.3463(28)	0.2963(16)	0.6345(46)
C14	-0.2379(30)	0.3732(17)	0.8528(53)
C15	-0.0834(29)	0.3515(17)	1.0226(63)
C16	-0.0432(29)	0.2564(19)	0.9745(60)
C17	-0.5172(31)	0.3123(19)	0.4162(60)
C18	-0.6133(27)	0.3732(17)	0.5769(54)

TABLE CIII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (ROOM TEMPERATURE)

ATOM	U11	U22	U33	U12	U13	U23
I1	14(0)	48(1)	27(1)	3(0)	0(0)	0(0)
Cu1	27(1)	45(1)	46(1)	15(1)	-2(1)	0(1)
N11	18(9)	33(10)	36(10)	11(8)	-2(8)	0(8)
N19	31(13)	79(17)	75(16)	37(12)	2(12)	5(13)
C12	29(13)	35(12)	24(11)	4(10)	11(10)	5(9)
C13	23(11)	43(13)	20(10)	14(10)	7(9)	8(9)
C14	25(12)	36(12)	39(13)	2(10)	6(10)	3(10)
C15	15(11)	35(13)	65(16)	0(10)	4(11)	-3(11)
C16	10(10)	53(15)	52(14)	10(10)	-6(10)	-11(12)
C17	24(13)	50(15)	53(15)	24(11)	-4(11)	-4(11)
C18	8(10)	37(12)	45(14)	9(9)	-8(10)	3(10)

Anisotropic thermal parameters in the form:

$$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$$ for I, Cu; $\times 10^3$ for C and N.

TABLE CIV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (ROOM TEMPERATURE)

I1 - Cu1	2.626(3)	Cu1 - I1 - Cu1'	63.17(9)
I1 - Cu1'	2.708(3)	Cu1 - I1 - Cu1''	66.7(9)
I1 - Cu1''	2.641(3)	Cu1' - I1 - Cu1''	105.36(9)
Cu1 - Cu1'	2.795(4)	I1 - Cu1 - I1'	116.8(1)
Cu1 - Cu1''	2.902(5)	I1 - Cu1 - I1''	113.1(1)
Cu1 - N11	2.05(2)	I1' - Cu1 - I1''	105.36(9)
N11 - C12	1.33(3)	I1 - Cu1 - N11	108.9(5)
N11 - C16	1.33(3)	I1' - Cu1 - N11	101.0(5)
C12 - C13	1.38(3)	I1'' - Cu1 - N11	110.9(5)
C13 - C14	1.38(3)	Cu1 - N11 - C12	122(2)
C13 - C17	1.54(3)	Cu1 - N11 - C16	120(2)
C14 - C15	1.38(3)	C12 - N11 - C16	118(2)
C15 - C16	1.37(3)	N11 - C12 - C13	122(2)
C17 - C18	1.45(4)	C12 - C13 - C14	120(2)
C18 - N19	1.13(4)	C12 - C13 - C17	118(2)
		C14 - C13 - C17	123(2)
		C13 - C14 - C15	117(2)
		C14 - C15 - C16	120(2)
		C15 - C16 - N11	122(2)
		C13 - C17 - C18	113(2)
		C17 - C18 - N19	179(2)

Symmetry Operations:

TABLE CIV (Continued)

' = -x, -y, 2 - z

'' = -x, -y, 1 - z

TABLE CV

CRYSYAL DATA FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (ROOM TEMPERATURE - UV IRRADIATED)

Formula	$(CuIC_7H_6N_2)_n$
Mwt	308.5879
<u>a</u>	7.897(2) Å
<u>b</u>	13.134(5)
<u>c</u>	4.256(1)
α	91.54(2)$^\circ$
β	101.14(2)
γ	101.85(2)
V	422.9(2) Å^3
F(000)	288
μMoK_α	61.3820 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.4229 g cm^{-1}
Z	2
Meas refl	1118
Obs refl	1035
R	8.3%
R_w	12.0
Space Group	$P\bar{1}$
Octants meas	$\pm h$, k, $\pm l$

TABLE CVI

POSITIONAL PARAMETERS FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (ROOM TEMPERATURE - UV IRRADIATED)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.2546(2)	0.0617(1)	0.8279(3)
Cu1	-0.0904(4)	0.0386(2)	0.7294(1)
N11	-0.1510(21)	0.1817(13)	0.7676(42)
N19	-0.3136(29)	0.7873(19)	-0.6981(58)
C12	-0.3017(27)	0.2016(16)	0.5990(47)
C13	-0.3469(28)	0.2955(16)	0.6367(45)
C14	-0.2373(30)	0.3737(17)	0.8524(52)
C15	-0.0825(28)	0.3521(18)	1.0270(64)
C16	-0.0438(28)	0.2560(17)	0.9740(60)
C17	-0.5170(32)	0.3117(19)	0.4160(59)
C18	-0.6135(28)	0.3735(17)	0.5794(53)

TABLE CVII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (ROOM TEMPERATURE - UV IRRADIATED)

ATOM	U11	U22	U33	U12	U13	U23
I1	15(0)	49(1)	28(1)	3(0)	0(0)	0(0)
Cu1	28(1)	46(1)	46(1)	15(1)	-2(1)	0(1)
N11	15(9)	38(10)	39(10)	10(8)	0(8)	0(8)
N19	35(13)	79(16)	73(16)	32(12)	5(11)	2(13)
C12	27(12)	39(12)	24(10)	9(9)	12(9)	7(8)
C13	21(10)	35(12)	23(10)	8(9)	7(8)	4(8)
C14	31(12)	38(12)	35(12)	3(10)	9(10)	2(10)
C15	18(11)	40(13)	68(16)	0(10)	13(11)	2(11)
C16	13(10)	40(13)	61(15)	6(9)	-9(10)	-2(11)
C17	34(14)	54(15)	52(15)	30(12)	-4(11)	0(12)
C18	16(10)	34(12)	43(13)	12(9)	-7(10)	2(10)

Anisotropic thermal parameters in the form:

$$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$$ for I, Cu; $\times 10^3$ for C and N.

TABLE CVIII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 3-PYRIDYLACETONITRILE (ROOM TEMPERATURE - UV IRRADIATED)

I1 - Cu1	2.627(3)	Cu1 - I1 - Cu1'	63.05(9)
I1 - Cu1'	2.700(3)	Cu1 - I1 - Cu1''	66.86(9)
I1 - Cu1''	2.632(3)	Cu1' - I1 - Cu1''	105.04(9)
Cu1 - Cu1'	2.786(4)	I1 - Cu1 - I1'	116.9(1)
Cu1 - Cu1''	2.897(5)	I1 - Cu1 - I1''	113.1(1)
Cu1 - N11	2.04(2)	I1' - Cu1 - I1''	105.04(9)
N11 - C12	1.34(3)	I1 - Cu1 - N11	109.1(4)
N11 - C16	1.33(3)	I1' - Cu1 - N11	101.0(5)
C12 - C13	1.37(3)	I1'' - Cu1 - N11	110.9(5)
C13 - C14	1.38(3)	Cu1 - N11 - C12	122(1)
C13 - C17	1.54(3)	Cu1 - N11 - C16	120(1)
C14 - C15	1.39(3)	C12 - N11 - C16	119(2)
C15 - C16	1.38(3)	N11 - C12 - C13	122(2)
C17 - C18	1.46(4)	C12 - C13 - C14	121(2)
C18 - N19	1.11(4)	C12 - C13 - C17	117(2)
		C14 - C13 - C17	122(2)
		C13 - C14 - C15	117(2)
		C14 - C15 - C16	119(2)
		C15 - C16 - N11	123(2)
		C13 - C17 - C18	113(2)
		C17 - C18 - N19	179(2)

Symmetry Operations

TABLE CVIII (Continued)

' = -x, -y, 2 - z

'' = -x, -y, 1 - z

TABLE CIX

CRYSTAL DATA FOR COPPER IODIDE ISOPROPYL NICOTINATE (CUBE)

Formula	$(CuIC_9H_{11}NO_2)_4$
Mwt	1422.5667
a	12.678(4) Å
b	12.678(4)
c	37.966(8)
α	90.0 °
β	90.0
γ	90.0
V	6103(3) $Å^3$
F(000)	5440
μMoK_α	68.3818 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	3.0958 g cm^{-1}
Z	8
Meas refl	2586
Obs refl	1884
R	6.4%
R_w	10.3
Space Group	$I4_1/a$
Octants meas	±h, k, l

TABLE CX

POSITIONAL PARAMETERS FOR COPPER IODIDE ISOPROPYL NICOTINATE (CUBE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.0811(1)	0.0902(1)	0.6660(0)
Cu1	0.0509(2)	0.1575(2)	0.6003(1)
O18	0.1613(14)	-0.2546(11)	0.6027(4)
O19	0.1549(17)	-0.3203(12)	0.5458(4)
N11	0.0995(10)	0.0448(10)	0.5655(4)
C12	0.1090(13)	-0.0568(13)	0.5800(5)
C13	0.1359(14)	-0.1358(14)	0.5503(7)
C14	0.1467(18)	-0.1106(18)	0.5160(5)
C15	0.1359(19)	-0.0107(16)	0.5076(4)
C16	0.1141(16)	0.0626(15)	0.5300(4)
C17	0.1488(17)	-0.2502(15)	0.5680(8)
C20	0.1819(26)	-0.3591(17)	0.6173(7)
C21	0.3008(25)	-0.3782(23)	0.6177(9)
C22	0.1386(28)	-0.3516(20)	0.6505(7)

TABLE CXI

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE ISOPROPYL NICOTINATE (CUBE)

ATOM	U11	U22	U33	U12	U13	U23
I1	62(0)	65(1)	49(0)	5(0)	-2(0)	8(0)
Cu1	83(1)	52(1)	54(1)	9(1)	7(1)	-4(1)
O18	164(15)	67(9)	74(10)	2(9)	-10(9)	3(7)
O19	228(20)	45(8)	143(15)	28(10)	-15(4)	-31(9)
N11	60(8)	44(8)	72(10)	3(6)	-6(7)	-7(6)
C12	49(10)	51(10)	101(14)	-8(8)	-11(9)	-12(9)
C13	65(12)	48(11)	157(22)	14(9)	-5(12)	-41(12)
C14	157(22)	106(17)	20(9)	25(15)	-1(10)	-9(10)
C15	176(22)	56(12)	36(10)	17(13)	8(11)	-8(9)
C16	103(15)	75(13)	43(10)	0(11)	-8(9)	8(9)
C17	96(16)	31(11)	173(25)	17(10)	19(16)	-10(14)
C20	198(32)	53(13)	104(20)	-2(15)	-1(19)	30(13)
C21	126(24)	117(22)	187(32)	40(19)	28(20)	42(21)
C22	232(34)	99(19)	105(21)	-6(20)	38(23)	52(16)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*$ $+ 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C, N, and O.

TABLE CXII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE ISOPROPYL NICOTINATE (CUBE)

I1 - Cu1	2.667(2)	Cu1 - I1 - Cu1''	59.97(7)
I1 - Cu1''	2.671(2)	Cu1 - I1 - Cu1'''	59.02(6)
I1 - Cu1'''	2.746(3)	Cu1'' - I1 - Cu1'''	59.20(7)
Cu1 - Cu1'	2.676(3)	I1 - Cu1 - I1''	111.56(8)
Cu1 - Cu1''	2.667(3)	I1 - Cu1 - I1'''	113.97(8)
Cu1 - Cu1'''	2.667(3)	I1'' - Cu1 - I1'''	114.06(8)
Cu1 - N11	2.04(1)	I1 - Cu1 - N11	109.8(4)
N11 - C12	1.41(2)	I1'' - Cu1 - N11	100.6(4)
N11 - C16	1.38(2)	I1''' - Cu1 - N11	105.8(4)
C12 - C13	1.55(3)	C12 - N11 - Cu1	114(1)
C13 - C14	1.35(3)	C16 - N11 - Cu1	124(1)
C13 - C17	1.61(3)	C12 - N11 - C16	121(1)
C14 - C15	1.31(3)	N11 - C12 - C13	109(2)
C15 - C16	1.29(3)	C12 - C13 - C14	125(2)
C17 - O18	1.33(3)	C12 - C13 - C17	107(2)
C17 - O19	1.23(3)	C14 - C13 - C17	128(2)
O18 - C20	1.46(3)	C13 - C14 - C15	117(2)
C20 - C21	1.53(4)	C14 - C15 - C16	124(2)
C20 - C22	1.38(4)	C15 - C16 - N11	124(2)
		C13 - C17 - O18	118(2)
		C13 - C17 - O19	112(2)
		O18 - C17 - O19	130(2)
		O18 - C20 - C21	109(2)

TABLE CXII (Continued)

O18 - C20 - C22	102(2)
C21 - C20 - C22	113(3)

Symmetry Operations

' = -x, 0.5 - y, z

'' = -0.25 + y, 0.25 - x, 1.25 - z

''' = 0.25 - y, 0.25 + x, 1.25 - z

TABLE CXIII

CRYSTAL DATA FOR COPPER IODIDE PHENYL NICOTINATE

Formula	$(Cu_2I_2(C_{12}H_9NO_2)_2)_2$
Mwt	1558.6355
a	21.442(4) Å
b	15.289(6)
c	20.708(6)
α	90.0°
β	128.70(2)
γ	90.0
V	5298(2) $Å^3$
F(OOO)	2976
μMoK_α	39.4788 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.9537 g cm^{-3}
Z	4
Meas. Refl.	3499
Obs. Refl.	2585
R	6.1%
R_w	9.2%
Space Group	$P2_1/c$
Octants Meas.	±h, k, ±l

TABLE CXIV

POSITIONAL PARAMETERS FOR COPPER IODIDE PHENYL NICOTINATE

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.8895(1)	0.2181(1)	0.2345(1)
I2	1.0819(1)	0.4310(1)	0.3886(1)
Cu1	0.9337(1)	0.3848(1)	0.2445(2)
Cu2	1.0465(2)	0.2670(1)	0.3369(1)
O118	0.8343(9)	0.7177(8)	0.1873(9)
O119	0.7675(11)	0.7499(9)	0.2327(12)
O218	1.1012(8)	-0.1043(8)	0.5138(8)
O219	0.9853(10)	-0.0521(10)	0.3990(11)
N111	0.8621(9)	0.4624(9)	0.2535(9)
N211	1.0954(9)	0.1880(9)	0.4376(10)
C112	0.8525(10)	0.5477(10)	0.2345(11)
C113	0.8116(11)	0.6018(11)	0.2464(12)
C114	0.7802(16)	0.5737(13)	0.2819(17)
C115	0.7888(15)	0.4853(15)	0.3015(16)
C116	0.8303(12)	0.4331(12)	0.2885(13)
C117	0.8005(13)	0.6995(12)	0.2216(13)
C120	0.8260(13)	0.8040(10)	0.1603(13)
C121	0.7660(13)	0.8225(14)	0.0805(14)
C122	0.7581(15)	0.9071(16)	0.0506(13)
C123	0.8115(15)	0.9675(15)	0.1009(16)
C124	0.8726(15)	0.9498(14)	0.1797(17)
C125	0.8819(12)	0.8618(13)	0.2123(12)

TABLE CXIV (Continued)

C212	1.0629(15)	0.1063(11)	0.4238(11)
C213	1.0940(11)	0.0454(12)	0.4864(11)
C214	1.1528(13)	0.0710(15)	0.5656(13)
C215	1.1848(16)	0.1547(15)	0.5817(15)
C216	1.1539(13)	0.2061(14)	0.5145(14)
C217	1.0526(14)	-0.0390(12)	0.4599(13)
C220	1.0703(12)	-0.1900(11)	0.4904(11)
C221	1.0624(13)	-0.2309(14)	0.4269(14)
C222	1.0349(14)	-0.3153(15)	0.4089(15)
C223	1.0160(15)	-0.3581(13)	0.4501(17)
C224	1.0250(16)	-0.3159(17)	0.5146(20)
C225	1.0540(15)	-0.2316(15)	0.5372(14)

TABLE CXV

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE PHENYL NICOTINATE

ATOM	X	Y	Z
H112	0.8763	0.5714	0.2106
H114	0.7530	0.6149	0.2936
H115	0.7652	0.4617	0.3259
H116	0.8384	0.3706	0.3050
H121	0.7267	0.7739	0.0445
H122	0.7088	0.9198	-0.0092
H123	0.8073	1.0262	0.0799
H124	0.9133	0.9967	0.2199
H125	0.9264	0.8455	0.2726
H212	1.0168	0.0876	0.3669
H214	1.1712	0.0308	0.6107
H215	1.2295	0.1766	0.6391
H216	1.1788	0.2655	0.5256
H221	1.0771	-0.2036	0.3960
H222	1.0316	-0.3450	0.3647
H223	0.9886	-0.4171	0.4297
H224	1.0165	-0.3498	0.5499
H225	1.0604	-0.2012	0.5850

TABLE CXVI

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE PHENYL NICOTINATE

ATOM	U11	U22	U33	U12	U13	U23
I1	46(0)	20(0)	60(0)	-3(0)	38(0)	2(0)
I2	70(0)	25(0)	59(0)	-13(0)	46(0)	-14(0)
Cu1	68(1)	20(1)	79(1)	8(1)	59(1)	4(1)
Cu2	70(1)	24(1)	54(1)	0(1)	42(1)	4(1)
O118	88(10)	20(6)	91(10)	18(6)	74(9)	15(6)
O119	151(16)	35(8)	166(17)	37(9)	145(15)	27(9)
O218	57(8)	42(8)	42(8)	5(7)	23(7)	14(6)
O219	65(10)	43(9)	78(12)	1(8)	6(9)	18(8)
N111	59(9)	24(8)	62(10)	6(7)	50(9)	1(7)
N211	56(10)	18(7)	51(10)	-1(7)	35(9)	-3(10)
C112	51(11)	8(8)	58(12)	1(7)	44(10)	2(7)
C113	55(12)	20(9)	67(13)	3(8)	50(11)	3(9)
C114	137(22)	24(10)	160(25)	23(12)	138(22)	16(13)
C115	119(20)	54(14)	123(20)	23(13)	110(19)	22(14)
C116	68(13)	31(11)	79(15)	5(9)	61(13)	11(10)
C117	69(14)	35(11)	75(15)	8(10)	57(13)	-3(10)
C120	58(12)	15(9)	51(12)	8(9)	36(11)	4(9)
C121	71(15)	44(13)	63(16)	-16(11)	36(14)	-10(11)
C122	85(17)	63(16)	39(12)	13(14)	31(12)	9(11)
C123	81(17)	49(14)	87(19)	30(13)	64(16)	43(14)
C124	88(17)	37(12)	98(20)	-22(12)	63(17)	-10(13)

TABLE CXVI (Continued)

C125	65(14)	31(11)	46(12)	-2(10)	23(11)	1(9)
C212	51(12)	27(10)	38(11)	8(9)	22(10)	5(8)
C213	50(11)	32(10)	38(11)	4(9)	24(9)	3(8)
C214	69(15)	55(15)	51(13)	-7(12)	17(12)	17(11)
C215	96(19)	40(13)	59(15)	-16(13)	-2(14)	17(12)
C216	52(14)	44(13)	65(16)	-27(11)	3(13)	-5(12)
C217	75(15)	25(10)	51(13)	8(10)	38(13)	10(9)
C220	66(13)	23(10)	46(11)	-3(9)	37(11)	7(8)
C221	78(15)	53(13)	66(14)	0(11)	57(13)	5(11)
C222	86(17)	48(13)	82(17)	-13(12)	58(15)	-19(12)
C223	88(18)	23(11)	105(20)	-3(11)	58(17)	-11(12)
C224	117(22)	52(16)	145(26)	14(15)	107(22)	34(17)
C225	106(19)	55(15)	69(16)	0(13)	67(15)	-1(12)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2U_{12}hka^*b^*$
$+ 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$
for C, N, and O.

TABLE CXVII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE PHENYL NICOTINATE

I1 - Cu2	2.731(3)	Cu2 - I1 - Cu1	58.36(7)
I1 - Cu1	2.681(3)	Cu2 - I1 - Cu2'	62.84(9)
I1 - Cu2'	2.667(4)	Cu1 - I1 - Cu2'	59.9(1)
I2 - Cu1	2.764(2)	Cu2 - I2 - Cu1	58.37(6)
I2 - Cu2	2.644(3)	Cu2 - I2 - Cu1'	60.65(9)
I2 - Cu2'	2.656(4)	Cu1 - I2 - Cu1'	59.9(1)
Cu1 - Cu2	2.640(3)	I1 - Cu1 - I2	116.00(8)
Cu1 - Cu2'	2.676(5)	I1 - Cu1 - I2'	111.3(1)
Cu1 - Cu1'	2.707(5)	I2 - Cu1 - I2'	111.4(1)
Cu2 - Cu2'	2.820(4)	N111 - Cu1 - I1	108.1(5)
Cu1 - N111	2.04(2)	N111 - Cu1 - I2	100.1(4)
Cu2 - N211	2.04(2)	N111 - Cu1 - I2'	109.0(8)
N111 - C112	1.34(2)	I1 - Cu2 - I2	118.42(8)
N111 - C116	1.34(4)	I1 - Cu2 - I1'	107.68(9)
C112 - C113	1.34(3)	I2 - Cu2 - I1'	118.8(1)
C113 - C114	1.34(5)	N211 - Cu2 - I1	103.1(5)
C113 - C117	1.55(3)	N211 - Cu2 - I2	108.2(4)
C114 - C115	1.39(3)	N211 - Cu2 - I1'	106.6(6)
C115 - C116	1.34(4)	C112 - N111 - C116	116(2)
C117 - O118	1.32(4)	C112 - N111 - Cu1	122(2)
C117 - O119	1.16(4)	C116 - N111 - Cu1	121(1)
O118 - C120	1.40(2)	N111 - C112 - C113	123(2)
C120 - C121	1.34(2)	C112 - C113 - C114	121(2)

TABLE CXVII (Continued)

C120 - C125	1.33(2)	C112 - C113 - C117	121(3)
C121 - C122	1.40(3)	C114 - C113 - C117	118(2)
C122 - C123	1.32(3)	C113 - C114 - C115	117(3)
C123 - C124	1.33(3)	C114 - C115 - C116	120(4)
C124 - C125	1.46(3)	C115 - C116 - N111	112(2)
N211 - C212	1.37(2)	C113 - C117 - O118	111(2)
N211 - C216	1.30(2)	C113 - C117 - O119	124(3)
C212 - C213	1.38(3)	O118 - C117 - O119	125(2)
C213 - C214	1.36(2)	C117 - O118 - C120	116(2)
C213 - C217	1.46(3)	O118 - C120 - C121	118(2)
C214 - C215	1.39(3)	O118 - C120 - C125	118(1)
C215 - C216	1.36(4)	C121 - C120 - C125	123(2)
C217 - O218	1.37(2)	C120 - C121 - C122	120(2)
C217 - O219	1.20(2)	C121 - C122 - C123	119(2)
O218 - C220	1.41(2)	C122 - C123 - C124	122(2)
C220 - C221	1.36(4)	C123 - C124 - C125	120(2)
C220 - C225	1.37(5)	C124 - C125 - C120	116(2)
C220 - C222	1.37(3)	C212 - N211 - C216	115(2)
C222 - C223	1.32(5)	C216 - N211 - Cu2	128(1)
C223 - C224	1.38(5)	C212 - N211 - Cu2	117(1)
C224 - C225	1.39(5)	N211 - C212 - C213	122(1)
		C212 - C213 - C214	119(2)
		C212 - C213 - C217	115(1)
		C214 - C213 - C217	126(2)
		C213 - C214 - C215	120(2)

TABLE CXVII (Continued)

C214 - C215 - C216	116(2)
C215 - C216 - N211	128(2)
C213 - C217 - O218	111(1)
C213 - C217 - O219	126(2)
O218 - C217 - O219	123(2)
C217 - O218 - C220	116(1)
O218 - C220 - C221	120(2)
O218 - C220 - C225	117(2)
C221 - C220 - C225	122(2)
C220 - C221 - C222	118(3)
C221 - C222 - C223	123(3)
C222 - C223 - C224	119(2)
C223 - C224 - C225	122(4)
C224 - C225 - C221	117(3)

Symmetry Operations

' = 2 - x, y, 0.5 - z

TABLE CXVIII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE PHENYL NICOTINATE (HYDROGEN)

C112 - H112	0.98	N111 - C112 - H112	119
C114 - H114	0.99	C113 - C112 - H112	118
C115 - H115	0.98	C113 - C114 - H114	120
C116 - H116	0.99	C115 - C114 - H114	123
C121 - H121	1.02	C114 - C115 - H115	120
C122 - H122	1.03	C116 - C115 - H115	120
C123 - H123	0.98	C115 - C116 - H116	120
C124 - H124	1.03	N111 - C116 - H116	118
C125 - H125	1.02	C120 - C121 - H121	118
C212 - H212	1.00	C122 - C121 - H121	122
C214 - H214	0.97	C121 - C122 - H122	117
C215 - H215	1.01	C123 - C122 - H122	123
C216 - H216	1.00	C122 - C123 - H123	120
C221 - H221	0.97	C124 - C123 - H123	119
C222 - H222	0.98	C123 - C124 - H124	122
C223 - H223	1.01	C125 - C124 - H124	118
C224 - H224	1.00	C124 - C125 - H125	123
C225 - H225	1.02	C120 - C125 - H125	121
		C211 - C212 - H212	121
		C213 - C212 - H212	117
		C213 - C214 - H214	119
		C215 - C214 - H214	123
		C214 - C215 - H215	123

TABLE CXVIII (Continued)

C216 - C215 - H215	121
C215 - C216 - H216	116
N211 - C216 - H216	116
C220 - C221 - H221	123
C222 - C221 - H221	119
C221 - C222 - H222	117
C223 - C222 - H222	120
C222 - C223 - H223	120
C224 - C223 - H223	121
C223 - C224 - H224	119
C225 - C224 - H224	119
C224 - C225 - H225	121
C220 - C225 - H225	122

TABLE CXIX

CRYSTAL DATA FOR COPPER IODIDE DI-3-CYANOPYRIDINE

Formula	$Cu_2I_2C_{24}H_{16}N_8$
Mwt	797.3445
<u>a</u>	8.079(3) Å
<u>b</u>	8.928(5)
<u>c</u>	9.681(7)
α	87.68(5) °
β	95.45(5)
γ	71.33(4)
V	656.6(7) $Å^3$
F(000)	380
μMoK_α	39.7989 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.0161 g cm^{-1}
Z	1
Meas refl	3737
Obs refl	2904
R	4.9%
R_w	7.0
Space group	$P\bar{1}$
Octants meas	±h, k, ±l

TABLE CXX

POSITIONAL PARAMETERS FOR COPPER IODIDE DI-3-CYANOPYRIDINE

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I2	0.2450(1)	0.0326(1)	0.0919(1)
Cu2	0.0792(1)	-0.0516(1)	-0.1115(1)
N201	0.0763(8)	0.0828(7)	-0.2923(6)
N211	0.2352(7)	-0.2837(6)	-0.1328(6)
N208	0.5139(12)	0.2219(14)	-0.5150(9)
N218	0.8249(11)	-0.5172(10)	-0.2336(9)
C202	0.2215(9)	0.1049(9)	-0.3273(8)
C203	0.2252(10)	0.1913(10)	-0.4495(8)
C204	0.0692(11)	0.2616(11)	-0.5374(8)
C205	-0.0832(11)	0.2398(11)	-0.4995(8)
C206	-0.0728(9)	0.1486(9)	-0.3772(8)
C207	0.3876(12)	0.2061(13)	-0.4851(9)
C212	0.4027(9)	-0.3170(8)	-0.1600(8)
C213	0.5055(9)	-0.4678(8)	-0.1851(7)
C214	0.4367(10)	-0.5934(8)	-0.1777(8)
C215	0.2659(10)	-0.5585(8)	-0.1497(9)
C216	0.1690(9)	-0.4035(8)	-0.1263(8)
C217	0.6846(10)	-0.4947(9)	-0.2125(9)

TABLE CXXI

POSITIONAL PARAMETERS FOR COPPER IODIDE DI-3-CYANOPYRIDINE (HYDROGEN ATOMS)

ATOM	X	Y	Z
H212	0.4535	-0.2309	-0.1630
H214	0.5081	-0.7016	-0.1909
H215	0.2140	-0.6428	-0.1458
H216	0.0468	-0.3814	-0.1061
H202	0.3300	0.0594	-0.2647
H204	0.0664	0.3232	-0.6241
H205	-0.1938	0.2884	-0.5585
H206	-0.1799	0.1314	-0.3510

TABLE CXXII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE DI-3-CYANOPYRIDINE

ATOM	U11	U22	U33	U12	U13	U23
I2	27(0)	34(0)	43(0)	-10(0)	5(0)	-2(0)
Cu2	31(0)	27(0)	37(0)	-5(0)	8(0)	0(0)
N201	34(2))	31(2)	36(3)	-8(2)	9(2)	0(2)
N208	47(4)	129(8)	66(5)	-37(5)	-3(4)	31(5)
N211	32(2)	25(2)	30(2)	-3(2)	6(2)	0(2)
N218	48(4)	55(4)	70(5)	-13(3)	20(3)	-7(3)
C202	31(3)	43(4)	34(3)	-9(3)	0(2)	7(3)
C203	35(3)	53(4)	32(3)	-17(3)	4(2)	-6(3)
C204	44(4)	59(5)	33(3)	-18(3)	-3(3)	13(3)
C205	34(3)	69(5)	33(3)	-18(3)	-2(2)	8(3)
C206	29(3)	41(3)	39(3)	-9(2)	7(2)	0(3)
C207	39(4)	85(7)	49(4)	-35(4)	-1(3)	21(4)
C212	34(3)	26(3)	40(3)	-4(2)	11(2)	-3(2)
C213	32(3)	33(3)	32(3)	-3(2)	4(2)	-4(2)
C214	40(3)	20(3)	50(4)	-4(2)	6(3)	-5(2)
C215	39(3)	26(3)	51(4)	-9(2)	7(3)	1(3)
C216	31(3)	30(3)	39(3)	-5(2)	0(2)	3(2)
C217	37(3)	32(3)	49(4)	-5(2)	13(3)	-6(3)

Anisotropic thermal parameters in the form:

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

TABLE CXXII (Continued)

+ $2U_{13}hla^*c^*$ + $2U_{23}klb^*c^*$)) x 10^4 for I, Cu; x 10^3 for C, N, and O.

TABLE CXXIII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE DI-3-CYANOPYRIDINE

I2 - Cu2	2.642(2)	Cu2 - I2 - Cu2'	60.39(4)
I2 - Cu2'	2.646(2)	I2 - Cu2 - I2'	119.60(4)
Cu2 - Cu2'	2.660(2)	I2' - Cu2 - N201	108.1(1)
Cu2 - N201	2.076(6)	I2 - Cu2 - N201	106.9(2)
Cu2 - N211	2.082(5)	I2 - Cu2 - N211	106.2(2)
N201 - C202	1.32(1)	I2' - Cu2 - N211	107.7(2)
N201 - C206	1.338(8)	N201 - Cu2 - N211	107.6(2)
C202 - C203	1.39(1)	Cu2 - N201 - C202	121.0(4)
C203 - C204	1.39(1)	Cu2 - N201 - C206	120.7(6)
C203 - C207	1.43(1)	C202 - N201 - C206	118.2(6)
C204 - C205	1.38(1)	N201 - C202 - C203	122.5(6)
C205 - C206	1.38(1)	C202 - C203 - C204	119.2(8)
C207 - N208	1.13(2)	C202 - C203 - C207	120.2(7)
N211 - C212	1.34(1)	C204 - C203 - C207	120.4(7)
N211 - C216	1.34(1)	C203 - C204 - C205	117.9(8)
C212 - C213	1.382(9)	C204 - C205 - C206	118.4(7)
C213 - C214	1.40(1)	C205 - C206 - N201	123.4(8)
C213 - C217	1.44(1)	C203 - C207 - N208	178(1)
C214 - C215	1.37(1)	Cu2 - N211 - C212	121.0(5)
C215 - C216	1.39(1)	Cu2 - N211 - C216	120.9(4)
C217 - N218	1.12(1)	C212 - N211 - C216	117.9(6)
		N211 - C212 - C213	122.4(7)
		C212 - C213 - C214	119.6(7)

TABLE CXXIII (Continued)

C212 - C213 - C217	119.2(8)
C214 - C213 - C217	121.0(6)
C213 - C214 - C215	117.5(6)
C214 - C215 - C216	119.8(8)
C215 - C216 - N211	122.5(7)
C213 - C217 - N218	179(1)

Symmetry Operations:

' = -x, -y, -z

TABLE CXXIV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE DI-3-CYANOPYRIDINE - HYDROGEN AYOMS

C202 - H202	0.98	N201 - C202 - H202	119
C204 - H204	0.98	C203 - C202 - H202	119
C205 - H205	0.97	C203 - C204 - H204	122
C206 - H206	0.98	C205 - C204 - H204	120
C212 - H212	0.98	C204 - C205 - H205	120
C214 - H214	0.97	C206 - C205 - H205	122
C215 - H215	0.97	C205 - C206 - H206	119
C216 - H216	0.98	N201 - C206 - H206	118
		N211 - C212 - H212	119
		C213 - C212 - H212	119
		C213 - C214 - H214	121
		C215 - C214 - H214	121
		C214 - C215 - H215	119
		C216 - C215 - H215	121
		C215 - C216 - H216	118
		N211 - C216 - H216	119

TABLE CXXV

CRYSTAL DATA FOR COPPER IODIDE BENZYLNICOTINAMIDE (ROOM TEMPERATURE)

Formula	$Cu_4I_4(C_{13}H_{12}N_2O)_4$
Mwt	1618.7744
a	10.156(3) Å
b	16.460(5) Å
c	17.125(6) Å
α	101.30(2)°
β	104.97(2)
γ	88.33(2)
V	2711(1) $Å^3$
F(OOO)	1560
μMoK_α	38.6115 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.9726 g cm^{-3}
Z	2
Meas. Refl.	7138
Obs. Refl.	4514
R	7.3%
R_w	16.9%
Space Group	$P\bar{1}$
Octants Meas.	±h, k, ±l

TABLE CXXVI

POSITIONAL PARAMETERS FOR COPPER IODIDE BENZYLNICOTINAMIDE (ROOM TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.6961(3)	0.2170(2)	0.6158(2)
I2	0.9078(3)	0.3857(2)	0.5203(2)
I3	0.5477(3)	0.2550(2)	0.3340(2)
I4	0.8771(3)	0.0885(2)	0.4219(2)
Cu1	0.8905(5)	0.2332(3)	0.5453(3)
Cu2	0.6684(5)	0.3180(4)	0.4889(4)
Cu3	0.8077(6)	0.2323(4)	0.3858(3)
Cu4	0.6550(5)	0.1527(4)	0.4558(3)
O119	1.3685(26)	0.0478(18)	0.7836(18)
O219	0.6614(29)	0.5392(18)	0.7695(19)
O319	0.8450(28)	0.4956(19)	0.2537(17)
O419	0.1359(27)	-0.0829(21)	0.2118(21)
N111	1.0797(30)	0.2142(20)	0.6180(20)
N118	1.1510(32)	0.0613(21)	0.7969(22)
N211	0.5316(31)	0.3946(21)	0.5338(21)
N218	0.4479(31)	0.5544(20)	0.7853(21)
N311	0.9237(31)	0.2712(24)	0.3171(21)
N318	1.0497(32)	0.5115(21)	0.2346(21)
N411	0.4788(31)	0.0823(21)	0.4201(22)
N418	0.3433(29)	-0.0789(20)	0.1897(20)
C112	1.0999(35)	0.1586(24)	0.6695(21)

TABLE CXXVI (Continued)

C113	1.2316(39)	0.1389(24)	0.7123(23)
C114	1.3444(39)	0.1804(24)	0.7024(23)
C115	1.3246(39)	0.2378(28)	0.6530(27)
C116	1.1887(43)	0.2576(26)	0.6128(26)
C117	1.2566(39)	0.0799(23)	0.7690(24)
C120	1.1672(45)	0.0018(27)	0.8518(30)
C121	1.2091(48)	0.0420(28)	0.9386(27)
C122	1.3450(59)	0.0499(36)	0.9758(35)
C123	1.3848(72)	0.0860(42)	1.0559(44)
C124	1.2865(108)	0.1135(44)	1.0951(39)
C125	1.1461(89)	0.0978(49)	1.0599(48)
C126	1.1103(64)	0.0639(43)	0.9790(40)
C212	0.5715(38)	0.4386(25)	0.6161(28)
C213	0.4798(36)	0.4812(25)	0.6556(25)
C214	0.3435(41)	0.4744(25)	0.6150(27)
C215	0.3010(40)	0.4299(28)	0.5302(28)
C216	0.4000(41)	0.3906(23)	0.4926(27)
C217	0.5339(44)	0.5290(25)	0.7431(25)
C220	0.4973(48)	0.6062(38)	0.8713(29)
C221	0.3784(41)	0.6512(26)	0.8913(24)
C222	0.3008(46)	0.6188(26)	0.9322(32)
C223	0.1874(49)	0.6615(34)	0.9510(29)
C224	0.1540(57)	0.7359(38)	0.9322(32)
C225	0.2288(57)	0.7723(33)	0.8960(28)
C226	0.3463(60)	0.7313(33)	0.8720(27)

TABLE CXXVI (Continued)

C312	0.9037(45)	0.3455(27)	0.2948(31)
C313	0.9920(39)	0.3821(27)	0.2665(25)
C314	1.1071(47)	0.3435(28)	0.2521(31)
C315	1.1301(50)	0.2654(37)	0.2721(39)
C316	1.0415(46)	0.2291(29)	0.3028(32)
C317	0.9575(42)	0.4675(27)	0.2599(25)
C320	1.0317(48)	0.6012(26)	0.2258(35)
C321	0.9680(43)	0.6173(33)	0.1413(32)
C322	0.9171(45)	0.5576(29)	0.0773(32)
C323	0.8586(48)	0.5843(38)	0.0051(31)
C324	0.8534(51)	0.6653(44)	-0.0056(36)
C325	0.9121(58)	0.7218(36)	0.0643(37)
C326	0.9689(48)	0.7040(26)	0.1359(37)
C412	0.4344(39)	0.0362(25)	0.3442(25)
C413	0.3056(38)	-0.0011(23)	0.3165(27)
C414	0.2186(40)	0.0123(24)	0.3680(29)
C415	0.2623(43)	0.0554(31)	0.4461(36)
C416	0.4004(46)	0.0940(28)	0.4733(32)
C417	0.2557(38)	-0.0577(24)	0.2325(25)
C420	0.3122(46)	-0.1358(27)	0.1103(26)
C421	0.3858(39)	-0.2142(30)	0.1181(24)
C422	0.3353(52)	-0.2754(34)	0.1528(29)
C423	0.4125(64)	-0.3477(31)	0.1628(33)
C424	0.5262(67)	-0.3595(40)	0.1355(35)
C425	0.5725(54)	-0.3039(34)	0.0982(32)

TABLE CXXVI (Continued)

C426	0.5001(42)	-0.2342(26)	0.0892(27)

TABLE CXXVII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE BENZYLNICOTINAMIDE (ROOM TEMPERATURE)

ATOM	U11	U22	U33	U12	U13	U23
I1	28(1)	42(1)	33(1)	-5(1)	10(1)	-3(1)
I2	27(1)	34(1)	48(1)	0(1)	7(1)	10(1)
I3	27(1)	53(1)	35(1)	4(1)	6(1)	8(1)
I4	30(1)	32(1)	55(1)	4(1)	19(1)	2(1)
Cu1	20(2)	51(3)	47(3)	-1(2)	1(2)	19(2)
Cu2	23(2)	49(3)	55(3)	9(2)	10(2)	-11(2)
Cu3	37(3)	61(4)	56(3)	14(2)	27(2)	28(3)
Cu4	25(2)	51(3)	50(3)	-14(2)	16(2)	-7(2)
O119	20(16)	45(19)	56(20)	6(14)	8(14)	14(15)
O219	35(19)	43(19)	59(21)	-8(15)	18(16)	1(16)
O319	28(17)	62(21)	41(18)	1(15)	10(14)	-1(15)
O419	16(15)	71(24)	76(24)	-9(15)	0(15)	-8(19)
N111	21(17)	37(21)	35(20)	11(15)	4(15)	14(17)
N118	22(19)	38(22)	52(24)	-1(6)	7(17)	2(18)
N211	16(17)	45(22)	44(22)	9(15)	9(15)	10(18)
N218	20(18)	30(20)	44(22)	4(15)	13(16)	-8(17)
N311	18(18)	63(28)	37(21)	-2(18)	14(16)	2(19)
N318	27(19)	43(22)	52(24)	-7(16)	26(18)	-5(19)
N411	22(18)	42(22)	52(24)	-7(16)	26(18)	-5(19)
N418	14(17)	38(21)	44(21)	8(15)	18(16)	-7(17)
C112	16(19)	33(24)	15(20)	11(17)	-5(16)	0(18)

TABLE CXXVII (Continued)

C113	36(24)	26(23)	23(22)	-7(19)	16(19)	-17(18)
C114	35(24)	22(22)	25(22)	6(18)	6(18)	11(19)
C115	18(22)	52(31)	44(28)	-14(21)	10(20)	-18(24)
C116	43(27)	37(27)	40(27)	-10(21)	15(22)	5(21)
C117	24(24)	21(23)	35(25)	-4(19)	2(19)	0(19)
C120	48(28)	41(28)	68(34)	-5(23)	9(25)	51(26)
C121	51(31)	43(29)	40(28)	-8(24)	-3(25)	26(24)
C122	75(42)	72(41)	58(39)	-30(33)	-12(32)	12(32)
C123	97(52)	80(49)	75(49)	-21(40)	10(41)	11(39)
C124	171(86)	77(50)	48(42)	-33(56)	3(51)	-1(35)
C125	138(72)	117(63)	79(55)	26(55)	61(53)	45(48)
C126	88(46)	118(56)	73(45)	26(39)	52(38)	51(41)
C212	19(21)	27(24)	67(32)	3(18)	11(21)	19(23)
C213	13(20)	40(26)	49(27)	9(18)	24(20)	19(21)
C214	34(26)	30(25)	48(29)	8(19)	19(22)	12(22)
C215	25(23)	52(30)	58(31)	34(21)	18(22)	41(26)
C216	41(26)	17(22)	60(30)	7(19)	24(23)	26(21)
C217	38(28)	25(24)	33(26)	8(21)	-12(22)	12(20)
C220	37(28)	117(49)	34(29)	8(30)	3(23)	- 23(30)
C221	33(24)	37(26)	25(23)	-4(20)	-3(19)	-10(20)
C222	54(30)	32(26)	39(27)	-9(22)	17(24)	-5(21)
C223	49(31)	68(31)	24(26)	15(30)	-12(26)	-5(25)
C224	69(38)	74(42)	45(32)	-7(32)	18(29)	16(30)
C225	73(38)	61(36)	24(26)	15(30)	-12(26)	-5(25)
C226	93(43)	63(37)	22(25)	-24(32)	2(26)	-3(24)

TABLE CXXVII (Continued)

C312	42(28)	23(25)	73(35)	10(21)	15(25)	11(24)
C313	19(21)	48(29)	39(26)	-19(20)	15(19)	3(22)
C314	49(30)	34(29)	72(36)	12(23)	19(26)	26(26)
C315	40(30)	85(44)	126(53)	1(29)	60(34)	31(39)
C316	36(28)	45(31)	70(36)	10(23)	-6(25)	8(27)
C317	30(26)	43(29)	38(27)	-1(22)	21(21)	4(22)
C320	52(31)	18(24)	104(43)	-13(22)	34(30)	-4(26)
C321	30(25)	90(39)	37(28)	17(25)	28(22)	28(28)
C322	37(27)	47(30)	60(35)	-26(24)	17(26)	-23(28)
C323	41(29)	83(44)	47(33)	15(28)	16(25)	20(30)
C324	34(30)	108(53)	67(41)	-5(32)	26(28)	8(39)
C325	82(40)	81(42)	80(42)	21(33)	30(34)	79(37)
C326	48(30)	18(25)	131(50)	-9(21)	55(33)	4(28)
C412	25(23)	34(25)	35(26)	-10(19)	9(19)	-12(21)
C413	21(22)	17(22)	60(29)	0(17)	18(21)	9(20)
C414	22(22)	18(23)	65(32)	-13(18)	9(22)	-21(22)
C415	22(25)	54(33)	109(47)	-8(23)	37(28)	12(33)
C416	42(28)	40(29)	77(37)	1(23)	24(27)	18(26)
C417	25(22)	23(23)	35(25)	0(18)	-10(19)	-17(21)
C420	51(29)	49(28)	31(25)	21(23)	-16(2)	-17(22)
C421	20(23)	75(35)	18(22)	-20(22)	0(18)	-21(22)
C422	62(34)	70(38)	41(30)	-9(29)	20(26)	6(27)
C423	100(46)	34(31)	63(37)	3(31)	0(34)	34(28)
C424	87(47)	82(48)	53(37)	41(38)	16(34)	-7(33)
C425	64(36)	50(35)	51(33)	7(29)	8(27)	-5(27)

TABLE CXXVII (Continued)

C426	33(25)	30(26)	52(29)	-8(21)	11(22)	4(22)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2U_{12}hka^*b^*$
$+ 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$
for C, N, and O.

TABLE CXXVIII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE BENZYLNICOTINAMIDE (ROOM TEMPERATURE)

I1 - Cu1	2.611(7)	Cu1 - I1 - Cu2	57.4(2)
I1 - Cu2	2.940(7)	Cu1 - I1 - Cu4	61.6(2)
I1 - Cu4	2.665(6)	Cu2 - I1 - Cu4	56.6(2)
I2 - Cu1	2.646(7)	Cu1 - I2 - Cu2	61.6(2)
I2 - Cu2	2.586(6)	Cu1 - I2 - Cu3	54.5(2)
I2 - Cu3	3.062(6)	Cu2 - I2 - Cu3	56.4(2)
I3 - Cu2	2.632(6)	Cu2 - I3 - Cu3	62.2(2)
I3 - Cu3	2.600(6)	Cu2 - I3 - Cu4	57.3(2)
I3 - Cu4	2.910(7)	Cu3 - I3 - I4	58.2(2)
I4 - Cu1	2.838(6)	Cu1 - I4 - Cu3	57.9(2)
I4 - Cu3	2.592(7)	Cu1 - I4 - Cu4	59.3(2)
I4 - Cu4	2.615(6)	Cu3 - I4 - Cu4	62.3(2)
Cu1 - Cu2	2.680(7)	I4 - Cu1 - I1	106.4(2)
Cu1 - Cu3	2.637(8)	I4 - Cu1 - I2	124.0(2)
Cu1 - Cu4	2.706(7)	I1 - Cu1 - I2	111.8(2)
Cu2 - Cu3	2.702(9)	N111 - Cu1 - I4	97.3(9)
Cu2 - Cu4	2.669(8)	N111 - Cu1 - I1	112(1)
Cu3 - Cu4	2.69(1)	N111 - Cu1 - I2	104(1)
Cu1 - N111	2.06(3)	I1 - Cu2 - I2	103.8(2)
Cu2 - N211	2.04(3)	I1 - Cu2 - I3	120.1(2)
Cu3 - N311	2.06(4)	I2 - Cu2 - I3	120.1(2)
Cu4 - N411	2.05(3)	N211 - Cu2 - I1	93(1)
N111 - C112	1.37(5)	N211 - Cu2 - I2	113.4(9)

TABLE CXXVIII (Continued)

N111 - C116	1.36(6)	N211 - Cu2 - I3	106.7(8)
C112 - C113	1.41(5)	I4 - Cu3 - I2	117.6(2)
C113 - C114	1.42(6)	I4 - Cu3 - I3	116.2(2)
C113 - C117	1.47(6)	I2 - Cu3 - I3	103.8(2)
C114 - C115	1.36(7)	N311 - Cu3 - I4	113(1)
C115 - C116	1.43(6)	N311 - Cu3 - I2	89.0(9)
C117 - N118	1.35(6)	N311 - Cu3 - I3	114.2(90
C117 - O119	1.23(5)	I4 - Cu4 - I1	111.5(2)
N118 - C120	1.46(7)	I4 - Cu4 - I3	105.8(2)
C120 - C121	1.46(6)	I1 - Cu4 - I3	120.0(2)
C121 - C122	1.36(7)	N411 - Cu4 - I4	120(1)
C121 - C126	1.36(9)	N411 - Cu4 - I1	107(1)
C122 - C123	1.34(9)	N411 - Cu4 - I3	92(1)
C123 - C124	1.4(1)	C112 - N111 - C116	119(3)
C124 - C125	1.4(1)	C112 - N111 - Cu1	122(2)
C125 - C126	1.3(1)	C116 - N111 - Cu1	118(3)
N211 - C212	1.41(5)	N111 - C112 - C113	122(4)
N211 - C216	1.41(6)	C112 - C113 - C114	118(4)
C212 - C213	1.39(6)	C112 - C113 - C117	124(4)
C213 - C214	1.38(5)	C114 - C113 - C117	119(3)
C213 - C217	1.52(5)	C113 - C114 - C115	120(3)
C214 - C215	1.45(6)	C114 - C115 - C116	120(4)
C215 - C216	1.41(6)	N111 - C116 - C115	120(4)
C217 - N218	1.28(6)	C113 - C117 - N118	117(3)
C217 - O219	1.26(5)	C113 - C117 - O119	118(4)

TABLE CXXVIII (Continued)

N218 - C220	1.52(5)	N118 - C117 - O119	125(4)
C220 - C221	1.48(7)	C117 - N118 - C120	120(3)
C221 - C222	1.36(7)	C121 - C120 - N118	112(4)
C221 - C226	1.43(7)	C122 - C121 - C126	123(5)
C221 - C222	1.36(7)	C122 - C121 - C120	118(5)
C222 - C223	1.41(7)	C126 - C121 - C120	118(6)
C223 - C224	1.34(8)	C121 - C122 - C123	118(6)
C224 - C225	1.32(9)	C122 - C123 - C124	118(6)
C225 - C226	1.46(8)	C123 - C124 - C125	124(6)
N311 - C312	1.35(6)	C124 - C125 - C126	116(8)
N311 - C316	1.42(6)	C125 - C126 - C121	120(6)
C312 - C313	1.33(7)	C212 - N211 - C216	120(3)
C313 - C314	1.37(6)	C212 - N211 - Cu2	119(2)
C313 - C317	1.50(6)	C216 - N211 - Cu2	120(3)
C314 - C315	1.38(8)	N211 - C212 - C213	122(3)
C315 - C316	1.38(9)	C212 - C213 - C214	118(4)
C317 - N318	1.31(6)	C212 - C213 - C217	118(3)
C317 - O319	1.23(5)	C214 - C213 - C217	118(3)
N318 - C320	1.51(6)	C213 - C214 - C215	120(4)
C320 - C321	1.51(7)	C214 - C215 - C216	119(3)
C321 - C322	1.32(6)	C215 - C216 - N211	121(4)
C321 - C326	1.45(7)	C213 - C217 - N218	118(3)
C322 - C323	1.38(8)	C213 - C217 - O219	117(4)
C323 - C324	1.4(1)	N218 - C217 - O219	125(4)
C324 - C325	1.37(8)	C217 - N218 - C220	120(3)

TABLE CXXVIII (Continued)

C325 - C326	1.30(8)	C221 - C220 - N218	107(3)
N411 - C412	1.34(5)	C222 - C221 - C226	118(4)
N411 - C416	1.34(7)	C222 - C221 - C220	121(5)
C412 - C413	1.39(5)	C226 - C221 - C220	121(5)
C413 - C414	1.39(7)	C221 - C222 - C223	121(4)
C413 - C417	1.52(5)	C222 - C223 - C224	122(5)
C414 - C415	1.35(7)	C223 - C224 - C225	120(6)
C415 - C416	1.48(6)	C224 - C225 - C226	121(5)
C417 - N418	1.29(6)	C225 - C226 - C221	118(5)
C417 - O419	1.24(5)	C312 - N311 - C316	116(4)
N418 - C420	1.46(5)	C312 - N311 - Cu3	121(3)
C420 - C421	1.48(6)	C316 - N311 - Cu3	122(3)
C421 - C422	1.43(8)	N311 - C312 - C313	124(4)
C421 - C426	1.38(6)	C312 - C313 - C314	122(4)
C422 - C423	1.42(8)	C312 - C313 - C317	116(4)
C423 - C424	1.3(1)	C314 - C313 - C317	122(4)
C424 - C425	1.4(1)	C313 - C314 - C315	117(5)
C425 - C426	1.36(7)	C314 - C315 - C316	121(5)
		C315 - C316 - N311	120(5)
		C313 - C317 - N318	119(4)
		C313 - C317 - O319	120(4)
		N318 - C317 - O319	122(4)
		C317 - N318 - C320	123(4)
		N318 - C320 - C321	116(4)
		C322 - C321 - C326	123(5)

TABLE CXXVIII (Continued)

C322 - C321 - C320	123(5)
C326 - C321 - C320	113(4)
C321 - C322 - C323	115(5)
C322 - C323 - C324	126(5)
C323 - C324 - C325	114(6)
C324 - C325 - C326	125(6)
C325 - C326 - C321	117(4)
C412 - N411 - C416	121(3)
C412 - N411 - Cu4	123(3)
C416 - N411 - Cu4	116(3)
N411 - C412 - C413	122(4)
C412 - C413 - C414	119(4)
C412 - C413 - C417	123(4)
C414 - C413 - C417	118(3)
C413 - C414 - C415	120(4)
C414 - C415 - C416	119(5)
C415 - C416 - N411	118(4)
C413 - C417 - N418	118(3)
C413 - C417 - O419	118(4)
N418 - C417 - O419	125(3)
C417 - N418 - C420	124(3)
N418 - C420 - C421	110(3)
C422 - C421 - C426	118(4)
C422 - C421 - C420	120(4)
C426 - C421 - C420	123(5)

TABLE CXXVIII (Continued)

C421 - C422 - C423	118(5)
C422 - C423 - C423	120(6)
C423 - C424 - C425	123(6)
C424 - C425 - C426	118(6)
C421 - C426 - C425	124(5)

TABLE CXXIX

CRYSTAL DATA FOR COPPER IODIDE BENZYLNICOTINAMIDE (LOW TEMPERATURE)

Formula	$Cu_4I_4(C_{13}H_{12}N_2O)_4$
Mwt	1618.7744
<u>a</u>	10.123(3) Å
<u>b</u>	16.318(4) Å
<u>c</u>	16.981(6) Å
α	$101.47(2)^\circ$
β	105.38(2)
γ	87.49(2)
V	2651(1) $Å^3$
F(000)	1560
μMoK_α	39.4929 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.0278 g cm^{-3}
Z	2
Meas. Refl.	6929
Obs. Refl.	5177
R	4.7%
R_w	8.8%
Space Group	$P\bar{1}$
Octants Meas.	±h, k, ±l

TABLE CXXX

POSITIONAL PARAMETERS FOR COPPER IODIDE BENZYLNICOTINAMIDE (LOW TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.6981(1)	0.2189(1)	0.6165(1)
I2	0.9084(4)	0.3886(1)	0.5206(1)
I3	0.5463(1)	0.2559(1)	0.3300(1)
I4	0.8787(1)	0.0873(1)	0.4223(1)
Cu1	0.8904(2)	0.2350(1)	0.5441(1)
Cu2	0.6698(2)	0.3205(1)	0.4853(1)
Cu3	0.8069(2)	0.2317(1)	0.3842(1)
Cu4	0.6553(5)	0.1552(1)	0.4553(1)
O119	1.3713(12)	0.0459(8)	0.7843(8)
O219	0.6588(12)	0.5414(8)	0.7669(7)
O319	0.8471(12)	0.4985(7)	0.2561(7)
O419	0.1326(13)	-0.0809(8)	0.2125(8)
N111	1.0777(14)	0.2159(9)	0.6164(9)
N118	1.1523(14)	0.0611(9)	0.7936(9)
N211	0.5347(15)	0.3957(10)	0.5336(10)
N218	0.4419(15)	0.5549(9)	0.7832(9)
N311	0.9265(15)	0.2703(9)	0.3190(9)
N318	1.0566(15)	0.5113(9)	0.2352(9)
N411	0.4805(15)	0.0848(10)	0.4229(10)
N418	0.3429(14)	-0.0763(9)	0.1892(8)
C112	1.1021(18)	0.1607(11)	0.6666(11)

TABLE CXXX (Continued)

C113	1.2355(16)	0.1394(10)	0.7092(10)
C114	1.3464(18)	0.1802(11)	0.7092(10)
C115	1.3279(17)	0.2398(11)	0.6507(11)
C116	1.1898(19)	0.2548(11)	0.6085(12)
C117	1.2597(18)	0.0779(10)	0.7656(11)
C120	1.1706(20)	-0.0014(11)	0.8483(12)
C121	1.2124(19)	0.0396(11)	0.9392(12)
C122	1.3464(23)	0.0551(14)	0.9806(13)
C123	1.3847(26)	0.0939(16)	1.0620(14)
C124	1.2882(27)	0.1130(14)	1.1055(13)
C125	1.1555(26)	0.0993(16)	1.0665(12)
C126	1.1166(21)	0.0625(13)	0.9855(12)
C212	0.5706(17)	0.4405(10)	0.6092(11)
C213	0.4754(18)	0.4795(10)	0.6520(11)
C214	0.3360(17)	0.4710(11)	0.6112(11)
C215	0.2976(19)	0.4265(11)	0.5308(12)
C216	0.3970(18)	0.3895(11)	0.4899(11)
C217	0.5315(19)	0.5270(10)	0.7381(11)
C220	0.4888(20)	0.6073(13)	0.8661(13)
C221	0.3685(19)	0.6516(11)	0.8917(11)
C222	0.2942(19)	0.6170(11)	0.9337(12)
C223	0.1820(21)	0.6609(12)	0.9532(11)
C224	0.1449(19)	0.7352(10)	0.9329(12)
C225	0.2192(22)	0.7700(12)	0.8916(13)
C226	0.3310(20)	0.7296(12)	0.8712(12)

TABLE CXXX (Continued)

C312	0.9063(18)	0.3434(11)	0.2990(11)
C313	0.9959(18)	0.3827(11)	0.2682(10)
C314	1.1140(20)	0.3408(11)	0.2593(12)
C315	1.1358(20)	0.2622(13)	0.2782(12)
C316	1.0411(18)	0.2265(12)	0.3087(12)
C317	0.9599(20)	0.4690(11)	0.2529(11)
C320	1.0382(20)	0.5997(12)	0.2315(13)
C321	0.9735(17)	0.6204(12)	0.1483(11)
C322	0.9181(18)	0.5625(11)	0.0791(11)
C323	0.8537(20)	0.5856(13)	0.0028(12)
C324	0.8537(20)	0.6700(13)	-0.0021(12)
C325	0.9100(21)	0.7297(13)	0.0683(12)
C326	0.9682(20)	0.7055(11)	0.1406(13)
C412	0.4339(16)	0.0380(11)	0.3453(11)
C413	0.3067(17)	-0.0017(10)	0.3193(10)
C414	0.2231(18)	0.0104(11)	0.3728(11)
C415	0.2720(19)	0.0571(13)	0.4539(12)
C416	0.4041(18)	0.0933(11)	0.4761(11)
C417	0.2530(18)	-0.0561(10)	0.2358(12)
C420	0.3089(19)	-0.1354(12)	0.1100(12)
C421	0.3846(18)	-0.2171(11)	0.1171(11)
C422	0.3366(20)	-0.2729(13)	0.1575(11)
C423	0.4113(64)	-0.3450(31)	0.1705(12)
C424	0.5296(21)	-0.3628(13)	0.1431(13)
C425	0.5756(19)	-0.3088(11)	0.0909(11)

TABLE CXXX (Continued)

C426	0.5029(18)	-0.2344(11)	0.0909(11)

TABLE CXXXI

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE BENZYLNICOTINAMIDE (LOW TEMPERATURE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
H112	1.0326(160)	0.1343(95)	0.6768(93)
H114	1.7462(228)	0.3191(137)	0.6768(93)
H116	1.1753(145)	0.2951(87)	0.5788(85)
H1201	1.2281(158)	-0.0479(95)	0.8356(94)
H1202	1.0969(145)	-0.0251(88)	0.8392(85)
H122	1.3897(144)	0.0456(87)	0.9594(134)
H123	1.4600(156)	0.0848(94)	1.0822(91)
H124	1.3126(146)	0.1332(87)	0.9594(85)
H125	1.1082(145)	0.1123(88)	1.1001(85)
H126	1.0522(157)	0.0459(97)	0.9528(93)
H212	0.7379(544)	0.4997(317)	0.7325(312)
H215	0.2011(249)	0.1123(88)	1.1001(85)
H216	0.3740(145)	0.3516(88)	0.4181(85)
H2201	0.5555(146)	0.6562(87)	0.8696(86)
H2202	0.5361(169)	0.5704(102)	0.9063(100)
H222	0.3180(168)	0.5664(101)	0.9491(98)
H223	0.1672(175)	0.6488(105)	0.9806(103)

TABLE CXXXI (Continued)

H224	0.0755(192)	0.7622(115)	0.9564(111)
H225	0.2139(146)	0.8121(88)	0.3054(85)
H226	0.3849(178)	0.7586(108)	0.8452(105)
H312	0.8320(145)	0.3718(88)	0.3054(85)
H314	1.1628(226)	0.3503(135)	0.2157(132)
H315	1.2111(144)	0.2226(87)	0.2576(85)
H3201	1.1143(148)	0.6201(88)	0.2527(85)
H3202	1.0007(146)	0.6201(87)	0.2624(85)
H322	0.9326(145)	0.5073(88)	0.0790(86)
H323	0.8253(145)	0.5478(88)	-0.0434(85)
H324	0.8147(145)	0.6762(88)	-0.0544(85)
H325	0.9181(278)	0.7758(165)	0.0356(160)
H326	0.9996(146)	0.7360(88)	0.1763(85)
H414	-0.0563(606)	-0.1444(360)	-0.0294(350)
H415	0.2205(145)	0.0589(87)	0.4931(85)
H416	0.4539(171)	0.1239(102)	0.5401(99)
H4201	0.3296(145)	-0.1149(88)	0.0638(85)
H4202	0.2259(184)	-0.1400(112)	0.0882(109)
H422	0.2553(192)	-0.2608(116)	0.1612(113)
H423	0.3630(146)	-0.3777(88)	0.1854(86)
H424	0.5618(324)	-0.3653(326)	0.0158(323)
H425	0.5923(556)	-0.3653(326)	0.0158(323)
H426	0.5193(225)	-0.2078(136)	0.0434(131)

TABLE CXXXII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE BENZYLNICOTINAMIDE (LOW TEMPERATURE)

ATOM	U11	U22	U33	U12	U13	U23
I1	15(0)	18(0)	19(0)	-3(0)	6(0)	0(0)
I2	13(0)	16(0)	25(0)	-1(0)	4(0)	5(0)
I3	13(0)	23(0)	19(0)	0(0)	3(0)	4(0)
I4	16(0)	13(0)	29(0)	1(0)	10(0)	1(0)
Cu1	11(1)	20(1)	25(1)	-2(1)	2(1)	9(1)
Cu2	11(1)	21(1)	28(1)	2(1)	6(1)	-5(1)
Cu3	17(1)	27(1)	28(1)	5(1)	13(1)	13(1)
Cu4	15(1)	20(1)	25(1)	-9(1)	9(1)	-4(1)
O119	14(7)	22(7)	29(7)	3(5)	4(5)	10(6)
O219	8(7)	24(7)	24(7)	-9(5)	4(5)	-7(5)
O319	12(6)	11(6)	28(7)	-3(5)	3(5)	1(5)
O419	16(7)	28(8)	36(8)	-8(6)	0(6)	-9(6)
N111	10(8)	10(8)	33(9)	-6(6)	8(6)	0(7)
N118	5(7)	18(8)	22(8)	-6(6)	2(6)	9(6)
N211	9(8)	25(9)	38(10)	0(7)	18(7)	7(8)
N218	21(8)	15(8)	15(7)	0(6)	11(6)	-5(6)
N311	19(8)	15(8)	15(7)	0(6)	12(7)	6(6)
N318	20(8)	7(7)	26(8)	0(6)	12(7)	6(6)
N411	13(8)	24(9)	41(10)	-3(7)	19(7)	12(8)
N418	12(8)	22(8)	11(7)	3(6)	4(6)	2(6)
C112	18(10)	19(10)	14(9)	-9(8)	5(7)	1(8)

TABLE CXXXII (Continued)

C113	5(8)	13(9)	18(9)	4(7)	7(7)	1(7)
C114	13(9)	14(9)	12(9)	-6(7)	0(7)	-6(7)
C115	12(9)	14(9)	15(9)	-11(7)	0(7)	-4(7)
C116	25(11)	7(9)	30(11)	4(8)	11(9)	10(8)
C117	17(9)	4(9)	17(9)	-1(7)	0(7)	-4(7)
C120	26(11)	15(10)	27(11)	-3(8)	2(9)	9(8)
C121	25(11)	13(10)	30(11)	4(8)	11(9)	10(8)
C122	37(13)	39(13)	29(11)	0(10)	5(10)	8(10)
C123	50(16)	54(16)	34(13)	-12(13)	-11(11)	15(12)
C124	73(17)	31(14)	22(12)	-6(12)	9(11)	-4(10)
C125	67(17)	60(17)	22(12)	18(13)	18(11)	17(11)
C126	34(12)	32(12)	27(11)	-6(10)	7(9)	9(9)
C212	11(9)	5(9)	27(11)	-5(7)	4(8)	-2(8)
C213	17(10)	7(9)	24(10)	-2(7)	11(8)	7(8)
C214	4(9)	22(10)	21(10)	-5(7)	-1(7)	7(8)
C215	21(10)	8(9)	32(11)	2(8)	8(9)	3(8)
C216	15(10)	22(10)	21(10)	-2(8)	11(8)	10(8)
C217	22(11)	3(9)	32(11)	2(7)	16(9)	9(8)
C220	17(11)	31(12)	36(12)	-2(9)	6(9)	5(10)
C221	21(10)	18(10)	12(9)	-2(8)	8(8)	-2(8)
C222	22(11)	13(10)	28(11)	0(8)	8(8)	-11(7)
C223	34(12)	29(11)	15(10)	-6(9)	8(8)	-14(8)
C224	26(11)	0(9)	35(11)	2(8)	5(9)	-1(8)
C225	42(13)	11(10)	32(11)	-3(9)	-2(9)	3(9)
C226	29(11)	22(11)	25(10)	-16(9)	9(9)	8(9)

TABLE CXXXII (Continued)

C312	13(9)	11(9)	18(9)	0(7)	2(7)	7(7)
C313	13(9)	18(10)	14(9)	-6(8)	-2(7)	0(8)
C314	34(12)	13(10)	28(11)	-5(8)	12(9)	15(8)
C315	24(11)	29(12)	30(11)	1(9)	12(9)	6(9)
C316	8(9)	33(12)	33(11)	3(8)	14(8)	4(9)
C317	32(11)	7(9)	19(10)	0(8)	8(8)	-4(7)
C320	23(12)	18(11)	49(13)	-13(9)	14(10)	0(9)
C321	5(9)	28(11)	25(10)	2(8)	8(8)	5(9)
C322	14(10)	14(9)	27(11)	-6(8)	8(8)	-6(8)
C323	25(11)	33(13)	21(10)	-19(9)	3(9)	-16(9)
C324	24(11)	42(14)	23(10)	-7(9)	17(8)	8(9)
C325	33(12)	41(13)	28(11)	5(10)	16(9)	19(10)
C326	23(11)	15(10)	41(13)	-8(8)	20(10)	-5(9)
C412	2(8)	18(10)	21(10)	-3(7)	1(7)	0(8)
C413	10(9)	0(8)	19(9)	-1(6)	4(7)	-3(7)
C414	15(10)	41(13)	-8(8)	2(7)	21(8)	1(8)
C415	19(11)	36(12)	23(10)	-14(9)	12(8)	-1(9)
C416	18(10)	25(11)	17(9)	-1(8)	14(8)	5(8)
C417	14(9)	3(9)	36(11)	6(7)	9(8)	7(8)
C420	16(10)	23(11)	28(11)	6(8)	-1(8)	-1(9)
C421	13(9)	25(10)	15(9)	-10(8)	5(7)	0(8)
C422	19(11)	33(12)	17(10)	-9(9)	0(8)	-4(9)
C423	34(12)	26(12)	24(11)	-13(9)	-9(9)	14(9)
C424	26(12)	30(12)	40(13)	8(9)	17(10)	5(10)
C425	18(10)	17(10)	22(10)	-3(8)	1(8)	-1(8)

TABLE CXXXII (Continued)

C426	19(10)	17(10)	21(10)	-6(8)	8(8)	3(8)

Anisotropic thermal parameters in the form:

$\exp(-2\pi(U_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^4$ for I, Cu; $\times 10^3$ for C, N, and O.

TABLE CXXXIII

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE BENZYLNICOTINAMIDE (LOW TEMPERATURE)

I1 - Cu1	2.604(3)	Cu1 - I1 - Cu2	56.21(7)
I1 - Cu2	2.980(3)	Cu1 - I1 - Cu4	61.47(8)
I1 - Cu4	2.651(3)	Cu2 - I1 - Cu4	56.69(7)
I2 - Cu1	2.638(3)	Cu1 - I2 - Cu2	61.13(7)
I2 - Cu2	2.575(3)	Cu1 - I2 - Cu3	53.45(7)
I2 - Cu3	3.096(3)	Cu2 - I2 - Cu3	55.00(7)
I3 - Cu2	2.625(2)	Cu2 - I3 - Cu3	61.26(7)
I3 - Cu3	2.594(3)	Cu2 - I3 - Cu4	56.92(7)
I3 - Cu4	2.905(3)	Cu3 - I3 - I4	57.77(8)
I4 - Cu1	2.830(2)	Cu1 - I4 - Cu3	57.41(8)
I4 - Cu3	2.588(3)	Cu1 - I4 - Cu4	58.91(7)
I4 - Cu4	2.620(3)	Cu3 - I4 - Cu4	61.67(8)
Cu1 - Cu2	2.652(3)	I4 - Cu1 - I1	105.91(9)
Cu1 - Cu3	2.611(3)	I4 - Cu1 - I2	125.6(1)
Cu1 - Cu4	2.686(3)	I1 - Cu1 - I2	112.40(9)
Cu2 - Cu3	2.659(4)	N111 - Cu1 - I4	95.8(4)
Cu2 - Cu4	2.646(3)	N111 - Cu1 - I1	111.5(4)
Cu3 - Cu4	2.670(4)	N111 - Cu1 - I2	103.2(4)
Cu1 - N111	2.02(1)	I1 - Cu2 - I2	103.02(8)
Cu2 - N211	2.02(2)	I1 - Cu2 - I3	119.70(9)
Cu3 - N311	2.04(2)	I2 - Cu2 - I3	119.7(1)
Cu4 - N411	2.04(1)	N211 - Cu2 - I1	90.2(5)
N111 - C112	1.33(2)	N211 - Cu2 - I2	112.8(4)

TABLE CXXXIII (Continued)

N111 - C116	1.37(3)	N211 - Cu2 - I3	107.8(4)
C112 - C113	1.42(2)	I4 - Cu3 - I2	117.33(9)
C113 - C114	1.39(3)	I4 - Cu3 - I3	116.62(9)
C113 - C117	1.49(3)	I2 - Cu3 - I3	104.08(8)
C114 - C115	1.38(3)	N311 - Cu3 - I4	112.6(4)
C115 - C116	1.43(2)	N311 - Cu3 - I2	87.4(4)
C117 - N118	1.36(3)	N311 - Cu3 - I3	115.3(4)
C117 - O119	1.21(2)	I4 - Cu4 - I1	110.82(9)
N118 - C120	1.49(3)	I4 - Cu4 - I3	105.8(1)
C120 - C121	1.51(2)	I1 - Cu4 - I3	121.56(8)
C121 - C122	1.36(3)	N411 - Cu4 - I4	119.5(4)
C121 - C126	1.40(3)	N411 - Cu4 - I1	106.1(5)
C122 - C123	1.34(3)	N411 - Cu4 - I3	92.9(5)
C123 - C124	1.36(4)	C112 - N111 - C116	117(1)
C124 - C125	1.34(3)	C112 - N111 - Cu1	123(1)
C125 - C126	1.35(3)	C116 - N111 - Cu1	119(1)
N211 - C212	1.31(2)	N111 - C112 - C113	123(2)
N211 - C216	1.39(2)	C112 - C113 - C114	118(2)
C212 - C213	1.41(3)	C112 - C113 - C117	122(2)
C213 - C214	1.40(2)	C114 - C113 - C117	119(1)
C213 - C217	1.49(2)	C113 - C114 - C115	121(2)
C214 - C215	1.37(2)	C114 - C115 - C116	116(2)
C215 - C216	1.42(3)	N111 - C116 - C115	124(2)
C217 - N218	1.35(3)	C113 - C117 - N118	117(1)
C217 - O219	1.27(2)	C113 - C117 - O119	120(2)

TABLE CXXXIII (Continued)

N218 - C220	1.46(2)	N118 - C117 - O119	123(2)
C220 - C221	1.51(3)	C117 - N118 - C120	118(1)
C221 - C222	1.37(3)	C121 - C120 - N118	112(1)
C221 - C226	1.40(3)	C122 - C121 - C126	117(2)
C221 - C222	1.37(3)	C122 - C121 - C120	121(2)
C222 - C223	1.40(3)	C126 - C121 - C120	122(2)
C223 - C224	1.34(3)	C121 - C122 - C123	122(2)
C224 - C225	1.36(3)	C122 - C123 - C124	120(2)
C225 - C226	1.37(3)	C123 - C124 - C125	120(2)
N311 - C312	1.30(2)	C124 - C125 - C126	120(2)
N311 - C316	1.37(2)	C125 - C126 - C121	121(2)
C312 - C313	1.40(3)	C212 - N211 - C216	120(2)
C313 - C314	1.38(3)	C212 - N211 - Cu2	121(1)
C313 - C317	1.49(2)	C216 - N211 - Cu2	118(1)
C314 - C315	1.38(3)	N211 - C212 - C213	123(2)
C315 - C316	1.40(3)	C212 - C213 - C214	118(1)
C317 - N318	1.35(3)	C212 - C213 - C217	117(1)
C317 - O319	1.23(2)	C214 - C213 - C217	124(2)
N318 - C320	1.46(2)	C213 - C214 - C215	119(2)
C320 - C321	1.49(3)	C214 - C215 - C216	121(3)
C321 - C322	1.36(2)	C215 - C216 - N211	119(1)
C321 - C326	1.42(3)	C213 - C217 - N218	117(2)
C322 - C323	1.40(3)	C213 - C217 - O219	121(2)
C323 - C324	1.39(3)	N218 - C217 - O219	122(1)
C324 - C325	1.39(2)	C217 - N218 - C220	120(1)

TABLE CXXXIII (Continued)

C325 - C326	1.34(3)	C221 - C220 - N218	110(1)
N411 - C412	1.36(2)	C222 - C221 - C226	119(2)
N411 - C416	1.32(3)	C222 - C221 - C220	122(2)
C412 - C413	1.39(2)	C226 - C221 - C220	119(2)
C413 - C414	1.38(3)	C221 - C222 - C223	118(2)
C413 - C417	1.49(2)	C222 - C223 - C224	123(2)
C414 - C415	1.41(2)	C223 - C224 - C225	119(2)
C415 - C416	1.41(3)	C224 - C225 - C226	121(2)
C417 - N418	1.35(3)	C225 - C226 - C221	120(2)
C417 - O419	1.24(3)	C312 - N311 - C316	120(2)
N418 - C420	1.46(2)	C312 - N311 - Cu3	119(1)
C420 - C421	1.52(3)	C316 - N311 - Cu3	120(1)
C421 - C422	1.41(3)	N311 - C312 - C313	124(2)
C421 - C426	1.38(3)	C312 - C313 - C314	117(2)
C422 - C423	1.39(3)	C312 - C313 - C317	117(2)
C423 - C424	1.39(3)	C314 - C313 - C317	126(2)
C424 - C425	1.37(3)	C313 - C314 - C315	119(2)
C425 - C426	1.41(3)	C314 - C315 - C316	120(2)
		C315 - C316 - N311	119(2)
		C313 - C317 - N318	116(2)
		C313 - C317 - O319	121(2)
		N318 - C317 - O319	121(2)
		C317 - N318 - C320	120(2)
		N318 - C320 - C321	117(1)
		C322 - C321 - C326	119(2)

TABLE CXXXIII (Continued)

C322 - C321 - C320	124(2)
C326 - C321 - C320	118(2)
C321 - C322 - C323	122(2)
C322 - C323 - C324	119(2)
C323 - C324 - C325	120(2)
C324 - C325 - C326	120(2)
C325 - C326 - C321	122(1)
C412 - N411 - C416	121(1)
C412 - N411 - Cu4	122(1)
C416 - N411 - Cu4	118(1)
N411 - C412 - C413	122(2)
C412 - C413 - C414	119(1)
C412 - C413 - C417	124(2)
C414 - C413 - C417	117(2)
C413 - C414 - C415	120(2)
C414 - C415 - C416	118(2)
C415 - C416 - N411	122(2)
C413 - C417 - N418	116(1)
C413 - C417 - O419	121(2)
N418 - C417 - O419	123(2)
C417 - N418 - C420	122(1)
N418 - C420 - C421	111(1)
C422 - C421 - C426	120(2)
C422 - C421 - C420	118(2)
C426 - C421 - C420	122(2)

TABLE CXXXIII (Continued)

	C421 - C422 - C423	119(2)
	C422 - C423 - C423	121(2)
	C423 - C424 - C425	120(2)
	C424 - C425 - C426	120(2)
	C421 - C426 - C425	120(2)

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