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LUMINESCENCE OF CUPROUS IODIDE COMPLEXES
AND X-RAY STRUCTURE DETERMINATIONS OF
COMPLEXES CONTAINING POTENTIALLY
BIDENTATE LIGANDS

BY

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LUMINESCENCE OF CUPROUS IODIDE COMPLEXES
AND X-RAY STRUCTURE DETERMINATIONS OF
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Preface

This work had its beginnings one early spring morning four years ago as I was folding up a plastic waterbed mattress at the warehouse in which I was working. With the wise counsel of Mr. Kenneth Webster, who visited with me later that day, I was able to see that the time had come for me to make that career change which I had talked about before. In the early part of the summer of that year after conversations with Dr. L. G. Hepler and Dr. Gilbert Mains, who was visiting the University of Lethbridge, I began sending letters of enquiry to various universities, one of which was Oklahoma State. The enthusiastic response from Dr. K. D. Berlin to one of these letters led to my enrollment at OSU.

This thesis is a report of work begun two summers ago, although concrete results did not arise until last summer. Special thanks go to my advisor Dr. Elizabeth Holt who suggested this project to me and who has patiently guided me through all the aspects of it. The moral support and helpful suggestions of Drs. Warren T. Ford and Neil Purdie, who served on my Thesis Committee, is appreciated.

This undertaking would not have been possible without the financial support from the Department of Chemistry, Oklahoma State University, and the Petroleum Research Fund.

I have many friends here at OSU, not only in the Chemistry Department, and their encouragement over the past three years has been so very helpful.

Finally, I would like to thank my mother, Mrs. Elaine Tompkins for her moral support, whose visit this spring encouraged me in making that final last effort necessary for the completion of my course requirements.

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CHAPTER I

INTRODUCTION

It has been known since 1938 that cuprous chloride and some cuprous chloride complexes are luminescent, upon excitation with low frequency ultra-violet radiation and that this luminescence changes when the temperature is lowered to that of liquid nitrogen (-196°C) (1) (2). Until the 1970's, little other work appeared in the literature concerning this phenomenon. Beginning in 1970, numerous publications by H. D. Hardt and his group appeared on the emission and structural properties of a variety of compounds of copper in the (+1) oxidation state.

The earliest work of this group dealt with the luminescence of a cuprous acetate complex which was prepared by the action of hydrazine (a strong reducing agent) on cupric acetate (3) (4). Other copper(I) carboxylates have since been prepared by a variety of methods, the most popular being the reaction of ammonium carboxylates with aqueous cupric sulfate and sodium ascorbate or ascorbic acid (5) (6) (7). All of the carboxylates reportedly emitted at both room temperature and at liquid nitrogen temperature and in those cases where the substance emitted at a different wavelength at -196°C , the shift of emission was reversible

on return to room temperature (8) (9). Most carboxylates showed a small red shift in emitted frequency with cooling but copper(I) valerate and copper(I) 3-hydroxybenzoate both exhibited a blue shift (8) (9). In these cases, this blue shift was visually observed as a change in color from gold to green. This reversible change in color (red or blue shift) with temperature was originally called "fluorescence thermochromism".

After their initial work on cuprous acetate, Hardt and Pierre (10) observed that numerous aromatic and aliphatic nitrogen donor Lewis bases which reacted with copper(I) iodide test paper, formed complexes which were luminescent and which, in many cases, emitted a different color when the temperature was lowered to that of liquid nitrogen (-196°C). The complexes formed by cuprous iodide with pyridine and its alkyl substituted derivatives display a variety of stoichiometries and structural formats (11) (12). Stoichiometries of Cu:I:ligand, 1:1:0.5, 1:1:1, 1:1:1.5, 1:1:2, and 1:1:3 have been observed. Normally complexes of stoichiometry 1:1:3 are observed to be monomers, complexes of stoichiometry 1:1:2 are monomers or rhombs, and those of stoichiometry 1:1:1.5 are chairs, but complexes of stoichiometry 1:1:1 may crystallize as cubes, polymeric pleated sheets or rhombs (12) (13) (14) (15) (16) (17) (18) (19) (20). The complex, $(\text{CuI})_2(2\text{-methylpyridine})$ of stoichiometry 1:1:0.5 is a polymer of chairs linked side by side (21).

Previously reported CuIL complexes for which structural

results are known include, for L=pyridine: $\text{Cu}_4\text{I}_4\text{pyridine}_4$, cubic; $(\text{CuIpyridine})_x$, polymer, and $\text{Cu}_2\text{I}_2(\text{pyridine})_4$, rhomb; (the polymeric sheets where Cl or Br replace I are also known (12) (16) (18) (20). For L=2-methylpyridine, the $\text{Cu}_4\text{I}_4(2\text{-methylpyridine})_4$ cube; $\text{Cu}_4\text{I}_4(2\text{-methylpyridine})_6$ chair; $\text{Cu}_2\text{I}_2(2\text{-methylpyridine})_4$, rhomb and $(\text{CuI})_2(2\text{-methylpyridine})$ polymeric chair form are known as well as the bromide analogue of cubic format and the chloro and bromo forms (14) (15) (17) (21). $\text{CuI}(3\text{-picoline})_3$, a monomer and $\text{Cu}_4\text{I}_4(3\text{-picoline})_4$, a cube, are the reported forms of CuI and 3-picoline (13) (19). Complexes with 2,4-lutidine are known of rhombic format $\text{Cu}_2\text{X}_2(2,4\text{-lutidine})_4$ (X=I, Br, Cl) (15). The two known complexes, L=2,6-lutidine, show trigonal, three coordinate copper; $\text{CuI}(2,6\text{-lutidine})_2$ a monomer and $\text{Cu}_2\text{I}_2(2,6\text{-lutidine})_2$ a rhomb (12) (14). $\text{CuI}(\text{collidine})$ forms a single strand polymer of three coordinate copper atoms ligated to a single collidine (12).

The earliest explanations for the observed temperature dependent luminescence of the cuprous acetate complexes focused on comparisons of the powder diffraction patterns of other copper(I) carboxylate complexes with that of copper(I) acetate (8). Weber and Hardt (22) (23) found that a similar intense line in the diffraction patterns of copper(I) formate, acetate, propionate, and butyrate corresponded to diffraction from the copper containing lattice plane (001) of the copper(I) acetate lattice whose single crystal structure had previously been determined. Thus all of the Cu(I)

carboxylate structures were expected to be similar to that of copper(I) acetate with copper atoms lying on planes and bridged by carboxylate groups. Differences in structures were thus attributed to differences arising only from the packing of substituents attached to the carboxylate group. The difference in thermochromic behavior for each carboxylate was then correlated with the difference in packing of each aliphatic group by comparing the difference in Stokes shift between 300K and 77K for each carboxylate, with the melting point for each corresponding alkane (ie. acetate/ethane), Weber and Hardt (8) were able to see that those carboxylates with the largest difference in Stokes shift had the same carbon skeleton as alkanes with the highest melting point.

Thus:

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

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

while

C_4H_9COOCu $\Delta E_{77K} - \Delta E_{300K} = -.1 \text{ eV (lower)}$

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

and

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

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

where ΔE is the Stokes shift.

Alkanes with even numbers of carbon atoms have higher melting points, therefore the packing of carbon atoms is closer and their van der Waals forces will be larger. Pre-

sumably, in those carboxylates with the greater differences in Stokes shift, a lesser portion of the excitation energy is dissipated as oscillation energy than for the carboxylates containing odd numbers of carbon. With looser packing, there are greater opportunities for oscillation.

Four aromatic copper(I) carboxylates have also been prepared and studied; copper(I) benzoate, 2-hydroxybenzoate, 3-hydroxybenzoate, and 4-hydroxybenzoate (9). The benzoate and 4-hydroxybenzoate reportedly emitted yellow at both room temperature and at -196°C , while the 3-hydroxybenzoate emitted gold at room temperature and intense green at -196°C . The 2-hydroxybenzoate reportedly emitted yellow nonthermochromically, but a recent experiment produced only a red crystalline powder which was not luminescent (copper(I) salicylate is a red substance used in propellants (24)). The reason for the observed thermochromism of the 3-hydroxybenzoate was not clear but a decrease in the crystallographic symmetry was proposed (9).

The red shift in the emission of three copper(I) iodide complexes was correlated with various structural aspects of their single crystals (25). The Lewis bases were piperidine, morpholine, and pyridine. Piperidine showed the lowest red shift while pyridine (its complex had the lowest symmetry) displayed the highest red shift. The piperidine complex of copper(I) iodide whose space group is $P4_2/m$ displayed a red shift of 15 nm when cooled to -196°C , the morpholine complex with a space group of $B2/b$ showed a red shift of 35 nm,

while the pyridine complex with a space group of $P2_12_12_1$ had a red shift of 50 nm.

Crystallographic studies of these three $Cu_4I_4L_4$ cubic clusters showed a $\bar{4}$ symmetry element present in $Cu_4I_4(\text{piperidine})_4$ relating all four Cu - N bonds, whereas $Cu_4I_4(\text{morpholine})_4$ crystallized with a two-fold axis relating the Cu - N bonds in pairs and $Cu_4I_4(\text{pyridine})_4$ displayed no internal crystallographic symmetry elements. Thus the suggestion was made that the observation of significant thermochromism in the solid state depended upon the absence of crystallographic symmetry elements in the cluster and thus the presence of independent Cu - N bonds.

A common feature of many copper(I) complexes which has been brought to light by x-ray diffraction studies is the shortness of the interatomic distances between copper atoms within the clusters in many cases. Molecular orbital calculations have shown that in the Cu_4^{4+} clusters, Cu - Cu distances of 2.83 Å have an overlap population of 0.32 corresponding to a bond energy of -0.417 eV. This binding strength increases as the Cu - Cu distance is shortened (26).

The number of CuI complexes for which both the structure and luminescent properties are known has increased over the years and work in the past has indicated a correlation between the Cu - Cu distances and luminescent properties. Interest has lately been focused on those complexes formed by a single ligand but with varying stoichiometries or structural formats (27) (28) (29). From comparisons of

the structural and emission characteristics for members of these isoligand families, structural aspects have been correlated with characteristics of the emission spectra. One significant structural detail is the closeness of the copper atoms in the cluster. In cases where copper atoms are closer than 2.84 Å, the electronic interactions according to the M.O. calculations should increase. It is generally observed that complexes with Cu - Cu distances shorter than 2.8 Å display an emission band at 570 - 625 nm which is not seen in complexes with Cu - Cu distances greater than 2.8 Å (27). Thus the $\text{Cu}_4\text{I}_4(\text{pyridine})_4$ cube in which the Cu - Cu distances average 2.691(5) Å shows emission at 615 nm whereas the $(\text{CuI}(\text{pyridine}))_x$ polymeric pleated sheet with a Cu - Cu separation of 2.876(2) Å does not. This important phenomenon of luminescence (fluorescence or phosphorescence) in copper(I) systems has been attributed to a $3d^{10} \rightarrow 3d^9 4s^1$ transition (metal centered or MC) upon excitation with ultra-violet radiation. This emission has been observed in a crystal matrix of RbMgF_3 doped with a trace amount of copper. Two emission bands ($\lambda_{\text{em}} = 450 \text{ nm}$ and 575 nm) were believed to arise from a metal centered transition of Cu^{1+} at two different sites in the lattice (30). The luminescence observed in $\text{CuI}(\text{pyridine})_x$ at 449 nm has been attributed to a $3d^{10} \rightarrow 3d^9 \text{pi}^*$ transition (metal to ligand charge transfer or MLCT) (31). In $\text{Cu}_4\text{I}_4(\text{pyridine})_4$, which has a cubic structure, a similar MLCT appears at $\lambda_{\text{em}} = 436 \text{ nm}$ along with the metal centered phenomenon which was found to be at 615 nm.

The assignment of this emission is confirmed by the absence of a similar band for the $\text{Cu}_4\text{I}_4(\text{piperidine})_4$ and $\text{Cu}_4\text{I}_4(\text{morpholine})_4$ which do not have aromatic ligands and thus exhibit metal centered emission at 570 and 625 nm respectively consistent with the Cu - Cu distances of 2.657(2) and 2.65(3) Å (31).

A recent paper has shed light on the matter of electronic transitions and the role of the ligand in complexes of copper(I) iodide (32). Two different complexes containing quinoline as the ligand have been prepared. Their single crystal structures were determined and their emission spectra measured. The first complex; $(\text{CuI}(\text{quinoline})_2)_2$ (1) is a rhomb with two ligands per copper. The Cu - Cu distance was 3.364(5) Å, much longer than usual, presumably because of the bulkiness of the two quinoline molecules attached to each copper, and is a distance far greater than those representative of possible Cu - Cu interactions. From this alone, one can conclude that this particular complex might show luminescence which does not change with temperature, which indeed it does. The broad band emission spectrum for this complex shows a maximum at 625 nm at room temperature, indicative of a MLCT transition ($3d^{10} \rightarrow 3d^9\pi^*$) and at 15 K a maximum of 610 nm. The MLCT band appears at longer wavelengths than that observed with copper bound pyridine consistent with the more extended aromatic system of quinoline.

The second complex $(\text{Cu}_4\text{I}_4(\text{quinoline})_4)$ (2), displays a

structure, previously unknown in copper(I) iodide clusters, consisting of a parallelogram of copper atoms with two short sides, Cu1 - Cu2, 2.582(10) Å; Cu3 - Cu4, 2.545(15) Å, and two long sides, Cu2 - Cu3, 3.279(10) Å; Cu1 - Cu4, 3.325(12) Å. Cu1 and Cu2 are each bound to three iodine atoms but Cu3 and Cu4 are each bound to only two iodine atoms. Each copper is bound to a nitrogen of the quinoline and the geometry about each copper is, for Cu1 and Cu2, a distorted tetrahedron and for Cu3 and Cu4, a trigonal plane. The room temperature, broad band emission spectrum for this complex shows one sharp peak at 625 nm, indicative once again of a MLCT transition. It should be noted that this MLCT emission is of a lower frequency than is observed for pyridine because of the lower energy of the π^* level of the quinoline extended aromatic system (normally about 370 nm). The emission for the expected Cu - Cu interaction is probably superimposed on the peak observed for the MLCT transition. Normally the emission due to metal centered transitions occurs at 550-628 nm. The emission spectrum for (2) at 15 K shows a new set of peaks at a higher frequency which is consistent with that observed for quinoline alone in ethanol (33). One can see why this arises by examining the two structures and their packing diagrams. The packing diagram of (2) shows a parallel arrangement of planar quinoline molecules which are close enough to interact with each other especially at very low temperatures. On the other hand, the packing diagram of (1) shows that each quinoline molecule is

perpendicular to its nearest quinoline neighbor. Intermolecular interactions involving the pi electron clouds of the quinoline molecules are not possible in (1) as they are in (2). Thus intermolecular $\pi \rightarrow \pi^*$ excitation is possible only for (2).

For the complexes formed by CuI and quinoline, we see from the emission spectra that there are three possible origins for luminescence:

- 1) MLCT between Cu(I) and quinoline ($3d^{10} \rightarrow 3d^9\pi^*$)
- 2) interactions between ligands ($\pi \rightarrow \pi^*$)
- 3) metal centered transitions ($3d^{10} \rightarrow 3d^94s^1$)

In the case of copper(I) iodide quinoline complexes, the observed temperature dependent luminescence arises because of a change in the relative population of emitting states in going from high temperature to low temperature. In this particular complex the shortening of the ligand - ligand distances at low temperature results in ligand centered emission because of the close parallel packing of the ligand in the solid matrix which is possible only for this and several other structural matrices. In (1) the bulkiness of the quinoline molecule causes an opening of the L - Cu - L angle and a closing of the I - Cu - I angle with a resulting lengthening of the distance between the two copper atoms. Thus the emission spectrum of (1) has one component both at room temperature and at low temperature whereas (2) displays two components at room temperature and three at low temperature. The bulk of the previously published work on

the phenomenon of luminescent thermochromism of cuprous halides has relied on Lewis base donor ligands in which the only donor was nitrogen. The literature contains instances in which the donor ligand contains both oxygen and nitrogen but there has been some question as to whether the oxygen is coordinated to the copper or not. No structural work is reported for these materials.

Previous workers have reported two 1:1:1 complexes of CuI and methyl quinaldate (and similarly two 1:1:1 complexes each with Cl or Br replacing I) and two 1:1:1 complexes of CuI and ethyl quinaldate (but only one version when Cl or Br replaces I) (34). The two forms of the iodide complexes differ in color, a dark brown modification and an orange brown modification existing for the complex of each ester. These modifications also differ in melting or decomposition points. Because the carbonyl stretching vibrations of the uncomplexed ester and the Cu complexed ester differ only by 5 cm^{-1} from the $1715, 1710\text{ cm}^{-1}$ observed in the uncomplexed methyl and ethyl quinaldate, respectively, these workers suggest that the C=O group does not participate in complexation in their materials (34). The emission characteristics of the CuI complexes with quinaldate esters were not reported.

There have been previous reports of complexes of nicotinic esters and CuI. In 1973, Hardt and Gechnizdjani (35) reported the isolation of the CuI complexes of the methyl, ethyl, butyl, and hexyl esters of nicotinic acid, all of

which were luminescent under ultra-violet radiation, but only the hexyl ester displayed temperature sensitive emission. The other species were yellowish in color and emitted green at 20°C and at -196°C. The powder pattern d spacings of these solid materials were reported. A later work reports the isolation of pale yellow 1:1:1 complexes of ethyl nicotinate and CuCl, CuBr or CuI along with d spacings and IR peak positions (36). A further work reports the preparation of CuI methyl nicotinate complexes of 1:1:1 and 1:1:2 stoichiometries and one complex of CuI and ethyl nicotinate (1:1:1) (37). These workers suggest that the similar position of the C=O stretching absorption in the IR spectra of complexed and uncomplexed methyl nicotinate indicates the non-coordination of the carbonyl oxygens.

Quinaldic acid is known in quantitative analysis as a precipitating agent as well as an agent for some colorimetric determinations (38) (39) (40) (41) (42) (43). The aqueous quinaldate ion is bidentate and forms colored chelate compounds with divalent cations, the nitrogens of the two quinoline rings coordinating with the metal to form two five membered rings and occupy octahedral positions about the central atom (44) (45) (46) (47) (48). In their study of copper(I) halides, Goher and Hafez (34) found that quinaldic acid formed two complexes with copper(I) iodide, one with a 1:1:1 stoichiometry and an other with 1:1:0.5 stoichiometry. These complexes, like some of the esters, were colored brown to violet brown. Infrared absorption spectra

showed, for the 1:1:1 complex, a carbonyl absorption maximum at 1625 cm^{-1} instead of 1700 cm^{-1} . This was interpreted as indicative of carbonyl coordination with the copper. A broad band at 3450 cm^{-1} , indicative of a free OH was given as further evidence for C=O coordination. For the 1:1:0.5 complex, a carbonyl stretching vibration at 1680 cm^{-1} was indicative of a different kind of linkage, and a cubane structure like many of the other complexes studied was proposed. A bidentate structure similar to the octahedral bidentate structure for the complexes of the divalent cations was proposed for the 1:1:1 complex of copper(I) iodide.

To understand the effects on structure and emission properties of CuIL complexes when the donor ligand is mixed or bidentate, a study of copper iodide complexes of quinaldic acid and its esters, along with the esters of nicotinic acid and related systems was undertaken.

CHAPTER II

X-RAY CRYSTALLOGRAPHY

For single X-ray structure determination, a crystal of approximately 0.1 mm^3 is mounted on a glass fiber which is mounted on a brass nib. None of the compounds examined was sensitive to air or moisture within the time required for an X-ray analysis so most of the crystals were attached to the glass fiber using epoxy glue as the adhesive. In some cases, there was evidence that epoxy reacted with the crystal and in these cases, the crystal was wedged into the constriction of a small capillary tube and the ends of the tube sealed with epoxy glue, making sure that none of the glue touched the crystal. The mounted crystal was inserted into a goniometer head and the goniometer was then positioned on a four-circle Syntex P3 automated diffractometer. The mounted crystal was visually centered within the crosshairs of the microscope and a rotation photograph was taken to ascertain the crystal quality and to provide a starting point for the automated centering program of the diffractometer. A reflection of $\approx 90^\circ$ and 2θ less than 20° was selected and used to re-adjust the height of the crystal more accurately. Fifteen independent reflections (spots) were centered to determine

the optimum 2θ , ω , ϕ , and χ angles for each reflection. An indexing routine provided possible cell edges from which a set with maximum symmetry and minimum volume was chosen (49). 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 (49). If the errors (standard deviations) of the cell dimensions were unacceptably high, a fast data scan was carried out to find fifteen intense reflections with 2θ values which were greater than 20° . The cell determination procedure was repeated using these new reflections to yield a cell with acceptable errors. Depending on the crystal class, a set of data was collected such that the diffraction symmetry of the cell generated a complete sphere of data (50). The details of data collection for each compound are shown in crystal data tables.

The diffractometer records the intensity data, I_{hkl} , associated with each reflection in the following format: sequence number, (negative for standard reflections), 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 $1^\circ/\text{minute}$ 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 (51). These four corrections are for (i) back-

ground, (ii) polarization, (iii) Lorentz effect, and (iv) crystal decomposition.

Correction for left and right background (i) is calculated as follows:

$$I_{\text{int}} = (I_{\text{meas}} - L_{\text{bg}} - R_{\text{bg}}) \times \text{Scan speed} \quad (1)$$

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

where:

I_{int} = Integrated Intensity

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

I_{meas} = Measured Intensity

L_{bg} = Left Background

R_{bg} = Right Background

The reflection is considered observed if:

$$I_{\text{int}} > 3\sigma(I_{\text{int}}) \quad (3)$$

The polarization term (ii) 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:

$$p = (1 + \cos^2 2\theta)/2 \quad (4)$$

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

The Lorentz effect (iii) 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 (F) is given by:

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

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

$$L_p = (1 + \cos^2 2\theta)/2 \times \sin 2\theta \quad (6)$$

A final correction (iv) 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:

$$I_{\text{orig}} / I_{\text{ave}} \quad (7)$$

where:

$$I_{\text{orig}} = \text{original intensity of the std. reflection} \quad (8)$$

$$I_{\text{ave}} = \text{Average current intensity of the std reflection} \quad (9)$$

These four corrections are combined to form the following expression

$$I_{\text{cor}} = I_{\text{int}} \times (L_p)^{-1} \times (I_{\text{orig}}/I_{\text{ave}}) \quad (10)$$

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

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

The error in $|F_{hkl}|$, is σF and is calculated according to the following (50):

$$\sigma F = (1/2) (k/L_p)^{1/2} ((N_t' + N_{\text{Rbg}} + N_{\text{Lbg}} + (0.01N_{\text{pk}})^2) / (N_t - N_{\text{Lbg}} - N_{\text{Rbg}})^{1/2} \quad (12)$$

where:

N_t = no. of counts

N_{Lbg} = no. of left background counts

N_{Rbg} = no. of right background counts

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

Although the structure factor $|F|$ can be derived from the measurements made from the diffractometer, the measurements contain no information about the phase (α), because phases cannot be measured (50). 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, we need to have information about the phase, at least for enough reflections, so that when a Fourier transform of the αF is made we will generate an interpretable electron density map and hence show the atomic positional parameters.

The structure factor $|F_{hkl}|$ (it contains no information about phases) is used to find the co-ordinates of atoms by either of two procedures, Patterson mapping or Direct methods. A Patterson map is the Fourier transform of $|F|^2$ (squaring the structure factor eliminates the phase). The Patterson map locates the positions of the ends of vectors between atoms, translated to the origin. Because the vectors between heavy atoms are most visible on the maps, use of the knowledge of the space group general equivalent positions allows calculation of Harker planes and lines from

which positional parameters can be determined. This method of obtaining a solution is known as the "Heavy Atom Method" (51).

The second tactic used to obtain positional parameters for atoms is "Direct Methods". The principle behind this method is the concept that the relationships between the intensities themselves 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. Using the Harker-Kasper inequalities (50), intensities and phases can be correlated. Normalized structure factors, E_{hkl} are calculated by the equation:

$$E_{hkl}^2 = (F_{hkl})^2 / \sum f_i \quad (13)$$

By use of the sigma1, and sigma2 relationships and symbolic addition procedures, the phases associated with a sufficient number of reflections can be determined (52).

Once the heaviest atoms are positioned by either the "Heavy Atom Method" or "Direct Methods", 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:

$$R_f = (\sum ||F_{obs}| - |F_{calc}||) / (\sum |F_{obs}|). \quad (14)$$

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

When some atoms are correctly placed, the phases being nearly correct, a Fourier transform of the observed minus

the calculated structure factor, F_{cal} , gives rise to an electron density map which shows the positions of missing atoms and a least squares refinement of the positional parameters, x , y , z , and the thermal parameter, U (isotropic), is carried out. The magnitude of the thermal parameter is an indication of the correctness of the identity of the atom. After several cycles of least-squares refinement of the positional parameters for the complete set of atoms and their associated anisotropic thermal parameters (U_{11} , U_{22} , U_{33} , U_{12} , U_{13} , U_{23}) are completed, an acceptable final R_f should have a value of less than 10%, and the bond angles and distances should be chemically reasonable. The refined positional parameters along with their anisotropic thermal parameters are used to obtain a projection view of the molecule in which the atoms are drawn as ellipsoids whose boundaries enclose the 90% probability density of the shell electron's location.

CHAPTER III

EXPERIMENTAL

Syntheses

(CuI(methylquinaldate))_x. Quinaldic acid (1 gm) was dissolved in 10 ml methanol, followed by addition of 3 ml conc. sulfuric acid, following the procedure of Mills et al. and the resulting solution was heated under reflux for two hours (38). The solution was then poured into distilled water cooled to 0° C and neutralized with solid Na₂CO₃ until effervescence ceased. The methyl ester was extracted into 30 ml of ether, from which it was isolated on evaporation of the organic solvent (mp 86-87° C) and was used without further purification. CuI (0.15 g) and methyl quinaldate (0.147 g) (1:1 molar ratio) were dissolved in acetonitrile giving a yellow orange solution. Purple-brown crystals of (CuI(methylquinaldate))_x suitable for single X-ray analysis were obtained upon slow evaporation of the solvent; decomp. 180° C; IR 1718 vs, 1620, 1595, 1505, 1460, 1433 s, 1388, 1318 vs, 1308 vs, 1262s, 795 s, 772 vs, 639, 600 cm⁻¹ KBr.

Cu₂I₂(isopropylquinaldate)₂. The isopropyl ester of quinaldic acid was prepared by an acid catalysed procedure as above and used as isolated. Five drops of the ester and

0.1 g. of CuI (molar ratio approx. 1:1) were dissolved in 40 ml of acetonitrile, giving an orange solution. Deep red purple crystals were obtained upon slow evaporation of the solvent melting with dec. $187-190^{\circ}$ C, color change to light orange with melting; IR 1695 vs, 1613, 1593, 1505, 1463 s, 1435, 1398 s, 1306 vs, 1300 vs, 1255 s, 1218, 1178 s, 1125, 1110 vs, 1098 vs, 970, 925, 883, 852, 795, 775 vs, 638, 627 cm^{-1} KBr.

$\text{Cu}_2\text{I}_2(\text{n-butylquinaldate})_2$. N-butyl quinaldate was prepared by the acid catalysed esterification of quinaldic acid with n-butanol. The crude ester was added to a solution of CuI (0.1 g) in acetonitrile to give a solution of molar ratio 1:1, ester:CuI. Purple brown crystals formed on slow evaporation of the solvent; dec. $195-200^{\circ}$; IR 1695, 1590, 1503, 1458 s, 1435, 1395, 1380, 1305 vs, 1258 s, 1217 s, 1178 s, 1129 s, 1060, 1023, 970 s, 950 s, 875, 841, 795, 775 vs, 737, 635, 625 cm^{-1} KBr.

$\text{Cu}_4\text{I}_4(\text{methylnicotinate})_4$. Nicotinic acid (1 gm) 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 diethylether, from which it was isolated upon distillation of the organic solvent and used without further purification. The crude methyl nicotinate (0.4 ml, 3.0

mmoles) was dissolved in acetonitrile and a slight excess of copper(I) iodide was added (0.1 gm, 3.1 mmoles). The yellow precipitate which formed was dissolved in acetonitrile and crystals suitable for X-ray analysis were formed upon slow evaporation of the solvent (decomp. 250°C). The solid crystalline material emitted a pale green color under a low frequency ultra-violet lamp at room temperature and at low temperature (-195°C) the emission intensified but with no significant change in observable color.

$\text{Cu}_4\text{I}_4(\text{isopropyl nicotinate})_4$. The isopropyl ester of nicotinic acid was prepared by the acid catalysed esterification procedure as above and used as isolated without further purification. The ester (0.5 ml) and CuI (0.6 gm, slight excess) was dissolved in acetonitrile and filtered. Yellow brown octahedral crystals were obtained upon slow evaporation of the solvent (mp. $135-137$ with decomp.). The crystalline material emitted dull green-brown at room temperature under low frequency ultra-violet radiation changing to intense pale green at -196°C . These crystals appeared to be unstable with respect to disproportionation over a long period of time (6 months). A modification of this complex was formed when excess isopropyl nicotinate was added to a solution of copper(I) iodide in acetonitrile. It decomposed at $130-133^{\circ}\text{C}$. Crystals suitable for X-ray analysis were formed by slow evaporation of the solvent. The excess ligand was washed from the crystals with a small amount of cold acetonitrile. These crystals emitted intense

pale green-blue at room temperature and at -196°C but emitted light brown (similar to the first modification) after they had been heated to 200°C (which is higher than the decomposition temperature). At -196°C , this residue emitted intense pale green-blue.

$\text{Cu}_4\text{I}_4(\text{n-butyl nicotinate})_4$. N-butyl nicotinate was prepared by the acid catalyzed esterification of nicotinic acid with n-butanol. The crude ester (0.5 ml) was added to an acetonitrile solution of CuI (0.1 gm, slight excess). Yellowish opaque octahedral crystals formed upon slow evaporation of the solvent (acetonitrile). Clear colorless crystals, suitable for X-ray analysis, were obtained by slow evaporation of a toluene/acetonitrile solvent (mp $132-135^{\circ}\text{C}$).

$\text{Cu}_2\text{I}_2(\text{pyrazinamide})_2$. Copper(I) iodide (0.1 gm) plus pyrazinamide (0.11 gm) were stirred for six hours in acetonitrile. The red-orange powder was only slightly soluble in this solvent and a great excess had to be used. Scarlet red crystals suitable for X-ray analysis were obtained upon slow evaporation of the solvent (decomp. 270°C).

$\text{Cu}_3\text{I}_2(\text{quinaldic acid})_3(\text{H}_2\text{O})$. Quinaldic acid (0.22 gm, 1.3 mmoles) was dissolved in acetonitrile which contained CuI (0.1 gm, 0.5 mmoles). A yellow solution resulted. Purple-brown crystals suitable for x-ray diffraction formed upon slow evaporation of the solvent (mp. $208-210^{\circ}\text{C}$ with effervescence).

CHAPTER IV

RESULTS AND DISCUSSION

Three different, potentially bidentate compounds were studied as ligands in this project; six esters, a carboxylic acid and an amide. All six compounds were similar in having a heterocyclic ring system with at least one nitrogen and in having a carbonyl containing group substituted on the aromatic ring. All of these acted as Lewis bases toward copper in the (+1) oxidation state and complexed easily with cuprous iodide. No significant disproportionation or oxidation to the (+2) state was experienced.

The first class of compounds to be studied were the methyl, isopropyl and n-butyl esters of quinaldic acid. Various spectral properties of some quinaldic esters have been reported and from the observed frequencies of the carbonyl stretching vibrations, it was concluded that these esters coordinate with the copper atom only through the nitrogen (34).

Cuprous iodide(methylquinaldate)₂ (I) (Figure 1.) crystallizes with a chain of alternating copper and iodine atoms, each copper atom displaying tetrahedral coordination to two iodine atoms and the carbonyl oxygen and nitrogen atoms of a single methyl quinaldate molecule. The I-Cu-I

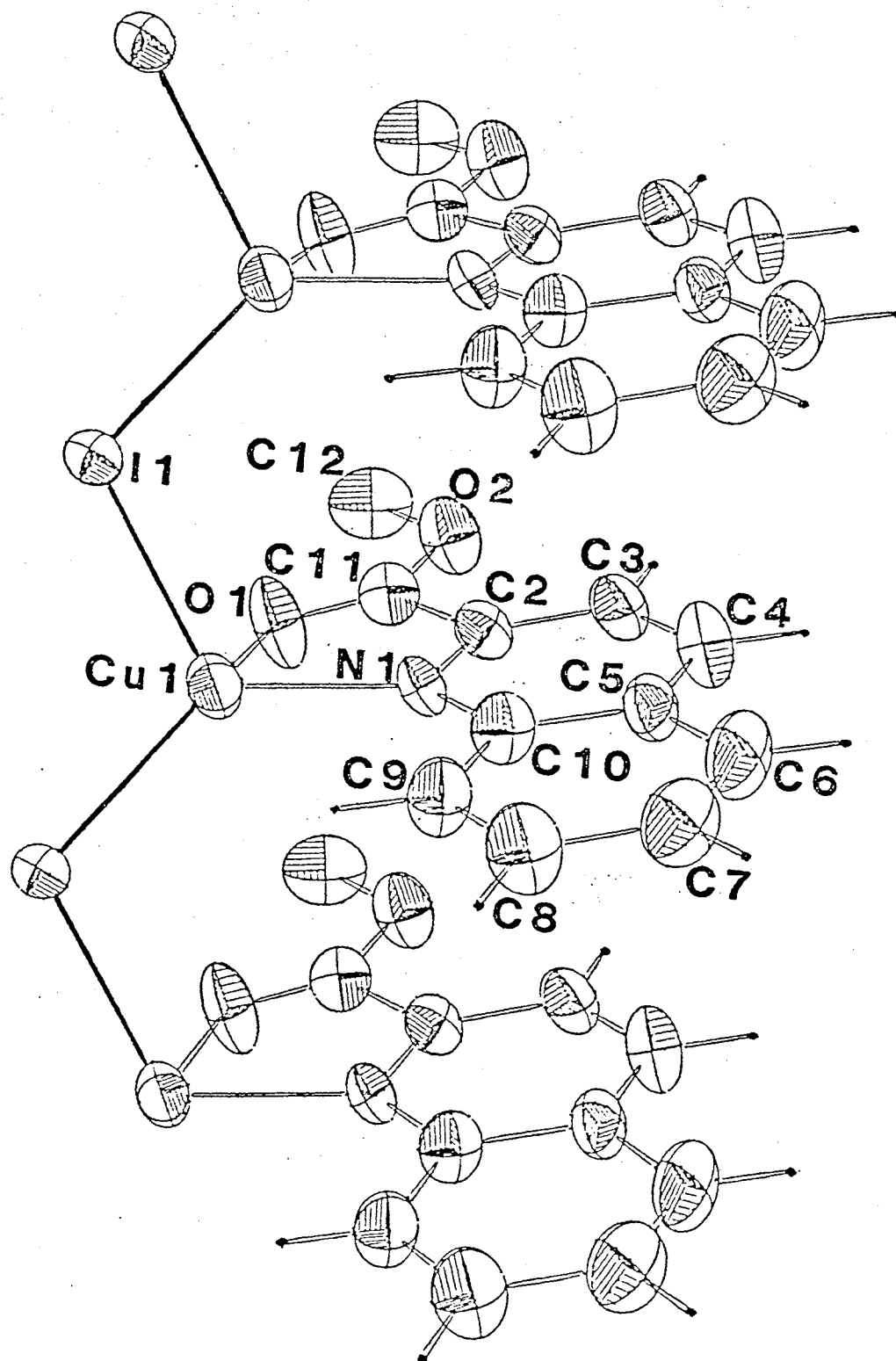


Figure 1. Projection View of (I)

angle is $107.84(9)^\circ$ and the angle at iodine, $107.84(8)^\circ$ (Table IV). Copper atoms along the chain are separated by the c cell edge, 4.108 Å. The single strand or split stair polymeric combination of copper and iodine has been previously observed for $(\text{CuIacridine})_x$ and for $(\text{CuIcollidine})_x$, both of which show three coordinate copper, presumably due to the steric demands of pyridine with methyl groups at both ortho positions (12) (17). The steric demands of diortho substituents have been observed to lead to three coordinate copper in the $(\text{CuI}(2,6\text{-dimethylpyridine}))_x$ rhombohedron as well (12).

Structure (I) displays similarities to $(\text{CuIacridine})_x$ and $(\text{CuIcollidine})_x$ despite the differences in coordination number for copper. These similarities include: Cu - I distances; 2.514(2), 2.549(2), and 2.543(9) Å; Cu - N distances; 2.01(1), 1.990(7), and 2.01(2) Å; I - Cu - I angles; $107.84(9)^\circ$, $107.70(5)^\circ$, and $109.7(1)^\circ$; and Cu - I - Cu angles; $107.84(8)^\circ$, $107.70(5)^\circ$, and $109.7(1)^\circ$ respectively.

CuI distances for these three single strand polymers average 2.535 Å, shorter than those normally observed in CuIligand cubes and polymeric pleated sheets where each Cu atom has three iodine neighbors (av. 2.698(3) and 2.706(3) Å respectively) but longer than those observed (2.388(2) Å) in CuI_2^- where copper has two neighbors (both iodine) and presumably exhibits multiple bond character (28) (53) (54). (Tables of bond distances and angles, anisotropic thermal parameters, positional parameters, and crystal data

for all structures appear at the end of this chapter.)

(CuIisopropylquinaldato)₂ (II) (Figure 2.) and (CuI(n-butylquinaldato))₂ (III) (Figure 3.) crystallize with planar rhombohedra of alternating copper and iodine atoms (Cu - I 2.585(3) (II), 2.57(8) Å (III); I - Cu - I' 120.9(2) (II), 121.0(1)° (III); Cu - I - Cu' 59.1(1) (II), 58.9(1)° (III)) (Tables VIII and XII) to which are bound two molecules of alkylquinaldato via coordination of the carbonyl oxygen (Cu - O 2.33(1) (II), 2.26(6) Å (III)) and nitrogen atoms (Cu - N 2.06(1) (II), 2.04(2) Å (III)) of a single organic molecule to each copper atom. The planes of the quinoline rings (std. dev. 0.02 (II), 0.02 (III)) are nearly perpendicular to the planes of the Cu₂I₂ rhombs, subtending angles of 85.8 (II) and 88.6° (III) to those planes. The carbonyl groups (C,C,O,O std. dev. 0.05 (II), 0.005 (III)) are close to coplanar with the quinoline rings (interplanar angle 7.38 (II), 1.26° (III) and thus resonance delocalization of electron density over the ten membered ring and the conjugated carbonyl group is possible. Similarly in (I), the atoms of the quinoline ring (std. dev. 0.01) subtend to an angle of 4.96° with the plane of the atoms (C,C,O,O) of the ester group (std. dev. 0.006). Carbonyl bonds are 1.18(2), 1.21(2) (II) and 1.15(4) Å (III) as compared to the normal C=O bond lengths of 1.23(1) Å for esters indicating little delocalization of the normal electron density from this carbonyl bond (55). Thus structures (I), (II), and (III) all show coordination of the carbonyl oxygen to copper

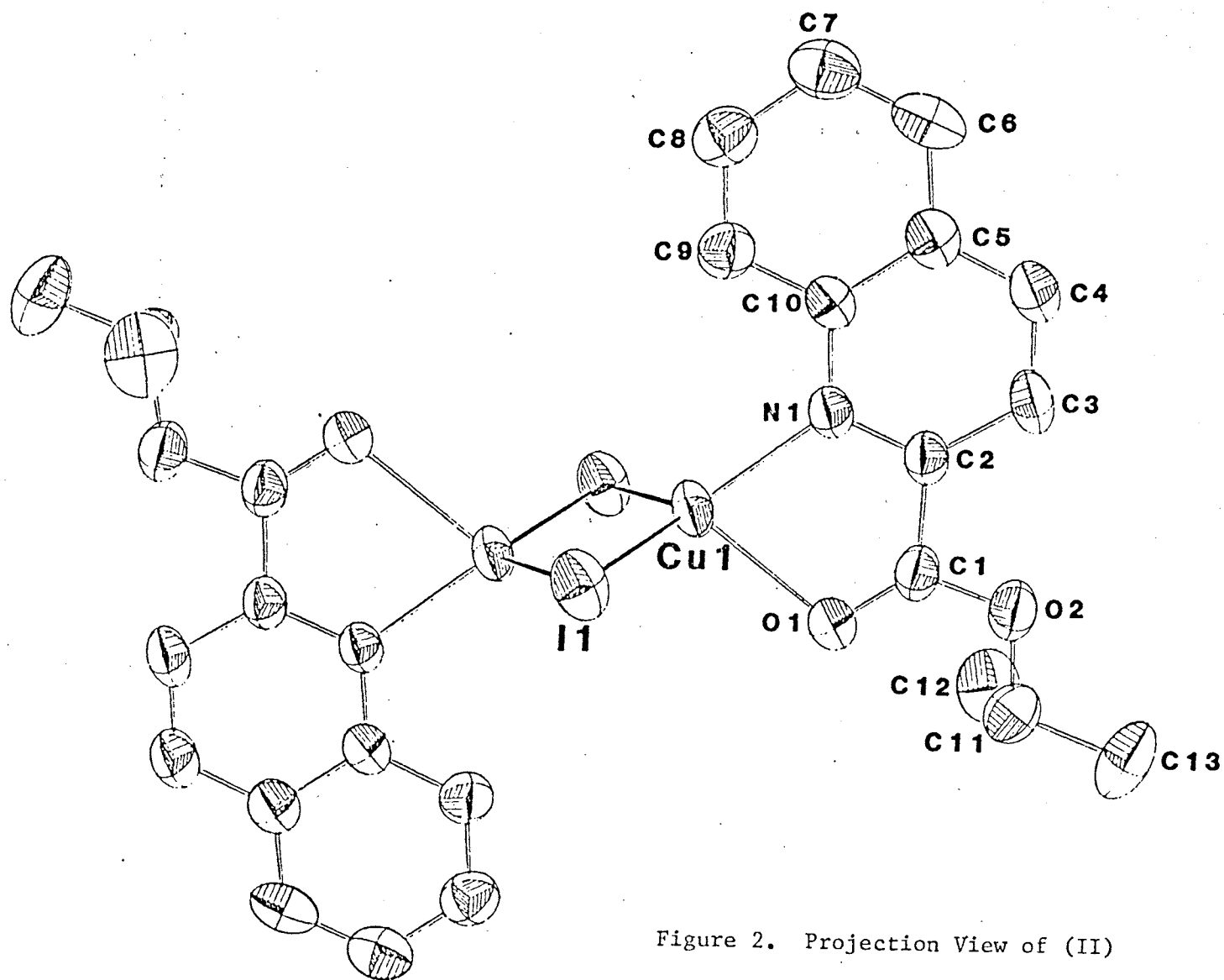


Figure 2. Projection View of (II)

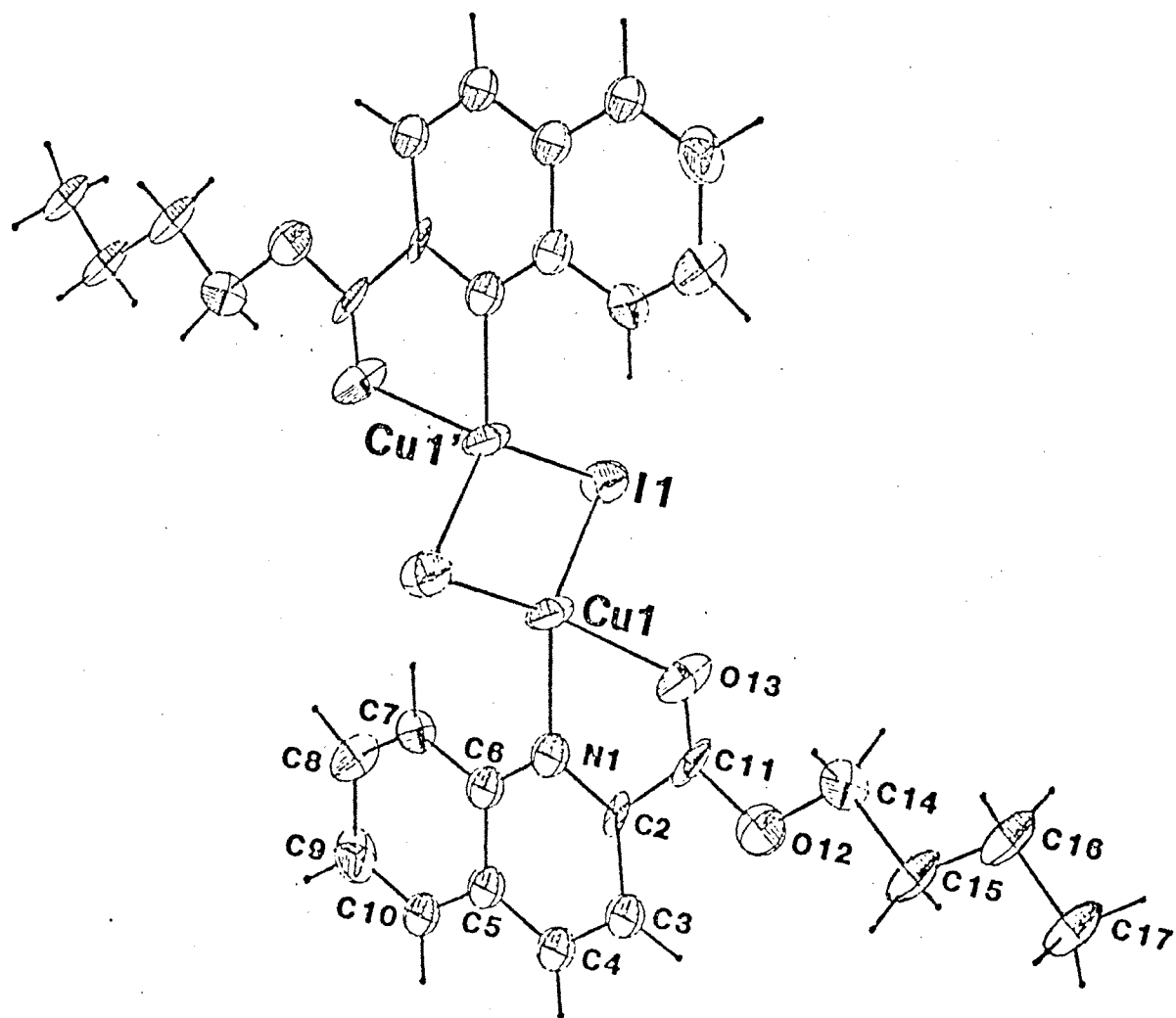


Figure 3. Projection View of (III)

without any significant change in the electron density of the carbonyl bond. This view is reinforced by the observation of the C=O stretching band in complexed and uncomplexed methyl quinaldate at similar positions 1718 (I) and 1715 cm^{-1} respectively.

Nevertheless, the Cu - O distance represents an interactive distance. similar Cu - carbonyl distances in the complex of Bis(10-methylisoalloxazine) with copper(I) are 2.27(2) and 2.21(2) Å (56). In this complex a similar (-Cu-N=C-C=O-) five membered ring is observed with both N and carbonyl oxygen involvement with Cu(I). (Copper - nitrogen distances are 1.94(2) and 1.92(2) Å). The structure of cuprous acetate shows copper atoms bridged in pairs by acetate groups (Cu - O, 1.89(2), 1.90(2) Å) but with a Cu - O distance of 2.31(2) Å to neighboring acetate oxygen atom (22).

Copper iodide rhombic structures such as (II) and (III) are common in the literature of CuI nitrogen donor ligand structures. Cu - Cu distances observed range from 2.535(9) to 3.576(2) Å. Thus these structures display flexible Cu - I - Cu angles and the ability to change the proximity of copper atoms in response to structural parameters which are not entirely obvious. It appears that ligands of smaller bulk permit opening of the I - Cu - I angle and closer Cu - Cu involvement. Thus 2,9-dimethylphenanthroline (Cu - Cu 3.083(3); pyridine (Cu - Cu 2.699(5) Å, in complexes of type Cu:ligand, 1:2 and 2,6-dimethylpyridine (Cu:ligand, 1:1

with tricoordinate copper) (Cu - Cu 2.586(4) Å) form a series of decreasing ligand bulk at copper and the Cu - Cu distances decrease with decreasing bulk. Less obvious is the reason for the copper - copper separation of 3.364(5) Å observed in $\text{Cu}_2\text{I}_2\text{quinoline}_4$ but 2.866(3) Å observed in $\text{Cu}_2\text{I}_2\text{quinoline}_4\cdot\text{quinoline}$ and 3.137(2) Å in $\text{Cu}_2\text{I}_2\text{quinoline}_4\cdot\text{CH}_3\text{CN}$. The inclusion of a molecule of quinoline or acetonitrile in the unit cell causes changes in the Cu - Cu proximity. Structures (II) and (III) (Cu - Cu 2.544(2) Å (II) and 2.53(1) Å (III) display close copper - copper distances compared to others observed in Cu_2I_2 rhombohedra.

The structures of CuI and quinaldic esters in which substitution is at the ortho positions of the pyridine ring provides a second ligation site and limits further Cu binding to a maximum of two iodine atoms. Single strand polymeric and rhombic forms are observed but chair, pleated sheets, or cube forms are not. The complexes of CuI and quinaldate esters (I), (II), and (III) display no emission upon excitation with a hand held black light (wavelength 366 nm).

The three structural features identified with components of emission in copper(I) iodide complexes are:

- 1) Copper binding to aromatic ring systems (MLCT or $3d^{10} \rightarrow 3d^9\pi^*$)
- 2) Cu - Cu distances of less than 2.7 Å (MC or $3d^{10} \rightarrow 3d^94s^1$)
- 3) interligand excitation ($\pi \rightarrow \pi^*$).

The luminescence attributed to 3) occurs when the aromatic ligands are packed in parallel planes and separated by 3.325(12), 3.279(19) Å, a separation which is apparently decreased on cooling to an interactive one, resulting in the emission spectrum of the ligand alone, slightly shifted in wavelength from that arising from the noncomplexed ligand. Complex (I), with a metal - metal separation of 4.108(2) Å is not a candidate for emission due to the second of these phenomena but might be expected to demonstrate visible evidence of 1) and 3) types of excitation. Complexes (II) and (III), without suitable packing of aromatic ligands might be expected to display evidence of excitation of types 1) and 2). However the energy levels of the aromatic rings of the quinoline molecule would be expected to be changed by the effects of the electron withdrawing ester groups and thus the energy levels of the aromatic ring are somehow altered to make this excitation of greater energy or to make other, radiationless, decay mechanisms more efficient. Thus inter-ligand transitions and metal to ligand charge transfer mechanisms are somehow unfavorable or do not result in visible emission. The lack of evidence of metal to metal interactions is apparently due to alteration of the metal energy levels by the coordination to oxygen. This view is supported by the observation of emission from nicotinic esters.

Three nicotinate esters were used as ligands with CuI to form a second class of compounds. All three of the

resulting complexes emit when excited at 366 nm.

Copper(I) iodide methyl nicotinate (IV) (Figure 4.) crystallizes as a polymeric pleated sheet of edge sharing Cu_2I_2 rhombohedra with each copper atom bound to three iodine atoms and to the nitrogen atom of the pyridine molecule substituted at the meta position with a methyl carboxyl group. The oxygen atoms of the carboxyl group do not participate in bonding unlike the carbonyl oxygen atom of crystalline $(\text{CuImethylquinolinate})_x$ in which both nitrogen and carbonyl oxygen atoms ligate to a single copper atom. Possibilities for nitrogen and oxygen complexation to two different copper atoms were not exploited in the structure observed. Cu - I distances, 2.67 Å (av) and the Cu - N distance of 2.07(1) Å are normal. Cu - Cu distances across rhombohedra are 2.872(3) and 2.800(2) Å (Table XVII), relatively similar values, greater than those observed in $(\text{CuI}(2\text{-picoline}))_x$ but less than those observed in $(\text{CuI}(\text{CH}_3\text{CN}))_x$ (27).

A Cu - Cu separation of 2.8 Å or greater is considered to be too large for metal to metal interactions. In $(\text{CuImethylnicotinate})_x$ (IV) the Cu - Cu separation of 2.800(2) Å is an indication that any luminescence observed is due to MLCT only. The emission observed for this complex was pale green and of low intensity but at -196°C the intensity greatly increased although there was no noticeable change in the color. The parallel arrangement of the ligands is suggestive of possible ligand - ligand interactions

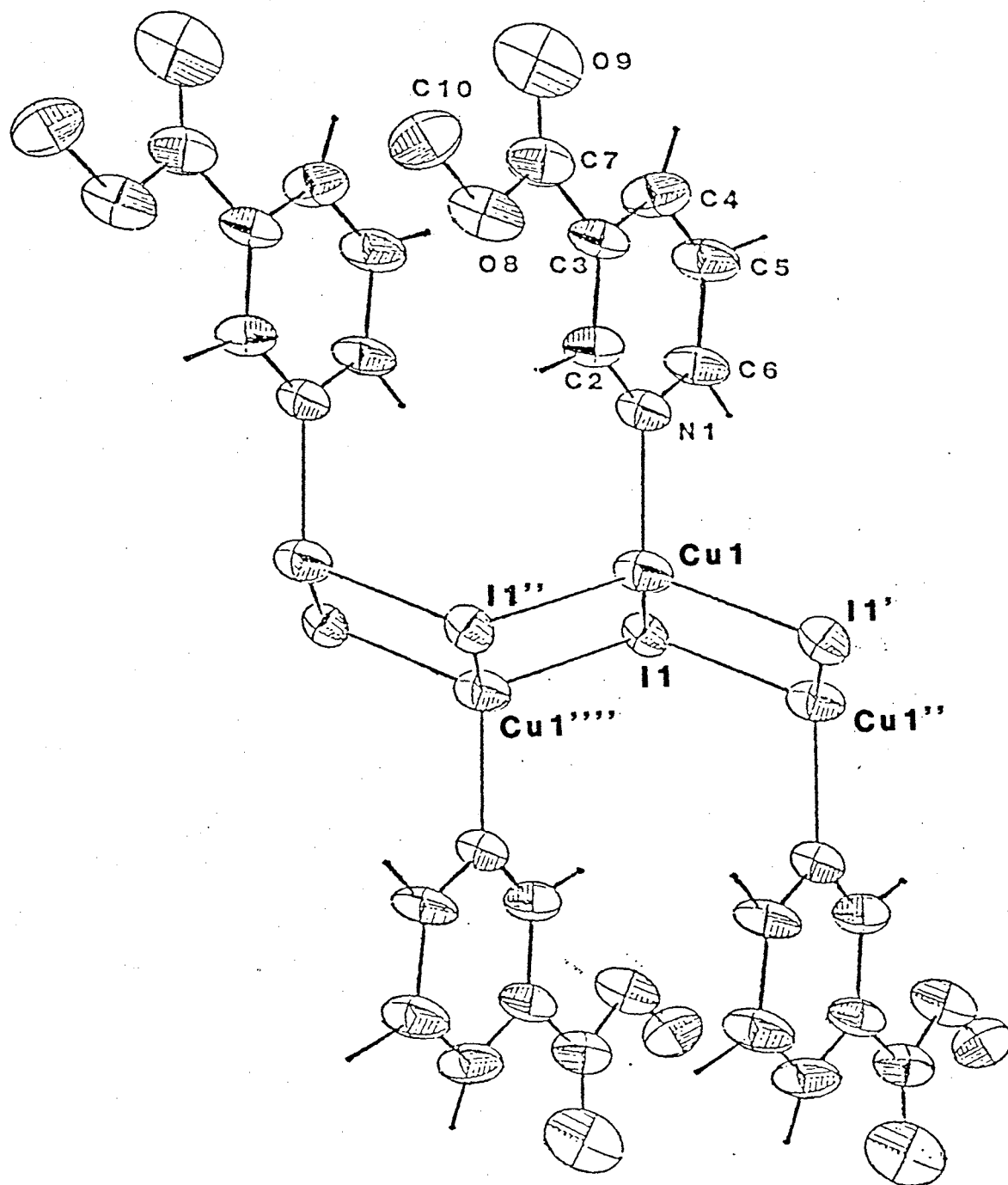


Figure 4. Projection View of (IV)

especially at low temperature ($\pi \rightarrow \pi^*$). The luminescent and structural properties of $(\text{CuImethylnicotinate})_x$ compare favorably to those of $(\text{CuI}(2,4\text{-lutidine}))_x$ which has a Cu - Cu separation of 2.734 Å and emit white-blue at room temperature and blue at -196°C ; and $(\text{CuI}(2\text{-picoline}))_x$ which has a Cu - Cu separation of 2.708(5) Å and emits blue-white at room temperature and blue at -196°C (27).

$\text{Cu}_4\text{I}_4(\text{isopropyl nicotinate})_4$ (V) (Figure 5.) and $\text{Cu}_4\text{I}_4(\text{n-butyl nicotinate})_4$ (VI) (Figure 6.) both crystallize as cubes with alternating copper and iodine atoms. The Cu - I separations of 2.70(av) (V) and 2.68(av) (VI) Å are, as in (IV), normal as are the Cu - N distances of 2.05(av) (V) and 2.04(av) (VI) Å (Tables XXI and XXV). The oxygen atoms do not coordinate with the copper atoms in these two nicotinate complexes. The copper - copper separations for (V) are 2.66(av) and for (VI), 2.67(av) Å. These distances are much shorter than in (V) showing the presence of strong interactions between the copper atoms. Luminescence in these two complexes is expected to arise from both MLCT and MC transitions. Preliminary results on a modification of (V) in which crystals were formed in excess ligand (isopropyl nicotinate) show a pleated sheet similar to (IV) with copper - copper separations of 2.85(av) Å.

Under a black light (366 nm), the emission of (V) was colored brown-green but changed to blue at -196°C , while the modification of (V) emitted blue both at room temperature and at that of liquid nitrogen. The intensity of emission

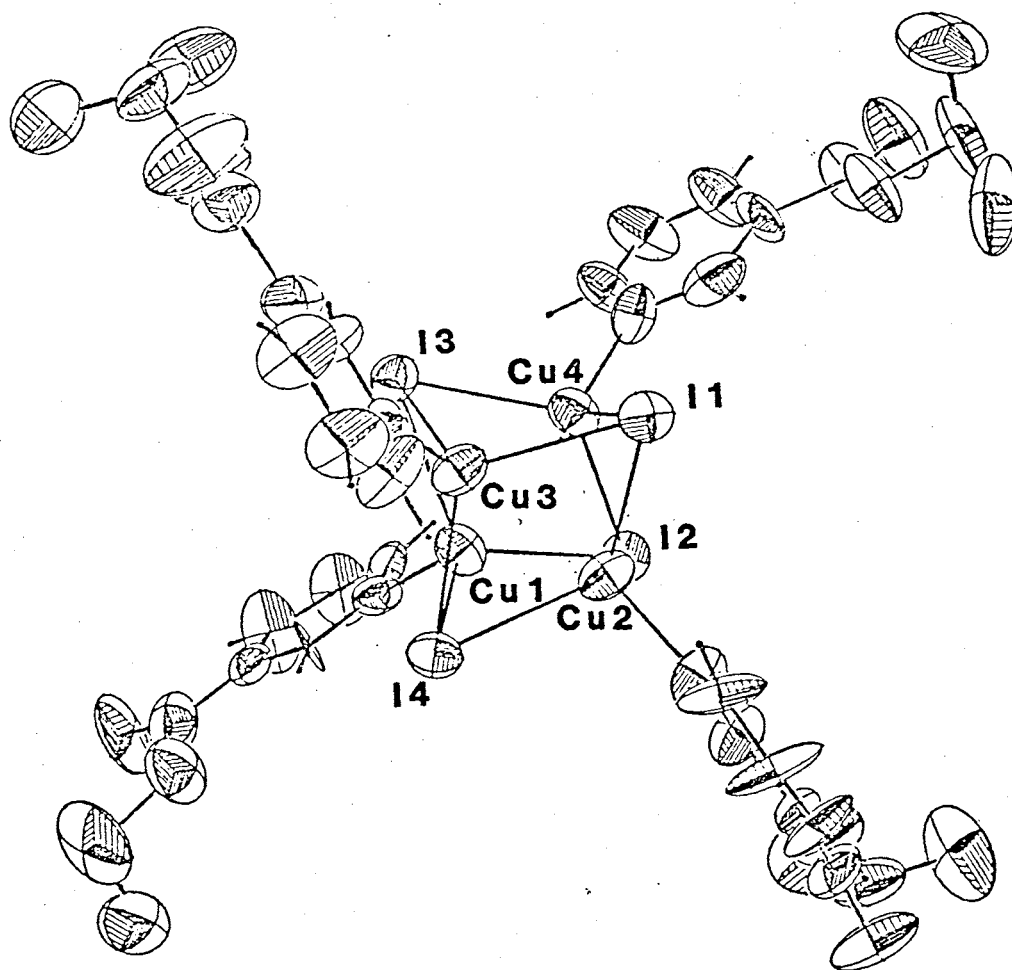


Figure 5. Projection View of (V)

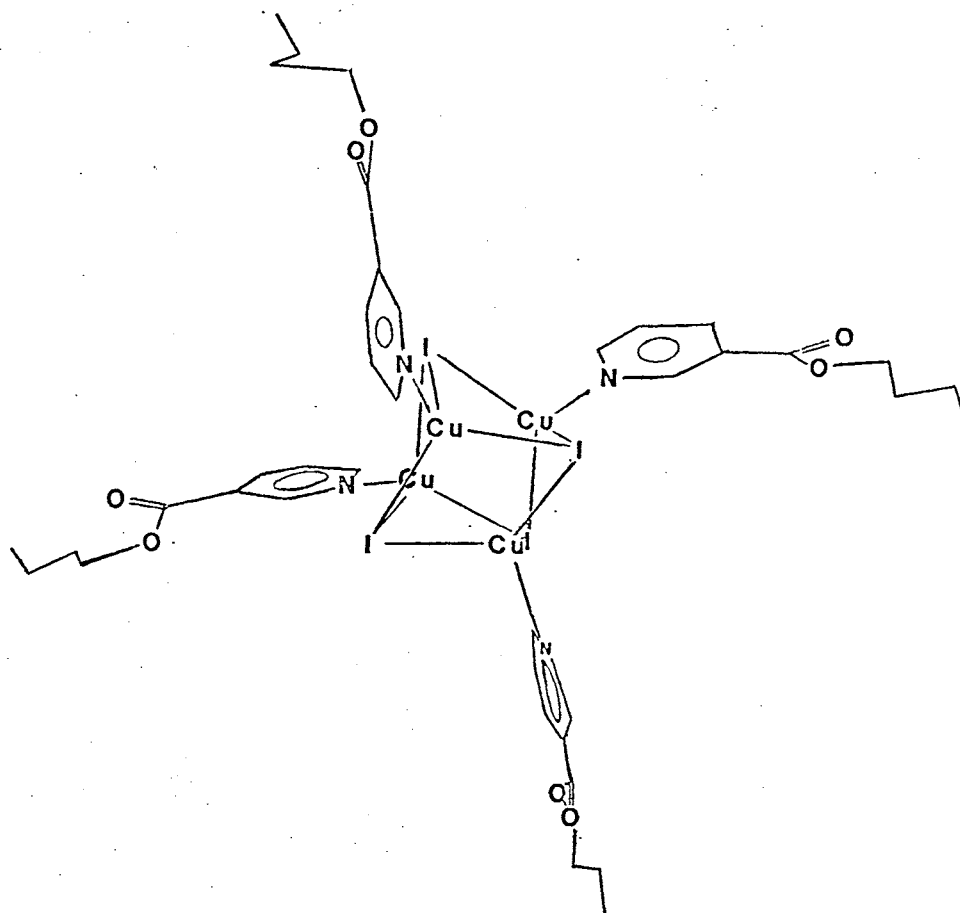


Figure 6. Schematic Diagram of (VI)

from this modification did not appear to change as in (V). The emission from (VI) showed no significant change in color with change in temperature, but like (IV) and (V) the intensity did change. The emission and structural properties of (VI) compare well with those of a previous study in which Cu_2I_2 (p-chloroaniline)(acetonitrile) and Cu_4I_4 (p-toluidine) $_2$ (acetonitrile) $_2$, both cubane type structures, were found to emit at 630 nm and 584 nm respectively under ultraviolet excitation of 370 nm and 365 nm respectively with no significant change in emitted wavelength at low temperature (15K) but a dramatic change in the intensity (27). The copper - copper separations averaged 2.68 Å for both complexes and the broad band emission spectrum for each showed only one significant broad and featureless band so both a MC (close copper - copper distances) and MLCT transition were assigned to the maxima.

The colors that are visually observed in any emission spectrum represent an average of the various maxima which are present. Copper(I) iodide isopropyl nicotinate appears to be anomalous in that its cubane modification displays a temperature dependent luminescence while its pleated sheet modification does not. From the visual observation of colors alone it is not possible to tell if this shift in emitted wavelength is due to a change in the relative population of excited states as in the copper(I) iodide quinoline case which has been previously reported. A detailed study involving broad band emission spectra for all of the

nicotinic ester complexes is necessary in order to get a clearer picture of the transitions involved which are responsible for the observed luminescence; and a correlation between structure and emission can be made.

$\text{CuI}(\text{pyrazinamide})_x$ (VII) (Figure 7.) is almost identical to (V) structurally; it crystallizes in a polymeric pleated sheet with Cu - I distances of 2.63(av) Å, Cu - N distances of 2.065(av) Å and Cu - Cu distances of 2.84 Å (Table XXIX). But the similarity ends here. Pyrazinamide is a derivative of the heterocycle pyrazine which contains two nitrogen atoms para to each other in the six membered ring. The amide group is ortho to one of the nitrogens (N1), and meta to the other (N4). Surprisingly, this Lewis base coordinated to copper at the nitrogen in the "four" position rather than the nitrogen in the "one" position and consequently the oxygen did not coordinate with copper at all. Since the complex is scarlet red in color, and was nonluminescent, it was expected from experience with the quinaldates that this complex would coordinate through both oxygen and the nitrogen at the "one" position. The red color that is observed arises from absorption of radiation in the visible range which would be brought about by MLCT transition. As in the quinaldates, the energy of the excited state is dissipated by some mechanism other than luminescence. An intermediate product has been observed in the preparation of this complex which is yellow and emits intense yellow under a black light. Crystals which were

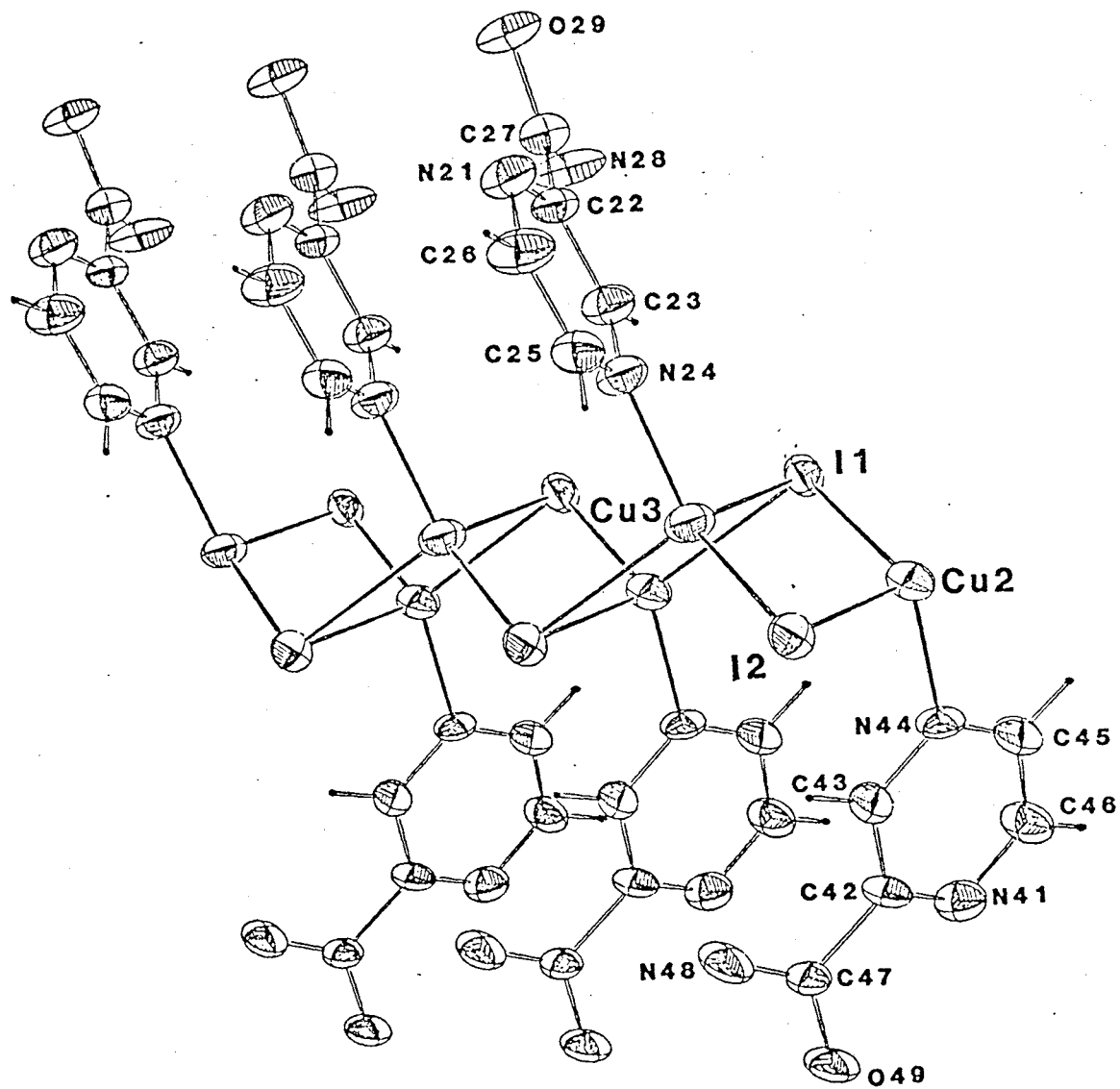


Figure 7. Projection View of (VII)

suitable for mounting were produced but they proved to be unstable and within a few minutes after being removed from the mother liquor, changed into the red complex (acetonitrile was the solvent). These crystals are possibly of mixed pyrazinamide and acetonitrile and are structurally of cubane format. If this is the case, then copper - copper interactions are expected as well as MLCT between the copper and the acetonitrile, these two only contributing to luminescence.

Copper iodide quinaldic acid (VIII) (Figure 8.), crystallized from acetonitrile, does not form a complex in the usual sense but instead forms an inclusion compound. Copper, in this complex, is of a mixed oxidation state, (+1) and (+2); Cu1 is coordinated to three iodine atoms, and Cu2 is coordinated to four iodine atoms, forming a polymeric lattice $(\text{Cu}_2\text{I}_3)_x$. This copper iodide lattice is included into a quinaldic acid lattice which is held together by hydrogen bonding and London dispersion forces (Figure 9.), three quinaldic acid molecules per (Cu_2I_3) unit. A molecule of water is also included into this quinaldic acid system. Two of the quinaldic acid molecules are parallel to each other and a third is perpendicular to the two parallel molecules, with the carboxyl group of this quinaldic acid hydrogen bonded to the carboxyl groups of the other two molecules. The two inner quinaldic acid molecules are held in a parallel orientation by London dispersion forces.

Complex (VIII) is purple-brown in color as is the

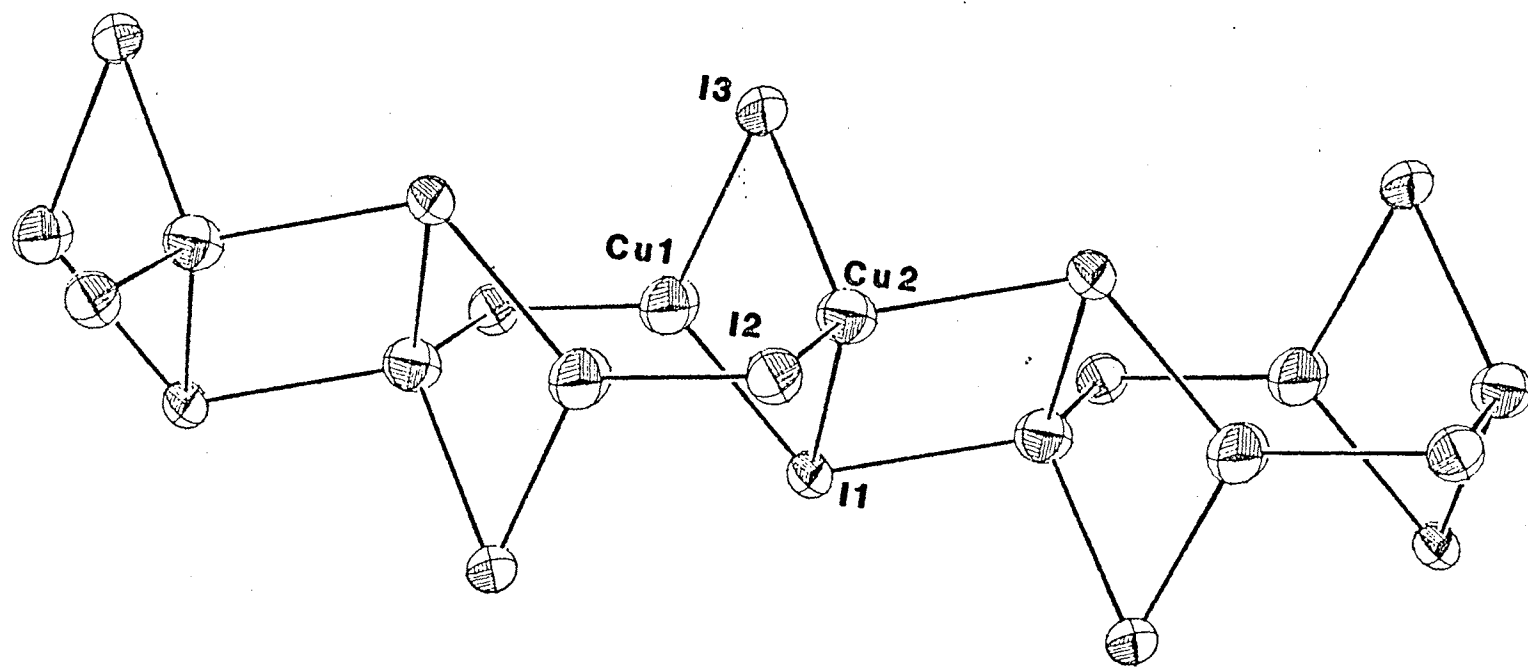


Figure 8. Projection View of (VIII). $(\text{Cu}_2\text{I}_3)_x$ Lattice.

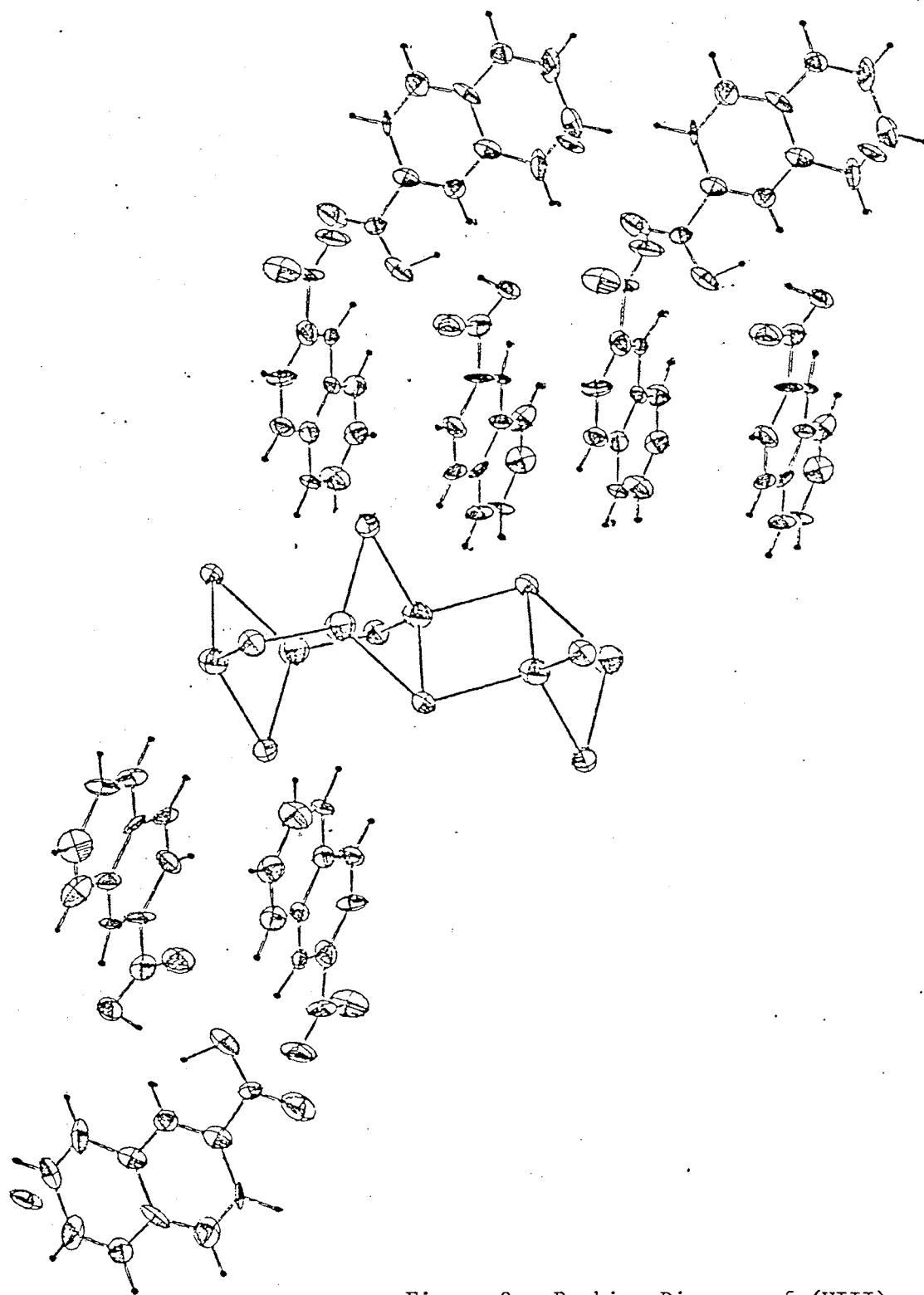


Figure 9. Packing Diagram of (VIII)

methyl ester complex, but unlike it, there is no coordination between the copper atoms and the quinaldic acid. The observation made by Goher and Hafez (34) that the 1:1:1 complex of copper, iodine and quinaldic acid displays coordination through the carbonyl oxygen and that the 1:1:0.5 complex displayed a different type of linkage cannot be confirmed or disputed since our complex had a stoichiometry which was different from that previously reported (1:1.5:1.5).

The copper iodide complexes which have been synthesized display a variety of properties and structural motifs. The structures, for the most part, have been similar to CuI patterns observed in the past, mainly rhombs, cubes, pleated sheets, and polymeric chains. That of quinaldic acid however, is previously unobserved. The emission properties of these complexes have not, in general, followed patterns observed before; the isopropyl nicotinate complex, for example, has displayed thermochromic emission, yet its cubane structure suggests that it should not be. A detailed study of the luminescence of all of the nicotinate complexes is needed to fully understand these properties, and a reliable correlation between their structures and luminescence, is not possible without measurement of the emission spectra to observe the numbers of components of these spectra and their maximum wavelengths.

Previous studies of copper iodide complexes have mostly involved donor ligands where there has been only one nitro-

gen in a heterocyclic ring and where the only heteroatom has been nitrogen. All of the ligands in this study have contained oxygen and one of these also contained a second nitrogen in the heterocyclic ring (pyrazinamide). This ligand was unusual in that, although the structural motif was of one of those observed before (pleated sheet), it did not display any of the luminescence seen in the nicotines and the other pyridine type derivatives. The fact that this complex coordinated through a nitrogen atom alone and not through both nitrogen and oxygen as in the quinaldines was also unexpected.

Structural work on the quinaldines has led to the finding that both nitrogen and oxygen coordinate to a copper atom in the solid copper(I) iodide complex. Using the results from infrared studies alone, it was predicted that the carbonyl oxygen did not coordinate to the copper (34). The complexes are totally non emitting. Their lack of emission may be due to a lowering of the π^* energy levels due to the influence of the electron withdrawing ester group situated ortho to the coordinated nitrogen atom or to some alteration of the copper energy levels due to oxygen coordination. Further work will focus on this phenomenon.

Copper(+1) is normally unstable and work in the past has been hindered by this fact. All of the compounds in this study have been remarkably stable, making X-ray analyses possible. It is reasonable to anticipate that the effect of the carbonyl group as a deactivator of the aroma-

tic ring, can be separated from its effect on copper when it is coordinating, by structural investigation of pyridine rings substituted in the para position by carbonyl substituents and by the investigation of pyridine substituted acetate esters in which a CH_2 group separates the potentially binding carbonyl from interaction with the heterocycle. With this recent understanding of the effect that oxygen has on some Lewis base donor ligands, more detailed studies which will correlate the structure of copper(I) iodide with their luminescent properties can proceed.

Table I.

CRYSTAL DATA FOR Copper Iodide Methyl Quinaldate(I)

Formula	$\text{CuIC}_{11}\text{H}_9\text{NO}_2$
M.W.	377.6
<u>a</u>	9.810(5) Å
<u>b</u>	15.486(14)
<u>c</u>	4.108(2)
α	81.32(4)
β	87.74(4)
γ	108.18(5)
V	583.7(7) Å ³
F(000)	360
$\mu_{\text{MoK}\alpha}$	44.76 cm ⁻¹
$\lambda_{\text{MoK}\alpha}$	0.71069 Å
D _{calc}	2.148 g cm ⁻³
Z	2
Meas refl	5611
Obs refl	2044
R	6.8%
R _w	9.3%
Space Group	P $\bar{1}$
Octants meas	<u>+</u> h, <u>k</u> , <u>+</u> l

TABLE II

POSITIONAL PARAMETERS FOR Copper Iodide Methyl Quinaldate(I)

ATOM	X(sig(X))	Y(sig(Y))	Z(sig(Z))
I1	1.2004(2)	0.4268(2)	0.5917(1)
Cu1	0.9288(4)	0.3972(3)	0.5095(2)
O13	0.782(2)	0.354(2)	0.605(1)
O12	0.648(2)	0.189(2)	0.641(1)
N1	0.857(2)	0.211(2)	0.482(1)
C2	0.773(3)	0.158(3)	0.528(2)
C3	0.716(3)	0.028(3)	0.517(1)
C4	0.762(3)	-0.042(3)	0.458(2)
C5	0.850(3)	0.011(2)	0.405(2)
C6	0.899(2)	0.145(2)	0.420(2)
C7	0.989(3)	0.195(3)	0.370(2)
C8	1.028(4)	0.135(3)	0.304(2)
C9	0.983(4)	0.000(3)	0.291(2)
C10	0.893(3)	-0.053(3)	0.341(2)
C11	0.735(3)	0.250(3)	0.597(2)
C14	0.604(3)	0.272(3)	0.710(2)
C15	0.525(3)	0.186(3)	0.761(2)
C16	0.470(3)	0.261(4)	0.831(2)
C17	0.411(4)	0.178(4)	0.887(2)
H3	-1.0548	0.4031	0.3036
H4	-1.2715	0.2842	0.5066
H6	-1.3920	0.1280	0.8396

TABLE II (Continued)

H7	-1.3745	-0.0047	1.1738
H8	-1.1448	-0.0088	1.3444
H9	-0.9342	0.1101	1.1200

TABLE III
ANISOTROPIC THERMAL PARAMETERS FOR
Copper Iodide Methyl Quinaldate(I)

ATOM	U11	U22	U33	U12	U13	U23
I1	348(9)	626(6)	309(4)	202(4)	-46(3)	-39(3)
Cu1	348(9)	516(11)	430(8)	162(8)	-74(6)	-11(7)
O1	36(5)	41(5)	89(7)	3(4)	-24(4)	11(5)
O2	46(5)	41(5)	68(6)	10(4)	-12(4)	6(4)
N1	28(5)	38(6)	37(5)	9(4)	-14(4)	-8(4)
C2	32(6)	32(7)	41(6)	1(5)	-10(4)	-12(5)
C3	44(7)	49(8)	46(7)	20(6)	-13(5)	-2(6)
C4	37(7)	44(9)	78(10)	14(6)	-19(7)	-10(7)
C5	30(6)	48(8)	49(7)	11(5)	-11(5)	-18(6)
C6	27(7)	59(10)	78(10)	-3(6)	0(6)	-12(8)
C7	40(8)	48(9)	70(10)	-3(7)	3(7)	-9(8)
C8	44(8)	42(8)	73(10)	3(6)	-2(7)	14(7)
C9	37(7)	48(8)	55(8)	13(6)	5(6)	17(6)
C10	33(6)	29(7)	52(7)	1(5)	0(5)	0(5)
C11	42(7)	27(6)	49(7)	10(5)	-6(5)	-12(5)
C12	77(11)	37(8)	62(9)	3(8)	4(8)	5(7)

Anisotropic thermal parameters in the form:

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

TABLE IV
BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
Copper Iodide Methyl Quinaldate(I)

Cu1 - I1	2.568(2)	Cu1 - I1 - Cu1'	107.84(8)
Cu1 - I1'	2.514(2)	I1 - Cu1 - I1'	107.84(9)
I1 - Cu1'	2.514(2)	I1 - Cu1 - O1	94.9(3)
Cu1 - O1	2.40(1)	I1' - Cu1 - O1	121.9(3)
Cu1 - N1	2.02(1)	I1 - Cu1 - N1	115.9(3)
N1 - C2	1.32(2)	I1' - Cu1 - N1	131.5(3)
C2 - C3	1.39(2)	N1 - Cu1 - O1	74.9(4)
C3 - C4	1.36(2)	Cu1 - N1 - C2	119.6(7)
C4 - C5	1.40(2)	Cu1 - N1 - C10	121.5(9)
C5 - C6	1.40(2)	N1 - C2 - C3	124(1)
C5 - C10	1.43(2)	C2 - C3 - C4	119(1)
C6 - C7	1.36(2)	C3 - C4 - C5	119(1)
C7 - C8	1.42(2)	C4 - C5 - C6	112(1)
C8 - C9	1.37(2)	C4 - C5 - C10	143.0(9)
C9 - C10	1.49(2)	C5 - C6 - C7	121(1)
C10 - N1	1.37(2)	C6 - C7 - C8	121(1)
C2 - C11	1.53(2)	C7 - C8 - C9	120(1)
C11 - O1	1.18(2)	C8 - C9 - C10	121(1)
C11 - O2	1.33(2)	C9 - C10 - C5	119(1)
O2 - C12	1.47(2)	C9 - C10 - N1	120(1)
		C10 - C5 - C6	119(1)
		C10 - N1 - C2	118(1)
		N1 - C10 - C5	121(1)

TABLE IV (Continued)

N1 - C2 - C11	113(1)
C2 - C11 - O2	111(1)
O1 - C11 - O2	126(1)
C11 - C2 - C3	123(1)
C11 - O2 - C12	114(1)
C11 - O1 - Cu1	106.0(8)

Table V

CRYSTAL DATA FOR Copper Iodide Isopropyl
Quinaldate(II)

Formula	$\text{CuIC}_{13}\text{H}_{13}\text{NO}_2$
M.W.	405.7
<u>a</u>	9.053(4) Å
<u>b</u>	22.554(10)
<u>c</u>	10.496(3)
α	52.37(3)
β	115.67(3)
γ	153.48(2)
V	717.9(5) Å ³
F(000)	392
$\mu_{\text{MoK}\alpha}$	36.46 cm ⁻¹
$\lambda_{\text{MoK}\alpha}$	0.71069 Å
D _{calc}	1.876 g cm ⁻³
Z	2
Meas refl	2928
Obs refl	2279
R	4.7%
R _w	6.3%
Space Group	P $\bar{1}$
Octants meas	<u>+</u> h, <u>k</u> , <u>+</u> l

TABLE VI
POSITIONAL PARAMETERS FOR Copper Iodide Isopropyl
Quinaldate(II)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.5525(1)	0.2228(1)	-0.0150(6)
Cu1	0.1010(2)	0.0660(1)	-0.1560(1)
O1	0.211(1)	0.236(1)	-0.3840(6)
O2	0.435(1)	0.391(1)	-0.6682(6)
N1	0.292(1)	0.140(1)	-0.3632(7)
C1	0.326(2)	0.285(1)	-0.5134(8)
C2	0.372(2)	0.237(1)	-0.5154(8)
C3	0.495(2)	0.293(1)	-0.670(1)
C4	0.530(2)	0.244(1)	-0.663(1)
C5	0.446(2)	0.140(1)	-0.504(1)
C6	0.483(2)	0.086(1)	-0.487(1)
C7	0.419(2)	-0.007(1)	-0.328(1)
C8	0.308(2)	-0.051(1)	-0.183(1)
C9	0.259(2)	-0.007(1)	-0.328(1)
C10	0.331(2)	0.092(1)	-0.354(1)
C11	0.448(2)	0.606(1)	-0.682(1)
C12	0.795(2)	0.606(1)	-0.666(1)
C13	0.410(3)	0.514(1)	-0.859(1)

TABLE VII
ANISOTROPIC THERMAL PARAMETERS FOR
Copper Iodide Isopropyl Quinaldate(II)

ATOM	U11	U22	U33	U12	U13	U23
I1	433(3)	533(3)	504(3)	392(3)	-159(2)	-335(3)
Cu1	550(5)	571(6)	293(4)	499(5)	-113(4)	-218(4)
O1	76(4)	73(3)	38(3)	69(3)	-11(2)	-22(2)
O2	66(3)	57(3)	37(3)	56(3)	-15(2)	-22(2)
N1	38(3)	42(3)	33(3)	35(3)	-12(2)	-22(2)
C1	41(3)	45(4)	32(3)	38(3)	-13(3)	-19(3)
C2	39(3)	43(3)	31(3)	36(3)	-13(3)	-21(3)
C3	47(4)	52(4)	31(4)	42(4)	-9(3)	-21(3)
C4	56(4)	58(4)	40(4)	50(4)	-13(4)	-26(4)
C5	39(3)	48(4)	47(4)	37(3)	-17(3)	-30(3)
C6	46(4)	60(4)	82(6)	44(4)	-20(4)	-47(4)
C7	49(4)	57(5)	76(6)	45(4)	-14(4)	-36(4)
C8	45(4)	51(4)	63(5)	42(4)	-18(4)	-31(4)
C9	45(4)	50(4)	51(4)	42(4)	-17(3)	-28(4)
C10	32(3)	39(3)	40(4)	29(3)	-13(3)	-26(3)
C11	55(4)	48(4)	54(4)	45(4)	-18(4)	-26(4)
C12	61(5)	63(5)	74(6)	51(5)	-27(4)	-46(5)
C13	81(6)	71(6)	56(5)	69(6)	-29(5)	-29(5)

Anisotropic thermal parameters in the form:

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

TABLE VII (Continued)

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

TABLE VIII
BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
Copper Iodide Isopropyl Quinaldate(II)

Cu1 - I1	2.585(3)	I1' - Cu1 - I1	120.9(2)
Cu1 - Cu1'	2.544(2)	I1 - Cu1 - O1	101.4(2)
Cu1 - N1	2.04(1)	I1 - Cu1 - N1	115.5(2)
Cu1 - O1	2.33(1)	O1 - Cu1 - N1	76.6(6)
N1 - C2	1.33(1)	O1 - Cu1 - I1'	112.0(3)
N1 - C10	1.36(3)	N1 - Cu1 - I1'	118.8(2)
C2 - C1	1.48(3)	Cu1 - I1 - Cu1'	59.1(1)
C2 - C3	1.42(2)	Cu1 - N1 - C10	123.8(5)
C3 - C4	1.37(4)	Cu1 - N1 - C2	117.6(15)
C4 - C5	1.41(2)	Cu1 - O1 - C1	107.4(15)
C5 - C10	1.43(2)	N1 - C10 - C5	121.3(11)
C5 - C6	1.41(4)	N1 - C10 - C9	118.8(14)
C6 - C7	1.38(2)	N1 - C2 - C3	123.8(20)
C7 - C8	1.41(3)	N1 - C2 - C1	114.8(13)
C8 - C9	1.37(4)	C2 - C3 - C4	118.2(12)
C9 - C10	1.42(2)	C3 - C4 - C5	119.8(15)
C1 - O1	1.21(2)	C4 - C5 - C10	118.3(21)
C1 - O2	1.32(1)	C4 - C5 - C6	122.6(16)
O2 - C11	1.48(3)	C6 - C5 - C10	119.0(11)
C11 - C12	1.52(1)	C5 - C6 - C7	120.4(18)
C11 - C13	1.55(2)	C6 - C7 - C8	119.5(25)
		C7 - C8 - C9	122.5(13)
		C8 - C9 - C10	118.6(14)

TABLE VIII (Continued)

C9 - C10 - C5	119.9(19)
C1 - C2 - C3	121.3(12)
O1 - C1 - C2	123.5(12)
O1 - C1 - O2	124.4(21)
C2 - C1 - O2	112.1(13)
C1 - O2 - C11	91.0(8)
O2 - C11 - C12	107.5(17)
O2 - C11 - C13	104.1(16)
C12 - C11 - C13	113.8(8)

Table IX

CRYSTAL DATA FOR Copper Iodide n-Butyl
Quinaldate(III)

Formula	$\text{CuIC}_{14}\text{H}_{15}\text{NO}_2$
F.W.	419.2
<u>a</u>	8.994(2) Å
<u>b</u>	10.336(3)
<u>c</u>	16.216(6)
α	90.0
β	101.0(2)
γ	90.0
V	1479.7(8) Å ³
F(000)	8016
$\mu_{\text{MoK}\alpha}$	35.40 cm ⁻¹
$\lambda_{\text{MoK}\alpha}$	0.71069 Å
D _{calc}	1.884 g cm ⁻³
Z	4
Meas refl	4122
Obs refl	1082
R	7.4%
R _w	9.8%
Space Group	P2 ₁ /c
Octants meas	<u>±</u> h,k,l

TABLE X
POSITIONAL PARAMETERS FOR Copper Iodide n-Butyl
Quinaldate(III)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	1.2004(2)	0.4268(2)	0.5917(1)
Cu1	0.9288(4)	0.3972(3)	0.5095(2)
O13	0.7826(25)	0.3546(20)	0.6055(12)
O12	0.6487(22)	0.1899(19)	0.6412(13)
N1	0.8578(25)	0.2117(18)	0.4821(13)
C2	0.7739(27)	0.1582(27)	0.5289(18)
C3	0.7168(27)	0.0287(27)	0.5178(14)
C4	0.7621(33)	-0.0428(27)	0.5178(14)
C5	0.8509(28)	0.0114(24)	0.4055(15)
C6	0.8991(25)	0.1454(23)	0.4206(15)
C7	0.9894(34)	0.1954(26)	0.3705(16)
C8	1.0288(35)	0.1355(30)	0.3041(16)
C9	0.9834(38)	0.0007(33)	0.2915(20)
C10	0.8943(38)	-0.0532(26)	0.3414(18)
C11	0.7356(29)	0.2506(31)	0.5971(19)
C14	0.6040(33)	0.2728(27)	0.7100(15)
C15	0.5255(33)	0.1860(30)	0.7618(19)
C16	0.4709(29)	0.2618(36)	0.8318(21)
C17	0.4118(41)	0.1788(36)	0.8871(23)

TABLE XI
ANISOTROPIC THERMAL PARAMETERS FOR
Copper Iodide n-Butyl Quinaldate(III)

ATOM	U11	U22	U33	U12	U13	U23
I1	43(1)	40(1)	47(1)	-5(1)	2(0)	3(1)
Cu1	47(2)	26(1)	48(2)	-14(1)	13(1)	1(1)
O13	69(15)	50(13)	33(12)	-33(11)	25(11)	-15(10)
O12	31(12)	44(12)	61(14)	-10(9)	0(11)	-11(10)
N1	42(15)	8(10)	41(14)	-10(9)	-6(12)	14(10)
C2	1(13)	43(16)	44(18)	-5(11)	2(12)	4(14)
C3	11(13)	62(19)	11(12)	-7(12)	10(10)	5(12)
C4	51(19)	48(19)	21(15)	-13(14)	19(13)	20(13)
C5	27(16)	29(13)	12(13)	8(1)	-17(11)	-8(12)
C6	4(12)	33(13)	8(12)	7(10)	-5(9)	-6(11)
C7	50(19)	35(15)	25(15)	0(13)	18(14)	-13(13)
C8	55(22)	56(19)	14(14)	15(16)	9(14)	0(14)
C9	50(21)	57(21)	61(22)	-1(17)	20(18)	-30(18)
C10	25(15)	38(17)	42(17)	-1(13)	3(12)	0(14)
C11	17(16)	52(19)	54(20)	-17(13)	10(15)	12(16)
C14	56(20)	40(16)	15(14)	1(14)	9(13)	-7(13)
C15	35(20)	59(20)	43(20)	-28(16)	4(16)	6(16)
C16	4(14)	106(28)	65(21)	2(16)	15(14)	-12(21)

Anisotropic thermal parameters in the form:

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

TABLE XI (Continued)

$$+ 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)) \times 10^3$$

TABLE XII
BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
Copper Iodide n-Butyl Quinaldate(III)

Cu1 - I1	2.56(8) Å	Cu1 - I1 - Cu1'	58.9(1) °
Cu1 - I1'	2.57(5)	I1 - Cu1 - I1'	121.0(1)
Cu1 - Cu1'	2.53(1)	I1 - Cu1 - O13	106.6(5)
Cu1 - N1	2.04(2)	I1' - Cu1 - O13	108.9(5)
Cu1 - O13	2.26(6)	I1 - Cu1 - N1	116.8(6)
N1 - C2	1.29(5)	I1' - Cu1 - N1	116.1(6)
C2 - C3	1.43(4)	N1 - Cu1 - O13	76.5(8)
C2 - C11	1.54(4)	Cu1 - N1 - C2	117(2)
C3 - C4	1.34(4)	Cu1 - N1 - C6	122(2)
C4 - C5	1.39(5)	C2 - N1 - C6	120(2)
C5 - C6	1.45(3)	N1 - C2 - C3	124(3)
C5 - C10	1.35(4)	N1 - C2 - C11	112(2)
C6 - N1	1.32(4)	C11 - C2 - C3	122(2)
C6 - C7	1.35(5)	C2 - C3 - C4	117(2)
C7 - C8	1.34(5)	C3 - C4 - C5	120(3)
C8 - C9	1.45(5)	C4 - C5 - C6	117(2)
C9 - C10	1.36(6)	C10 - C5 - C6	118(2)
C11 - O12	1.31(5)	C10 - C5 - C4	123(2)
C11 - O13	1.15(4)	N1 - C6 - C7	122(2)
O12 - C14	1.52(4)	C5 - C6 - C7	117(2)
C14 - C15	1.49(5)	C5 - C6 - N1	120(2)
C15 - C16	1.53(5)	C6 - C7 - C8	125(3)
C16 - C17	1.41(6)	C7 - C8 - C9	116(3)

TABLE XII (Continued)

C8 - C9 - C10	119(3)
C9 - C10 - C5	122(3)
C2 - C11 - O13	122(3)
C2 - C11 - O12	109(2)
O13 - C11 - O12	128(3)
C11 - O12 - C14	113(2)
O12 - C14 - C15	107(2)
C14 - C15 - C16	111(3)
C15 - C16 - C17	111(3)

TABLE XIII

Hydrogen Positional Parameters for Copper Iodide
n-Butyl Quinaldate(III)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(X))
H3	0.6502	-0.0061	0.5534
H4	0.7211	-0.1313	0.4470
H7	1.0273	0.2823	0.3844
H8	1.0790	0.1854	0.2630
H9	1.0230	-0.0520	0.2494
H10	0.8583	-0.1451	0.3297
H141	0.5457	0.3175	0.6775
H151	0.4405	0.1419	0.7392
H152	0.6100	0.1232	0.7980
H161	0.5769	0.3303	0.8551
H162	0.4653	0.3716	0.8215
H171	0.3481	0.1099	0.8610
H172	0.3939	0.1361	0.9459
H173	0.3459	0.2537	0.9169

Table XIV

CRYSTAL DATA FOR Copper Iodide Methyl
Nicotinate(IV)

Formula	$\text{CuIC}_7\text{H}_7\text{NO}_2$
F.W.	327.59
<u>a</u>	4.175(2) Å
<u>b</u>	12.197(5)
<u>c</u>	18.682(12)
α	90.0
β	106.07(4)
γ	90.0
V	914.2(8) Å ³
F(000)	616
$\mu_{\text{MoK}\alpha}$	56.96 cm ⁻¹
$\lambda_{\text{MoK}\alpha}$	0.71069 Å
D _{calc}	2.380 g cm ⁻³
Z	4
Meas refl	2351
Obs refl	1727
R	7.0%
R _w	8.9%
Space Group	P2 ₁ /n
Octants meas	<u>±</u> h,k,l

TABLE XV
POSITIONAL PARAMETERS FOR Copper Iodide Methyl
Nicotinate(IV)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.6647(2)	0.3731(1)	0.9305(1)
Cu1	0.2646(4)	0.4252(1)	1.0165(2)
N1	0.3787(25)	0.3192(8)	1.1066(6)
C2	0.2352(31)	0.2209(9)	1.1040(7)
C3	0.3219(33)	0.1463(9)	1.1597(7)
C4	0.5677(38)	0.1743(12)	1.2247(7)
C5	0.7200(37)	0.2736(11)	1.2294(8)
C6	0.6163(35)	0.3449(11)	1.1682(7)
C7	0.1605(37)	0.0373(11)	1.1550(7)
O8	0.2179(32)	-0.0303(9)	1.2050(6)
O9	-0.064(25)	0.0188(7)	1.0893(5)
C10	-0.2214(39)	-0.0875(11)	1.0799(9)
H2	0.0382	0.1900	1.0598
H4	0.6708	0.1300	1.2605
H5	0.9578	0.3013	1.2754
H6	0.7138	0.4200	1.1675

TABLE XVI
ANISOTROPIC THERMAL PARAMETERS FOR
Copper Iodide Methyl Nicotinate(IV)

ATOM	U11	U22	U33	U12	U13	U23
I1	338(4)	320(4)	326(4)	-28(3)	0(3)	-56(3)
Cu1	500(9)	366(8)	347(9)	-37(7)	-5(7)	41(6)
N1	42(5)	30(5)	31(5)	0(4)	0(4)	1(4)
C2	49(6)	29(5)	30(6)	-2(4)	9(5)	1(4)
C3	54(7)	28(5)	27(6)	12(4)	7(5)	1(4)
C4	67(9)	46(7)	23(6)	17(6)	0(5)	-1(5)
C5	64(8)	42(7)	32(7)	-8(6)	-10(6)	-5(5)
C6	60(8)	38(6)	24(6)	-1(5)	-5(5)	-4(4)
C7	64(8)	34(6)	36(7)	9(5)	11(6)	0(5)
O8	96(8)	51(6)	56(7)	-1(5)	3(6)	30(5)
O9	64(6)	35(4)	40(5)	-5(4)	0(4)	5(3)
C10	69(9)	31(6)	66(10)	-14(6)	25(8)	-3(6)

Anisotropic thermal parameters in the form:

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

TABLE XVII
BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
Copper Iodide Methyl Nicotinate(IV)

Cu1 - I1	2.695(2) Å	I1 - Cu1 - I1'	102.67(5) °
Cu1 - I1'	2.652(2)	I1 - Cu1 - I1''	114.85(6)
Cu1 - I1''	2.638(2)	I1' - Cu1 - I1''	116.08(7)
Cu1 - Cu1''	2.872(3)	I1 - Cu1 - N1	107.2(3)
Cu1 - Cu1'''	2.800(2)	I1' - Cu1 - N1	116.8(6)
Cu1 - N1	2.07(1)	I1'' - Cu1 - N1	107.5(3)
N1 - C2	1.34(2)	Cu1 - I1 - Cu1'''	102.67(5)
N1 - C6	1.33(2)	Cu1 - I1 - Cu1''	65.15(6)
C2 - C3	1.35(2)	Cu1'' - I1 - Cu1'''	63.92(5)
C3 - C4	1.40(2)	Cu1 - N1 - C2	122.1(7)
C4 - C5	1.36(2)	Cu1 - N1 - C6	120.3(8)
C5 - C6	1.41(2)	C2 - N1 - C6	117.4(10)
C3 - C7	1.48(2)	N1 - C2 - C3	123.6(10)
C7 - O8	1.22(2)	C2 - C3 - C7	122.4(10)
C7 - O9	1.34(2)	C2 - C3 - C4	118.6(11)
O9 - C10	1.44(2)	C7 - C3 - C4	118.9(11)
		C3 - C4 - C5	119.5(12)
		C4 - C5 - C6	117.6(11)
		C5 - C6 - N1	123.1(12)
		C3 - C7 - O8	124.9(11)
		C3 - C7 - O9	113.4(10)
		O8 - C7 - O9	121.7(12)

TABLE XVII (Continued)

C7 - O9 - C10	116.3(10)
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Symmetry operations:

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

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

$$''' = 1+x, y, z$$

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

Table XVIII

CRYSTAL DATA FOR Copper Iodide Isopropyl
Nicotinate(V)

Formula	$\text{CuIC}_9\text{H}_{11}\text{NO}_2$
F.W.	355.64
<u>a</u>	12.675(4) Å
<u>b</u>	20.920(9)
<u>c</u>	12.649(4)
α	107.64(3)
β	89.89(3)
γ	107.66(3)
V	3030.7(18) Å ³
F(000)	1360
$\mu_{\text{MoK}\alpha}$	34.42 cm ⁻¹
$\lambda_{\text{MoK}\alpha}$	0.71069 Å
D _{calc}	1.559 g cm ⁻³
Z	8
Meas refl	15539
Obs refl	4460
R	8.1%
R _w	12.2%
Space Group	P $\bar{1}$
Octants meas	<u>+</u> h, <u>k</u> , <u>+</u> l

TABLE XIX

POSITIONAL PARAMETERS FOR Copper Iodide Isopropyl
Nicotinate(V)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.2473(2)	0.3322(1)	0.7562(1)
I2	0.0850(2)	0.3324(1)	1.0761(2)
I3	-0.0760(2)	0.1678(1)	0.7529(2)
I4	0.2437(2)	0.1678(1)	0.9151(2)
Cu1	0.0496(4)	0.2007(2)	0.9432(4)
Cu2	0.2424(3)	0.2994(2)	0.9512(4)
Cu3	0.1508(4)	0.2006(2)	0.7574(3)
Cu4	0.0567(4)	0.2883(2)	0.8490(4)
N101	-0.0323(20)	0.1318(13)	1.0245(22)
C102	-0.0336(28)	0.1553(18)	1.1361(26)
C103	-0.0800(30)	0.1052(19)	1.1895(29)
C104	-0.1260(39)	0.0150(17)	1.0205(32)
C105	-0.1283(34)	0.0150(17)	1.0205(32)
C106	-0.0794(34)	0.0642(16)	0.9738(31)
C107	-0.0875(34)	0.1328(20)	1.3181(32)
O108	-0.1097(33)	0.0946(16)	1.3700(25)
O109	-0.0586(25)	0.2042(14)	1.3599(18)
C110	-0.0642(51)	0.2351(27)	1.4768(32)
C111	-0.1791(49)	0.2355(32)	1.4953(42)
C112	0.0144(51)	0.3022(30)	1.5031(39)
N201	0.3890(23)	0.3682(14)	1.0334(24)

Table XIX (Continued)

C202	0.4764 (35)	0.3434 (21)	1.0330 (30)
C203	0.5847 (24)	0.3930 (20)	1.0824 (31)
C204	0.5946 (31)	0.4629 (18)	1.1291 (37)
C205	0.5026 (32)	0.4817 (17)	1.1270 (36)
C206	0.4093 (29)	0.4372 (17)	1.0804 (31)
C207	0.6816 (25)	0.3666 (17)	1.0839 (35)
O208	0.7738 (21)	0.4048 (16)	1.1073 (31)
O209	0.6524 (18)	0.2067 (13)	1.0586 (24)
C210	0.7423 (34)	0.2629 (26)	1.0693 (51)
C211	0.7692 (54)	0.2645 (33)	1.1813 (49)
C212	0.6998 (45)	0.1967 (29)	0.9822 (49)
N301	0.1636 (24)	0.1316 (14)	0.6077 (23)
C302	0.1887 (32)	0.1549 (19)	0.5198 (29)
C303	0.1912 (28)	0.1071 (18)	0.4141 (27)
C304	0.1661 (38)	0.0364 (19)	0.4067 (29)
C305	0.1368 (40)	0.0172 (18)	0.4954 (26)
C306	0.1425 (34)	0.0633 (17)	0.5915 (26)
C307	0.2157 (39)	0.1344 (27)	0.3195 (29)
O308	0.2056 (30)	0.0964 (17)	0.2278 (20)
O309	0.2639 (25)	0.2057 (15)	0.3452 (22)
C310	0.3041 (44)	0.2371 (28)	0.2564 (32)
C311	0.2938 (53)	0.3065 (31)	0.3013 (48)
C312	0.4174 (43)	0.2361 (35)	0.2444 (54)
N401	-0.0258 (24)	0.3684 (13)	0.8327 (21)
C402	-0.1356 (22)	0.3429 (17)	0.8099 (29)

TABLE XIX (Continued)

C403	-0.1284 (35)	0.4625 (16)	0.8393 (42)
C404	-0.1284 (35)	0.4625 (16)	0.8393 (42)
C405	-0.0175 (34)	0.4881 (16)	0.8534 (37)
C406	0.0279 (28)	0.4372 (18)	0.8597 (28)
C407	-0.3162 (35)	0.3659 (25)	0.7842 (35)
O408	-0.3685 (23)	0.4040 (18)	0.7957 (31)
O409	-0.3592 (22)	0.2943 (15)	0.7341 (25)
C410	-0.4778 (31)	0.2657 (23)	0.6933 (45)
C411	-0.4930 (44)	0.2647 (31)	0.5802 (47)
C412	-0.5056 (37)	0.1953 (26)	0.7039 (50)
H102	-0.0031	0.2075	1.1798
H104	-0.1621	0.0029	1.1718
H105	-0.1635	-0.0354	0.9766
H106	-0.0799	0.0473	0.8899
H202	0.4662	0.2902	0.9992
H204	0.6683	0.4997	1.1634
H205	0.5060	0.5319	1.1652
H206	0.3444	0.4548	1.0781
H302	0.2043	0.2069	0.5300
H304	0.1702	0.0008	0.3360
H305	0.1078	-0.0344	0.4877
H306	0.1330	0.0463	0.6582
H402	-0.1777	0.2908	0.7895
H404	-0.1691	0.4973	0.8440
H405	0.0260	0.5370	0.8593

TABLE XIX (Continued)

H406	0.1092	0.4542	0.8868
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TABLE XX
ANISOTROPIC THERMAL PARAMETERS FOR
Copper Iodide Isopropyl Nicotinate(V)

ATOM	U11	U22	U33	U12	U13	U23
I1	57(1)	43(1)	62(1)	12(1)	11(1)	22(1)
I2	60(1)	44(1)	50(1)	18(1)	7(1)	5(1)
I3	56(1)	44(1)	53(1)	7(1)	-5(1)	10(1)
I4	69(1)	44(1)	56(1)	23(1)	1(1)	16(1)
Cu1	73(3)	51(2)	48(2)	13(2)	13(2)	19(2)
Cu2	51(2)	48(2)	66(3)	14(2)	-6(2)	11(2)
Cu3	82(3)	46(2)	45(2)	22(2)	11(2)	12(2)
Cu4	57(2)	51(2)	73(3)	23(2)	1(2)	23(2)
N101	40(16)	56(17)	60(20)	27(13)	6(13)	26(14)
C102	67(24)	58(22)	36(20)	20(18)	12(17)	18(17)
C103	70(25)	73(25)	51(24)	21(20)	0(19)	19(20)
C104	112(35)	33(19)	80(29)	-7(20)	18(25)	19(19)
C105	104(34)	22(18)	77(29)	-17(19)	-1(24)	-9(18)
C106	113(32)	26(17)	65(27)	7(19)	39(24)	8(17)
C107	86(31)	75(27)	58(27)	16(23)	3(23)	10(22)
O108	233(42)	101(25)	82(22)	49(26)	45(24)	66(20)
O109	145(26)	88(20)	27(13)	35(18)	23(15)	24(13)
C110	148(53)	107(38)	42(24)	56(38)	23(29)	3(24)
C111	134(50)	182(62)	76(38)	79(46)	14(35)	-21(36)
C112	179(58)	106(44)	62(33)	34(41)	3(34)	-14(30)
N201	63(19)	52(18)	72(20)	20(15)	19(16)	23(15)

Table XX (Continued)

C202	104(33)	76(28)	48(24)	22(24)	12(22)	-1(20)
C203	19(18)	83(27)	83(28)	2(17)	-11(17)	25(22)
C204	55(27)	42(21)	124(37)	1(19)	-37(24)	6(22)
C205	89(29)	31(20)	110(35)	12(19)	-46(25)	-6(21)
C206	60(24)	50(21)	87(28)	25(18)	-17(21)	14(19)
C207	25(19)	42(20)	131(36)	-31(15)	11(20)	31(22)
O208	51(17)	100(24)	194(37)	13(16)	-13(19)	36(23)
O209	31(13)	80(18)	139(25)	11(12)	-7(14)	46(17)
C210	59(28)	149(44)	188(61)	71(29)	22(33)	89(43)
C211	193(66)	182(61)	119(50)	112(53)	-23(45)	67(45)
C212	127(48)	146(52)	186(58)	105(43)	74(42)	55(44)
N301	87(22)	44(17)	64(20)	29(15)	24(17)	22(14)
C302	93(29)	60(23)	59(24)	35(21)	30(21)	34(19)
C303	54(22)	65(24)	42(21)	21(18)	6(17)	-11(17)
C304	139(39)	52(23)	40(23)	27(24)	31(23)	-19(17)
C305	196(46)	43(22)	15(17)	14(26)	13(22)	10(15)
C306	127(35)	48(21)	22(18)	-15(21)	-8(20)	22(16)
C307	114(39)	175(47)	33(21)	86(36)	28(23)	35(25)
O308	194(37)	139(29)	29(15)	43(26)	23(19)	21(17)
O309	122(25)	89(21)	62(18)	6(18)	18(16)	18(16)
C310	125(45)	117(42)	39(24)	12(34)	8(25)	27(26)
C311	207(65)	128(48)	123(48)	60(46)	32(43)	102(42)
C312	82(37)	247(73)	207(67)	42(42)	71(41)	181(61)
N401	73(21)	51(17)	37(16)	32(15)	-2(14)	0(13)
C402	10(15)	63(22)	82(25)	24(15)	0(15)	20(18)

Table XX (Continued)

C403	68(25)	91(27)	34(20)	45(21)	15(17)	24(18)
C404	83(31)	12(16)	190(50)	9(18)	32(30)	47(23)
C405	84(29)	15(17)	141(40)	-2(18)	24(26)	45(21)
C406	52(24)	63(23)	48(23)	8(18)	21(18)	0(18)
C407	86(34)	143(43)	86(32)	71(32)	35(26)	64(31)
O408	61(19)	141(29)	195(37)	74(20)	5(21)	35(26)
O409	78(19)	87(21)	121(25)	42(16)	-4(17)	2(18)
C410	42(23)	92(33)	126(45)	9(21)	0(26)	-2(31)
C411	102(44)	156(56)	101(43)	9(38)	1(35)	36(40)
C412	63(32)	104(40)	191(60)	-41(27)	-2(34)	28(39)

Anisotropic thermal parameters in the form:

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

TABLE XXI
BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
Copper Iodide Isopropyl Nicotinate(V)

Cu1 - I4	2.744(6) Å	I2 - Cu1 - I3	113.9(2) °
Cu1 - I3	2.673(1)	I2 - Cu1 - I4	111.7(2)
Cu1 - I2	2.657(5)	I3 - Cu1 - I4	114.1(2)
Cu2 - I4	2.657(5)	I2 - Cu1 - N101	108.9(7)
Cu2 - I2	2.667(5)	I3 - Cu2 - N101	106.7(7)
Cu2 - I1	2.79(6)	I4 - Cu1 - N101	100.2(8)
Cu3 - I4	2.674(5)	I1 - Cu2 - I2	113.7(2)
Cu3 - I3	2.742(5)	I2 - Cu2 - I4	114.2(2)
Cu4 - I3	2.655(4)	I2 - Cu2 - N201	108.2(2)
Cu4 - I2	2.740(5)	I2 - Cu2 - N201	106.1(8)
Cu4 - I1	2.675(5)	I4 - Cu2 - N201	109.6(0)
Cu1 - N101	2.05(3)	I1 - Cu3 - I3	111.8(2)
Cu2 - N201	2.02(2)	I1 - Cu3 - I4	113.8(2)
Cu3 - N301	2.04(2)	I3 - Cu3 - I4	114.0(2)
Cu4 - N401	2.08(3)	I1 - Cu3 - N301	109.1(8)
Cu1 - Cu2	2.656(5)	I3 - Cu3 - N301	100.2(8)
Cu1 - Cu3	2.674(6)	I4 - Cu3 - N301	106(1)
Cu1 - Cu4	2.656(7)	I1 - Cu4 - I2	113.7(2)
Cu2 - Cu3	2.666(5)	I1 - Cu4 - I3	114.0(2)
Cu2 - Cu4	2.685(7)	I2 - Cu4 - I3	111.8(2)
Cu3 - Cu4	2.657(7)	I1 - Cu4 - N401	104.4(8)
N101 - C102	1.30(4)	I2 - Cu4 - N401	101.3(6)
C102 - C103	1.40(5)	I3 - Cu4 - N401	108.3(2)

Table XXI (Continued)

C103 - C104	1.32(4)	Cu4 - I1 - Cu3	59.8(2)
C104 - C105	1.34(6)	Cu4 - I1 - Cu2	59.5(1)
C105 - C106	1.33(6)	Cu3 - I1 - Cu2	59.1(1)
C103 - C107	1.57(5)	Cu4 - I2 - Cu2	59.9(2)
C107 - O108	1.15(6)	Cu4 - I2 - Cu1	58.9(1)
C107 - O109	1.35(7)	Cu2 - I2 - Cu1	59.8(1)
O109 - C110	1.43(4)	Cu4 - I3 - Cu3	59.0(2)
C110 - C111	1.48(9)	Cu4 - I3 - Cu1	59.8(2)
C110 - C112	1.39(7)	Cu3 - I3 - Cu1	59.2(1)
N101 - C106	1.30(4)	Cu1 - I4 - Cu2	59.9(1)
N201 - C202	1.36(6)	Cu3 - I4 - Cu1	59.1(2)
N201 - C204	1.33(4)	Cu2 - I4 - Cu1	58.9(1)
C202 - C203	1.45(5)	C102 - N101 - C106	117(3)
C203 - C204	1.36(5)	N101 - C102 - C103	117(3)
C204 - C205	1.34(6)	C104 - C103 - C107	117(3)
C205 - C206	1.27(4)	C102 - C103 - C104	122(3)
C203 - C207	1.49(5)	C102 - C103 - C107	117(3)
C207 - O208	1.18(4)	C103 - C104 - C105	121(49)
C207 - O209	1.33(4)	C102 - N101 - C106	117(3)
O209 - C210	1.54(6)	C105 - C106 - N101	127(3)
C210 - C211	1.42(9)	C103 - C107 - O108	121(3)
C210 - C212	1.43(7)	C103 - C107 - O109	125(3)
N301 - C302	1.34(5)	C107 - O109 - C110	117(3)
N301 - C306	1.32(5)	O109 - C110 - C111	108(4)
C302 - C303	1.41(5)	O109 - C110 - C112	103(4)

Table XXI (Continued)

C303 - C304	1.39(6)	C112 - C110 - C111	114(6)
C304 - C305	1.32(5)	C202 - N201 - C206	116(3)
C305 - C306	1.29(4)	N201 - C202 - C203	118(3)
C303 - C307	1.47(6)	C202 - C203 - C204	118(4)
C307 - O308	1.17(4)	C202 - C203 - C207	119(3)
C307 - O309	1.36(6)	C204 - C203 - C207	121(3)
O309 - C310	1.48(6)	C203 - C204 - C205	117(3)
C310 - C311	1.44(9)	C204 - C205 - C206	121(3)
C310 - C312	1.45(8)	C205 - C206 - N201	125(4)
N401 - C402	1.33(4)	C203 - C207 - O208	122(3)
N401 - C406	1.33(4)	C203 - C207 - O209	113(2)
C402 - C403	1.45(6)	O208 - C207 - O209	124(4)
C403 - C404	1.33(6)	C207 - O209 - C210	118(3)
C404 - C405	1.33(6)	O209 - C210 - C211	110(5)
C405 - C406	1.38(6)	O209 - C210 - C212	100(4)
C403 - C407	1.52(5)	C211 - C210 - C212	120(6)
C407 - O408	1.16(8)	C302 - N301 - C306	120(3)
C407 - O409	1.37(5)	N301 - C301 - C303	120(3)
O409 - C410	1.47(5)	C302 - C303 - C304	116(3)
C410 - C411	1.44(9)	C302 - C303 - C307	118(4)
C410 - C412	1.45(8)	C304 - C303 - C307	124(3)
		C303 - C304 - C305	119(3)
		C304 - C305 - C306	121(4)
		C305 - C306 - N301	123(4)
		C303 - C307 - O308	121(5)

Table XXI (Continued)

C303 - C307 - O309	116 (3)
O308 - C307 - O309	121 (4)
C307 - O309 - C310	120 (3)
O309 - C310 - C311	101 (4)
O309 - C310 - C312	106 (5)
C311 - C310 - C312	114 (5)
C402 - N401 - C406	121 (3)
N401 - C402 - C403	115 (3)
C402 - C403 - C404	118 (3)
C402 - C403 - C407	115 (3)
C404 - C403 - C407	126 (4)
C403 - C404 - C405	127 (4)
C404 - C405 - C406	110 (3)
C403 - C404 - C405	127 (4)
C404 - C405 - C406	110 (3)
N401 - C406 - C405	125 (3)
C403 - C407 - O408	120 (4)
C403 - C407 - O409	116 (4)
O408 - C407 - O409	123 (4)
C407 - O409 - C410	117 (4)
O409 - C410 - C411	110 (4)
O409 - C410 - C412	101 (4)
C411 - C410 - C412	113 (4)

Table XXII

CRYSTAL DATA FOR Copper Iodide n-Butyl
Nicotinate(VI)

Formula	$\text{Cu}_4\text{I}_4(\text{C}_{10}\text{H}_{13}\text{NO}_2)_4$
M.W.	1478.7
<u>a</u>	12.271(10) Å
<u>b</u>	12.305(9)
<u>c</u>	20.594(12)
α	72.61(5)°
β	72.63(6)
γ	89.91(6)
V	2819(3) Å ³
F(000)	1340
$\mu_{\text{MoK}\alpha}$	36.91 cm ⁻¹
$\lambda_{\text{MoK}\alpha}$	0.71069 Å
D _{calc}	1.74 g cm ⁻³
Z	2
Meas refl	14391
Obs refl	4773
R	10.6%
R _w	13.8%
Space Group	PI*
Octants meas	h, ±k, l

* The original cell dimensions (triclinic cell) are being transformed to tetragonal so that a better refinement can be obtained.

Table XXIII

CRYSTAL DATA FOR Copper Iodide Pyrazinamide(VII)

Formula	$\text{CuIC}_5\text{H}_5\text{N}_3\text{O}$
M.W.	299.6
<u>a</u>	4.118(2) Å
<u>b</u>	14.927(6)
<u>c</u>	15.032(8)
α	71.22(4)°
β	105.99(4)
γ	82.09(3)
V	814.5(7) Å ³
F(000)	292
$\mu_{\text{MoK}\alpha}$	31.92 cm ⁻¹
$\lambda_{\text{MoK}\alpha}$	0.71069 Å
D _{calc}	1.278 g cm ⁻³
Z	2
Meas refl	4266
Obs refl	2814
R	6.8%
R _w	9.0%
Space Group	P $\bar{1}$
Octants meas	<u>+</u> h, <u>k</u> , <u>+</u> l

Table XXIV

POSITIONAL PARAMETERS FOR Copper Iodide Pyrazinamide (VII)

ATOM	X (SIG(X))	Y (SIG(Y))	Z (SIG(Z))
I1	-0.1210(2)	-0.0591(1)	0.3964(1)
I2	0.0264(2)	0.0592(1)	0.1033(1)
Cu2	0.2352(5)	0.0377(1)	0.2928(1)
Cu3	-0.3127(5)	-0.0377(1)	0.2069(1)
O29	-0.4999(38)	-0.3759(8)	0.4387(10)
N28	-0.3856(42)	-0.4990(10)	0.3858(11)
C27	-0.4250(38)	-0.4057(11)	0.3783(12)
C26	-0.2985(48)	-0.2962(12)	0.1386(13)
C25	-0.2769(39)	-0.2043(11)	0.1364(11)
N24	-0.2967(33)	-0.1783(9)	0.2101(10)
C23	-0.3504(41)	-0.2422(11)	0.2863(11)
C22	-0.3681(36)	-0.3365(10)	0.2903(11)
C21	-0.3461(36)	-0.3634(10)	0.2144(11)
O49	-0.7527(31)	0.3756(8)	0.0596(9)
N48	-0.6569(37)	0.4991(10)	0.1123(11)
C47	-0.5867(34)	0.4071(10)	0.1207(11)
C46	0.1317(42)	0.2968(12)	0.3614(11)
C45	0.2509(38)	0.2057(11)	0.3627(13)
N44	0.1032(31)	0.1773(8)	0.2894(9)
C43	-0.1712(34)	0.2433(11)	0.2104(11)
C42	-0.2806(36)	0.3361(10)	0.2105(11)

TABLE XXIV (Continued)

N41	-0.1443 (35)	0.3638 (10)	0.2836 (10)
H26	-0.2797	-0.3131	0.0818
H25	-0.2441	-0.1575	0.0785
H23	-0.3784	-0.2231	0.3411
H46	0.2464	0.3144	0.4179
H45	0.4529	0.1601	0.4193
H43	-0.2895	0.2256	0.1543

TABLE XXV
ANISOTROPIC THERMAL PARAMETERS FOR
Copper Iodide Pyrazinamide(VII)

ATOM	U11	U22	U33	U12	U13	U23
I1	24(0)	33(0)	32(0)	-4(0)	6(0)	-7(0)
I2	27(0)	34(0)	32(0)	-6(0)	12(0)	-7(0)
Cu2	31(0)	25(1)	44(1)	0(0)	9(0)	-9(0)
Cu3	41(1)	24(1)	42(1)	-10(0)	16(0)	-8(0)
O29	100(10)	20(6)	62(8)	-17(6)	47(7)	-14(5)
N28	81(10)	22(7)	52(9)	-18(6)	32(7)	-17(6)
C27	41(7)	27(7)	39(8)	-9(5)	19(6)	-12(6)
C26	70(11)	29(9)	47(10)	-6(7)	26(8)	-19(7)
C25	43(7)	27(8)	32(7)	-6(5)	13(6)	-5(6)
N24	46(7)	23(6)	39(7)	-12(5)	15(5)	-8(5)
C23	54(8)	25(7)	32(7)	-8(6)	14(6)	-12(6)
C22	37(7)	19(7)	36(7)	-7(5)	13(5)	-6(5)
N21	56(8)	26(7)	45(7)	-12(5)	18(6)	-16(6)
O49	58(7)	23(6)	54(7)	11(4)	-12(5)	-14(5)
N48	58(8)	17(7)	49(8)	5(5)	-12(6)	-7(6)
C47	30(6)	17(6)	43(8)	0(4)	9(5)	-7(6)
C46	55(9)	33(9)	23(7)	-2(6)	0(6)	-8(6)
C45	34(7)	25(8)	50(9)	4(5)	6(6)	-11(7)
N44	42(6)	14(6)	40(7)	-2(4)	10(5)	-12(5)
C43	29(6)	28(7)	38(8)	-1(5)	7(5)	-11(6)

Table XXV (Continued)

C42	37(7)	18(6)	31(7)	4(5)	9(5)	-5(5)
N41	50(7)	29(7)	40(7)	-8(5)	15(5)	-14(5)

Anisotropic thermal parameters in the form:

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

Table XXVI
BOND DISTANCES (\AA) AND BOND ANGLES ($^{\circ}$) FOR
Copper Iodide Pyrazinamide(VII)

I1 - Cu2	2.659(2) \AA	Cu2 - I2 - Cu3	65.62(7) $^{\circ}$
I1 - Cu3	2.636(3)	Cu2 - I2 - Cu3'	65.00(7)
I1 - Cu2'	2.600(2)	Cu3 - I2 - Cu3'	103.08(7)
I2 - Cu2	2.634(3)	Cu2 - I1 - Cu3	64.85(8)
I2 - Cu3	2.602(3)	Cu2 - I1 - Cu2'	103.11(7)
I2 - Cu3'	2.656(2)	Cu3 - I1 - Cu2	65.76(8)
Cu2 - Cu3	2.838(3)	I1 - Cu3 - I2	115.66(9)
Cu2 - Cu3'	2.843(3)	I1 - Cu3 - I2'	113.63(9)
Cu2 - N44	2.06(1)	I2 - Cu3 - I2'	103.08(7)
Cu3 - N24	2.07(1)	I1 - Cu3 - N24	104.4(4)
N41 - C42	1.30(2)	I2 - Cu3 - N24	115.5(4)
N41 - C46	1.36(2)	I2' - Cu3 - N24	104.2(3)
C42 - C43	1.39(2)	I1 - Cu2 - I2	113.84(9)
C42 - C47	1.52(2)	I1 - Cu2 - I1'	103.11(8)
C43 - N44	1.36(1)	I2 - Cu2 - I1'	115.6(1)
N44 - C45	1.33(2)	I2 - Cu2 - N44	104.3(4)
C45 - C46	1.37(2)	I1 - Cu2 - N44	104.0(4)
C47 - N48	1.32(2)	I1' - Cu2 - N44	115.7(3)
C47 - O49	1.25(2)	C42 - N41 - C46	115(1)
N21 - C22	1.35(3)	C43 - C42 - N41	124(1)
N21 - C26	1.33(2)	C47 - C42 - N41	119(1)
C22 - C23	1.40(2)	C47 - C42 - C43	117(1)

Table XXVI (Continued)

C22 - C27	1.49(2)	N44 - C43 - C42	119(1)
C23 - N24	1.33(2)	C45 - N44 - C43	117(1)
N24 - C25	1.30(2)	C43 - N44 - Cu2	118(1)
C25 - C26	1.38(3)	C45 - N44 - Cu2	124.4(8)
C27 - N28	1.34(2)	C46 - C45 - N44	112(1)
C27 - O29	1.22(3)	C45 - C46 - N41	121(2)
		N48 - C47 - C42	117(2)
		O49 - C47 - N48	124(1)
		O49 - C47 - C42	118(1)
		C22 - N21 - C26	116(2)
		C23 - C22 - N21	121(1)
		C27 - C22 - N21	120(1)
		C27 - C22 - C23	119(2)
		N24 - C23 - C22	121(2)
		C25 - N24 - Cu3	124(1)
		C23 - N24 - Cu3	118(1)
		C25 - N24 - C23	118(2)
		C26 - C25 - N24	121(3)
		C25 - C26 - N21	124(2)
		N28 - C27 - C22	116(2)
		O29 - C27 - N28	124(2)
		O29 - C27 - C22	120(2)

Table XXVI (Continued)

Symmetry operations:

$$\text{Cu2}' = x-1, y, z$$

$$\text{Cu3}' = x+1, y, z$$

$$\text{I1}' = x+1, y, z$$

$$\text{I2}' = x-1, y, z$$

Table XXVII

CRYSTAL DATA FOR Copper Iodide Quinaldic Acid(VIII)

Formula	$\text{Cu}_3\text{I}_2(\text{C}_{10}\text{H}_6\text{N}_2\text{O})_3\text{H}_2\text{O}$
M.W.	978.9
<u>a</u>	7.465(1) Å
<u>b</u>	18.602(8)
<u>c</u>	11.741(3)
α	79.492(3)°
β	82.84(2)
γ	83.33(3)
V	1583.5(8) Å ³
F(000)	688
$\mu_{\text{MoK}\alpha}$	32.96 cm ⁻¹
$\lambda_{\text{MoK}\alpha}$	0.71069 Å
D _{calc}	1.524 g cm ⁻³
Z	2
Meas refl	7702
Obs refl	3095
R	6.3%
R _w	7.9%
Space Group	P1
Octants meas	<u>+</u> h, <u>k</u> , <u>+</u> l

Table XXVIII

 POSITIONAL PARAMETERS FOR Copper Iodide
 Quinaldic Acid(VIII)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.1168(2)	0.0613(1)	0.0979(1)
I2	0.3820(2)	0.0333(1)	-0.2617(1)
I3	0.3797(2)	-0.1500(1)	0.0267(1)
Cu1	0.4008(4)	-0.0350(2)	0.1130(3)
Cu2	0.2086(4)	-0.0236(1)	-0.0664(2)
O1	-0.9879(18)	0.6061(7)	0.5036(12)
O112	-0.5087(18)	-0.4394(7)	0.3741(11)
O113	0.2531(20)	0.5049(8)	0.4209(13)
N101	0.6777(18)	0.5588(8)	0.2923(12)
C102	0.5044(25)	0.5672(9)	0.3349(15)
C103	0.4175(20)	-0.6379(10)	0.3329(17)
C104	0.5120(26)	-0.6962(11)	0.2884(18)
C105	0.6887(26)	0.6899(10)	0.2428(14)
C106	0.7963(24)	0.7477(10)	0.1889(16)
C107	0.9642(24)	0.7371(13)	0.1455(19)
C108	0.0572(27)	0.6635(12)	0.1471(20)
C109	0.9604(24)	0.6019(12)	0.2009(19)
C110	0.7793(25)	0.6170(9)	0.2467(14)
C111	0.4109(23)	0.4967(9)	0.3806(16)
O212	-0.3486(21)	0.5020(7)	0.1420(13)
O213	-0.7519(21)	0.5266(7)	0.0126(11)

Table XXVIII (Continued)

N201	0.3516(16)	0.3605(7)	0.2496(12)
C202	0.3049(24)	0.3763(11)	0.1399(16)
C203	0.2618(25)	0.3228(9)	0.0818(14)
C204	0.2661(24)	0.2522(10)	0.1354(16)
C205	0.3200(22)	0.2312(10)	0.2520(16)
C206	0.3277(22)	0.1575(9)	0.3110(27)
C207	0.3729(29)	0.1474(11)	0.4253(18)
C208	0.4078(25)	0.2025(11)	0.4834(16)
C209	0.3986(24)	0.2743(10)	0.4242(16)
C210	0.3558(20)	0.2881(9)	0.3123(13)
C211	0.3058(25)	0.4578(9)	0.0906(18)
O312	0.7634(21)	0.3967(7)	0.1097(13)
O313	0.9053(17)	0.4301(6)	0.2465(12)
N301	0.8915(17)	0.2961(7)	0.3740(12)
C302	0.8428(25)	0.3093(9)	0.2677(17)
C303	0.7955(25)	0.2491(10)	0.2210(17)
C304	0.8008(22)	0.1798(9)	0.2870(15)
C305	0.8498(21)	0.1688(9)	0.4008(16)
C306	0.8528(27)	0.0998(9)	0.4711(19)
C307	0.1041(28)	0.9095(9)	0.4151(19)
C308	0.0646(29)	0.8467(12)	0.3731(17)
C309	0.0631(26)	0.7800(11)	0.4386(16)
C310	0.8915(24)	0.2282(9)	0.4477(16)
C311	0.8353(24)	0.3867(10)	0.2019(15)

Table XXVIII (Continued)

H101	0.7434	0.5179	0.2707
H112	0.6205	0.4600	0.3873
H201	0.3978	0.4000	0.2840
H301	0.8951	0.3400	0.3993
H313	0.7932	0.4400	0.3036
H103	0.2895	0.6448	0.3640
H104	0.4492	0.7463	0.2873
H106	0.7394	0.7988	0.1843
H107	1.0961	0.7367	0.1274
H108	-0.0728	0.6619	0.1434
H109	1.0935	0.5929	0.1878
H203	0.2273	0.3369	0.0019
H204	0.2328	0.2144	0.0954
H206	0.3061	0.1165	0.2731
H207	0.3769	0.0964	0.4692
H208	0.4408	0.1897	0.5643
H209	0.4207	0.3150	0.4625
H303	0.7595	0.2575	0.1403
H304	0.7691	0.1380	0.2553
H306	0.8792	0.0465	0.5005
H307	0.0924	0.9606	0.4311
H308	0.0412	0.8533	0.2909
H309	-0.0456	0.7790	0.5030

Table XXIX
ANISOTROPIC THERMAL PARAMETERS FOR
Copper Iodide Quinaldic Acid(VIII)

ATOM	U11	U22	U33	U12	U13	U23
I1	34(0)	34(0)	51(0)	-3(0)	-9(0)	-18(0)
I2	44(0)	36(0)	38(0)	-7(0)	-12(0)	2(0)
I3	37(0)	30(0)	51(0)	-2(0)	-10(0)	0(0)
Cu1	58(1)	51(1)	54(1)	1(1)	-21(1)	-12(1)
Cu2	55(1)	39(1)	45(1)	-5(1)	-15(1)	-5(1)
O1	57(9)	24(7)	58(9)	-20(6)	-1(7)	-16(6)
O112	56(9)	35(8)	46(8)	-27(6)	-10(6)	0(6)
O113	62(10)	41(9)	63(10)	-25(7)	5(7)	-10(7)
N101	30(8)	28(9)	26(8)	-2(6)	-1(6)	-8(6)
C102	47(11)	22(10)	24(10)	-9(8)	-3(8)	-5(7)
C103	6(7)	36(11)	60(13)	-5(7)	-9(7)	-8(9)
C104	35(11)	39(12)	53(13)	-9(9)	0(9)	-4(10)
C105	52(11)	27(10)	20(9)	-25(8)	-9(8)	-2(7)
C106	36(10)	24(10)	38(11)	-8(7)	-9(8)	-7(8)
C107	17(10)	77(17)	60(14)	-8(9)	18(9)	-24(12)
C108	37(11)	60(15)	69(16)	-17(10)	-21(10)	-19(12)
C109	16(9)	65(15)	61(14)	-10(9)	-7(9)	-2(11)
C110	51(11)	22(10)	15(19)	-9(8)	-9(8)	3(7)
C111	27(10)	25(10)	42(11)	0(8)	0(8)	-20(8)
O212	80(11)	15(7)	68(10)	-10(7)	-20(8)	0(7)

Table XXIX (Continued)

O213	94(11)	38(6)	27(7)	-10(7)	-25(7)	9(6)
N201	13(6)	16(7)	43(9)	-1(5)	-4(5)	-1(6)
C202	33(10)	39(12)	37(11)	-6(8)	-15(8)	0(9)
C203	56(12)	18(9)	19(9)	8(8)	-15(8)	-8(7)
C204	41(10)	25(10)	36(11)	-4(8)	-10(8)	-11(8)
C205	25(9)	33(11)	38(11)	-3(7)	-3(7)	-12(8)
C206	29(9)	13(9)	50(12)	-6(7)	-4(8)	-9(8)
C207	62(14)	32(12)	41(13)	-15(10)	-6(10)	12(9)
C208	40(11)	39(12)	32(11)	2(9)	-11(8)	-6(9)
C209	36(10)	29(10)	33(11)	-3(8)	-3(8)	3(8)
C210	17(7)	20(9)	20(8)	-7(6)	5(6)	-2(6)
C211	43(11)	5(9)	48(13)	-5(7)	12(9)	5(8)
O312	73(10)	27(8)	69(10)	-6(7)	-31(8)	5(7)
O313	41(8)	19(7)	71(10)	-9(5)	-19(7)	3(6)
N301	24(7)	5(7)	43(9)	-4(5)	1(6)	-6(6)
C302	48(11)	4(8)	46(12)	-2(7)	5(9)	-4(7)
C303	38(10)	30(11)	46(12)	-13(8)	-13(9)	-7(9)
C304	27(9)	19(9)	30(10)	4(7)	9(7)	-10(7)
C305	19(8)	19(9)	49(12)	13(6)	0(7)	-6(8)
C306	54(12)	8(9)	63(14)	3(8)	-18(10)	7(8)
C307	58(13)	7(9)	66(14)	-7(8)	-8(10)	0(9)
C308	59(13)	51(14)	26(11)	-4(10)	1(9)	1(9)
C309	45(11)	44(12)	25(10)	12(9)	-1(8)	11(9)
C310	35(10)	13(9)	45(11)	-4(7)	4(8)	-3(8)

Table XXIX (Continued)

C311	39(10)	27(10)	30(10)	0(8)	-9(8)	10(8)
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Anisotropic thermal parameters in the form:

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

TABLE XXX
BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
Copper Iodide Quinaldic Acid(VIII)

Cu1 - I1	2.612(3)	I1 - Cu1 - I3	114.8(1)
Cu1 - I3	2.556(4)	I1 - Cu1 - I2	119.8(1)
Cu1 - I2'	2.533(4)	I3 - Cu1 - I2	121.8(1)
Cu2 - I1	2.636(3)	I1 - Cu2 - I2	117.9(1)
Cu2 - I2	2.596(3)	I1 - Cu2 - I3	109.2(1)
Cu2 - I3	2.656(3)	I1 - Cu2 - I1'	101.5(1)
Cu2 - I1'	2.690(3)	I2 - Cu2 - I3	111.5(1)
N101 - C102	1.33(2)	Cu1' - I1 - Cu2	121.5(1)
C102 - C103	1.39(2)	Cu2 - I1 - Cu2'	78.4(1)
C102 - C111	1.53(2)	Cu2 - I2 - Cu1	76.6(1)
C103 - C104	1.35(3)	Cu1 - I3 - Cu2	61.2(1)
C104 - C105	1.36(3)	Cu1 - I1 - Cu2	60.1(1)
C105 - C106	1.42(3)	C102 - N101 - C110	123(1)
C105 - C110	1.43(2)	H101 - N101 - C102	128(2)
C106 - C107	1.30(2)	H101 - N101 - C110	106(1)
C107 - C108	1.46(3)	N101 - C102 - C103	119(2)
C108 - C109	1.43(3)	N101 - C102 - C111	116(1)
C109 - C110	1.40(2)	C103 - C102 - C111	123(2)
C110 - N101	1.38(2)	C102 - C103 - C104	119(2)
C111 - O112	1.22(2)	C103 - C104 - C105	123(2)
C111 - O113	1.21(2)	C104 - C105 - C106	127(2)
N101 - H101	0.91(1)	C104 - C105 - C110	117(2)
O112 - H112	0.99(1)	C110 - C105 - C106	115(2)

Table XXX (Continued)

N201 - C202	1.34(3)	C105 - C106 - C107	123(2)
C203 - C204	1.34(2)	C106 - C107 - C108	121(2)
C204 - C205	1.44(3)	C107 - C108 - C109	118(2)
C202 - C211	1.52(2)	C108 - C109 - C110	117(2)
C205 - C206	1.41(2)	C109 - C110 - N101	118(2)
C206 - C207	1.39(3)	C105 - C110 - N101	117(2)
C207 - C208	1.39(3)	C105 - C110 - C109	123(2)
C208 - C209	1.38(3)	O112 - C111 - C102	114(1)
C209 - C210	1.36(2)	O113 - C111 - O112	128(2)
C210 - N201	1.41(2)	O113 - C111 - C102	116(2)
C211 - O212	1.19(3)	C111 - O112 - H112	94(1)
C211 - O213	1.30(2)	C202 - N201 - C210	121(2)
N201 - H201	1.01(1)	H201 - N201 - C202	119(1)
N301 - C302	1.31(3)	H201 - N201 - C210	119(1)
C302 - C303	1.42(3)	N201 - C202 - C203	122(2)
C302 - C311	1.50(2)	N201 - C202 - C211	111(2)
C303 - C304	1.37(2)	C211 - C202 - C203	125(2)
C304 - C305	1.40(3)	C202 - C203 - C204	119(2)
C305 - C306	1.39(2)	C203 - C204 - C205	120(2)
C305 - C310	1.41(3)	C204 - C205 - C206	122(2)
C306 - C307	1.38(3)	C204 - C205 - C210	118(2)
C307 - C308	1.42(3)	C206 - C205 - C210	119(2)
C308 - C309	1.33(3)	C205 - C206 - C207	114(2)
C309 - C310	1.39(3)	C206 - C207 - C208	125(2)
C310 - N301	1.37(2)	C207 - C208 - C209	118(2)

Table XXX (Continued)

C311 - O312	1.24(2)	C208 - C209 - C210	118(2)
C311 - O313	1.23(3)	C209 - C210 - C205	122(1)
N301 - H301	0.92(1)	C209 - C210 - N201	119(2)
O313 - H313	1.02(1)	C205 - C210 - N201	117(1)
		C202 - C211 - O213	123(2)
		C202 - C211 - O212	124(2)
		O212 - C211 - O213	124(2)
		C302 - N301 - C310	125(2)
		H301 - N301 - C310	123(2)
		N301 - C302 - C303	118(1)
		C311 - C302 - C303	122(2)
		H301 - N301 - C302	109(1)
		N301 - C302 - C311	118(2)
		C302 - C303 - C304	120(2)
		C303 - C304 - C305	119(2)
		C304 - C305 - C306	121(2)
		C305 - C306 - C307	120(2)
		C304 - C305 - C310	119(1)
		C306 - C305 - C310	118(2)
		C306 - C307 - C308	118(2)
		C307 - C308 - C309	123(2)
		C308 - C309 - C310	118(2)
		C309 - C310 - N301	122(2)
		C309 - C310 - C305	117(2)
		C305 - C310 - N301	116(2)

TABLE XXX (Continued)

C302 - C311 - O313	114(2)
C302 - C311 - O312	115(2)
O312 - C311 - O313	129(2)
H313 - O313 - C311	94(1)

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