CORRELATION OF STRUCTURE AND EMISSION IN SOLID STATE COPPER(I) COMPLEXES; ($Cu_4I_4(CH_3CN)_2(LIGAND)_2$, LIGAND = ANILINE DERIVATIVE)

By

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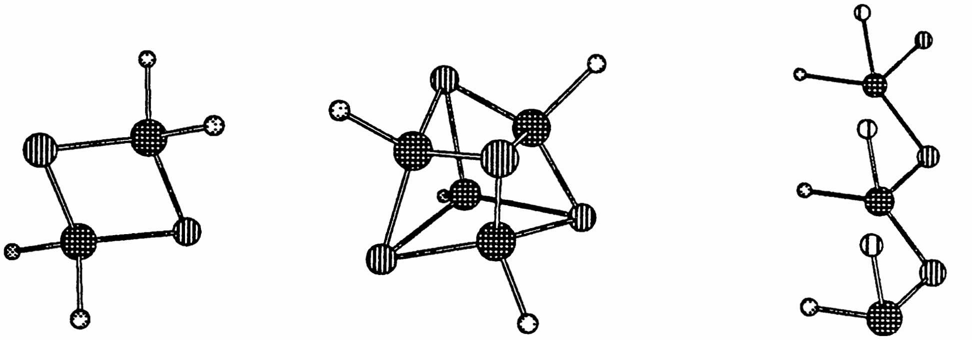
CHAPTER I

INTRODUCTION AND BACKGROUND

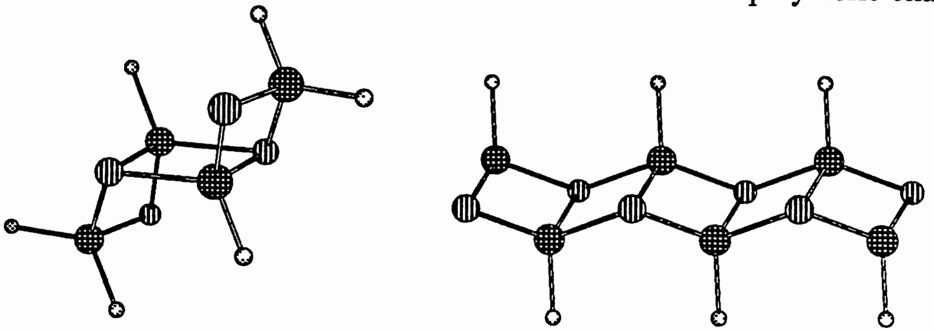
Complexes of cuprous halides and nitrogen donor ligands have been observed to display a wide variety of stoichiometries [1], structures [2, 3] and emission characteristics [4] in the solid state. There are several kinds of motifs; rhombs, chairs and cubes common for such copper(I) halide complexes. These complexes exhibit different Cu:X:L stoichiometries and may exhibit different emission properties. Stoichiometries, Cu:I:L of 1:1:0.5, 1:1:1, 1:1:1.5, 1:1:2, and 1:1:3 have been observed. Monomers may have stoichiometries of 1:1:2, or 1:1:3; rhombs of 1:1:2; chairs of 1:1:1.5 and cubes of 1:1:1. These motifs are illustrated in Figure 1.

These complexes are of interest because many of them, when excited by ultraviolet light, will emit in the visible range. This emission has potential application in the photosensitization of semiconductors. Luminescence of these complexes has been observed both in the solid state and in solution. Mechanisms related to the excitation and emission processes have been proposed to explain emission spectra. Excitation of a copper(I) halide Lewis base complex may arise from five mechanisms [5]:

1) Metal to Ligand Charge Transfer (MLCT) ----- MLCT refers to a $3d^{10}$-$3d^9\pi^*$ transition, in which an electron from the 3d orbital of the copper is excited to a π^* orbital of the ligand [6 - 8]. This transition exists in many copper(I) halide complexes with nitrogen donor ligands in which the nitrogen atom is part of an unsaturated system, such as pyridine, quinoline or acetonitrile. The emission seen for complexes, $Cu_4I_4(pyridine)_4$, at 560 nm (room temperature) [6, 9], $(CuI(quinoline)_2)_2$, at 620 nm



romb cube polymeric chain



chair polymeric pleated sheet

Figure 1. Motifis of Copper(I) Halide Complexes

[5] and Cu_4I_4(quinoline)$_4$, at 615 nm [5], were assigned to MLCT.

2) Ligand - Ligand Interaction (LLI) ----- ligand emission arising from electronic excited states derived from the ligand system. Ligand to ligand interaction is described as π - π^* transition between adjacent π systems. To observe this transition, it is necessary that the π systems of unsaturated ligands be packed in parallel fashion and close to each other so that interaction between π and π^* is possible. When Cu_4I_4(quinoline)$_4$ is cooled below 77K, its emission spectrum [10] matches that of quinoline alone in frozen ethanol solution [11]. In this complex, the ligands are lined up in parallel. Upon cooling, the separation between ligands is reduced and thus makes a π - π^* transition possible.

3) Metal - Metal Interaction (MMI) ----- d - d emission occuring from excited state essentially localized on one of two close metal ions. Metal to metal interaction was proposed for solid copper(I) halide complexes [12, 13] when the distance between two copper atoms is less than 2.6 Å. This transition may be represented as $3d^{10}3d^{10}$-$3d^{9}3d^{10}4s^{1}$ excitation. The existence of (MMI) in copper(I) clusters has also been supported by molecular orbital calculations[14]. If one considers only the 3d orbitals on Cu, interaction between two Cu atoms is repulsive as indicated by the binding energy becoming increasingly positive and the overlap population becoming increasingly negative as Cu atoms are brought closer together. However, if 4s and 4p orbitals are included in the calculation, the binding energy becomes more negative and the overlap population becomes more positive, indicating an increase in the attraction between Cu atoms.

4) Single Metal Excitation (SME) ----- has been discussed when the distance between two copper atoms is greater than 2.8 Å and, thus, interaction between two metals is unlikely. SME refers to single metal excitation and may be described as a $3d^{10}$-$3d^{9}4s^{1}$ transition. SME is considered to occur in the copper(I) complexes, Cu_4I_4(morpholine)$_4$(emits at 626 nm at room temperature) [12], and Cu_4I_4(piperidine)$_4$

(570 nm at room temperature) [15]. In these systems, no MLCT nor LLI is possible because the ligands are saturated.

5) Donor Acceptor Pair (DAP) mechanisms are operative when a ligand, I, donates an electron to the metal atom. In the systems Cu_2I_2(Lewis base)$_4$, *ab initio* calculations have shown that the HOMO orbital is dominated by iodine p orbitals whereas the LUMO orbitals are dominated by copper based p orbitals. Thus the excitation mechanism involves promotion of an electron from iodine to copper.

Luminescence of copper(I) halides was first noted in 1938 when J. T. Randall reported luminescence of the solid cuprous halides and their complexes [16, 17]. He observed that the color of luminescence changed with temperature, later to be called "fluorescence thermochromism". In the 1970's, H. D. Hardt and his colleagues published numerous papers in the field. Many complexes of copper(I) halide with Lewis bases [18 - 26], such as pyridine, pyridine derivatives, morpholine, piperidine, quinoline, pyrrolidine, etc. were synthesized and the colors of the emission of these complexes were tabulated. These authors observed that the emission of some copper(I) complexes was temperature dependent and coined the term "fluorescence thermochromism" to describe this phenomenon [19, 20]. The explanation of temperature dependent emission became an objective in research on the luminescence of copper(I) halide complexes at the time.

Weber and Hardt [25] offered the first explanation of the temperature dependent emission by comparing the powder diffraction patterns of formate, acetate, propionate, and butyrate salts of copper(I). Since these patterns seemed to have the same general motif for all of the carboxylate structures, differences in thermochromicity were thought to result from packing differences. These authors proposed that those carboxylates with odd numbers of carbon atoms pack more loosely than those with even numbers of carbon atoms. Tight packing was thought to give rise to thermochromic emission while loose packing resulted in non-thermochromic emission because loosely packed molecules are more likely to oscillate and to dissipate excited state energy non-radiatively.

Hardt and Gechnizdjani [26] concluded that mobility of the solid structure in the lattice could be a factor affecting thermochromicity after a study of the emission properties of copper(I) iodide hexamethylenetetraamine (HMTA) complex. They observed that the method of preparation and solvent used resulted in materials which displayed different fluorescent behavior with temperature. When the solid state structure was "tightened" by inclusion of additional HMTA or the presence of a second nitrogen base, such as pyridine, thermochromism of the complex disappeared. Their "framework hypothesis" suggested that if each copper atom in a complex has at least 1.33 ligands available, then the complex will not display thermochromism, due to the limited mobility in the lattice.

The next attempt to investigate thermochromism involved correlation of the symmetry of Cu(I) complexes with their thermochromism. Hardt and Pierre [27], and Schramm and co-workers [12, 15] suggested that the thermochromicity was related to crystallographic symmetry. After examining emission spectra of $Cu_4(py)_4(ClO_4)_4$, Hardt and Pierre concluded that the extent of the red shift of the emission peak with temperature depends more on the symmetry of the cluster than on copper-copper distances. The higher the symmetry of the cluster, the less the red shift. The reason for the red shift at lower temperature was presumed due to an increase in electronic interaction between adjacent ions (caused by short metal-metal distances) in the excited state.

Schramm and co-workers [12, 15] compared emission and crystal structures of Cu_4I_4(piperidine)$_4$, Cu_4I_4(morpholine)$_4$ and Cu_4I_4(pyridine)$_4$ and found no luminescence thermochromism in Cu_4I_4(piperidine)$_4$, which has a fourfold inversion axis (S_4) within the cubic cluster. The latter two complexes, which have a twofold axis or no symmetry element, respectively, showed luminescence thermochromism, thus authors proposed that if the point symmetry of a $(CuI)_4$ cluster is at least fourfold, thermochromism will not be observed.

To evaluate the influence of S_4 symmetry on thermochromicity as proposed by Hardt and Pierre, Rath et al [10] studied Cu_4I_4(p-tld)$_2$(acetonitrile)$_2$, (p-tld = paratoluidine) and $[Cu_2I_2$(p-ClAn)(acetonitrile)$]_2$, (p-ClAn = parachloroaniline) (II) complexes. In both complexes, the Cu_4I_4 cluster exists with mixed ligands so the existence of a S_4 internal symmetry element in the cluster is excluded. It was found that both complexes emitted yellow non-thermochromically and displayed no shift of emission maxima. But their wavelengths of maximum emission, 586 nm for (I), and 630 nm for (II), are different. One complex (I) had no internal symmetry. According to the thesis that absence of crystallographically related Cu - I bonds leads to thermochromism, it should emit thermochromically. The other complex (II) had two-fold symmetry but its emission behavior was similar to that of (I), thus, the presence or absence of a symmetry element in the cubic clusters of $(CuIL)_4$ was not the deciding factor in the thermochromicity of the systems. For these two tetrameric clusters, the average Cu···Cu separations are 2.699(3) and 2.682(7) Å respectively. Thus the two emission maxima were most likely due to metal centered interactions.

Tompkins et al [28] pursued investigation of the influences of a symmetry element on the emission of a compound. Three complexes with cubic motifs, but with different symmetry elements, were prepared. Cu_4I_4(isopropylnicotinate)$_4$ crystalizes with a S_4 symmetry element in the center of the tetramer; Cu_4I_4(phenylnicotinate)$_4$ has a twofold axis relating one-half of the cube to the other; Cu_4I_4(benzylnicotinamide)$_4$ has no symmetry element in the cube. These complexes show three different symmetry elements and thus gave the opportunity to verify the idea that symmetry can not be generally correlated with thermochromicity. It was observed that Cu_4I_4(isopropylnicotinate)$_4$ and

Cu_4I_4(benzylnicotinamide)$_4$ are thermochromic, but Cu_4I_4(phenylnicotinate)$_4$ is non-thermochromic.

Tompkins et al thought that temperature change may affect the crystal structure. Studies at both room and low temperatures represent a significant step to more complete understanding of these systems. The primary reason for low temperature studies is to observe the differences in structural details at the two extreme temperatures, especially for those complexes which emitted thermochromically. They found that the luminescence of some complexes of nicotinic acid esters and pyridine derivatives changes color at liquid nitrogen temperature (100K). A study of the Cu_4I_4(benzylnicotinate)$_4$ structure showed that both crystal structure and emission spectra changed with temperature. The room temperature crystal structure refined to an R factor of 7.3% in triclinic cell P1 bar. Data collected at liquid nitrogen temperature refined to R = 4.7%. The improvement in R factor with lowering of temperature is expected due to the decreased vibration of atoms in the solid. However a change in the geometry at copper also occured. The low temperature determination of the crystal structure shows distoration of angles about copper. This solid shows a yellow emission at room temperature and orange emission at 100K. The red shifting was suggested to correlate with the change in copper geometry.

Although crystallographic symmetry has not been previously related to thermochromicity, it may influence the wavelength of maximum emission. According to Bao et al [29], solid state symmetry may be a major factor affecting the wavelengths of maximum emission. These workers focused on the emission of copper(I) complexes due to nonligand based mechanisms only, by working with complexes containing aliphatic amines. In these systems, without ligand centered excited states, emission can only originate from metal centered electron transitions. Four systems with Cu_2I_2(ligand)$_4$ structure; Cu_2I_2(1-methylpiperazine)$_4$ (III), Cu_2I_2(4-methylpiperidine)$_4$ (IV), Cu_2I_2(3,3-dimethylpiperidine)$_4$ (V) and Cu_2I_2(3-azaspiro[5.5]undecane)$_4$ (VI) were studied. Structural details of bonding in the four clusters are identical within experimental error except for the crystallographic symmetry element present or absent within the Cu_2I_2 motif. Two of the complexes (V) and (VI) crystallize with a crystallographic center of symmetry within the Cu_2I_2 unit and emit at 650 nm when excited at 330 nm. Two others, (III) and (IV), crystallize without such a symmetry element and emit at 495-500 nm under the same conditions. The influence of crystallographic symmetry upon the wavelengths of maximum emission of the two types of solid materials is interpreted on the basis of *ab initio* calculations which suggest that the emission derives from a LUMO to HOMO transition in (III) and (IV) which is forbidden by selection rules in (V) and (VI). For (V) and (VI), crystallographic symmetry imposed upon orbital combination results in excitation to a LUMO of higher energy followed by reemission to an intermediate state and radiationless decay to the ground state. These emissions are of lower energy and thus occur at longer wavelength as observed. The same type of analysis was applied to cubic clusters which were interpreted on the basis of symmetry adapted combinations of atomic orbitals. Cu_4I_4(acetonitrile)$_2$(morpholine)$_2$, which does not have a symmetry element within the cube, shows emission at 575 nm, while Cu_4I_4(morpholine)$_4$, which has a twofold rotation axis within the cubic cluster, shows emission at 640 - 680 nm. The twofold axis in Cu_4I_4(morpholine)$_4$ raised the level of the HOMO and reduced the energy difference between HOMO and LUMO. Therefore, emission appears at a longer wavelength.

Previous studies showed that crystallographic symmetry may be a major factor affecting the wavelength of maximum emission in rhombohedral complexes, Cu_2I_2(ligand)$_4$, and in a few cases of Cu_4I_4(ligand)$_4$ cubes. The use of symmetry adapted combinations of atomic orbitals requires an initial assignment of the relative energies of Cu, I and N orbitals and permits the interaction of only one orbital per atom at a time. Furthermore the assignment of differences of energy levels are only speculative.

The energy level diagrams used by previous workers are only qualitative and the result based on them is speculative. So a more accurate way to evaluate the energy differences between molecular orbitals is needed.

The complexes Cu_4I_4(acetonitrile)$_2$(p-toluidine)$_2$ and Cu_4I_4(acetonitrile)$_2$(p-chloroaniline)$_2$ were prepared by Rath et al and were first identified in space group P1 bar and C2/c respectively. The differences in their emission spectra, λ_{max} 586 and 630 nm respectively, argued for an interpretation of the wavelength of maximum emission which derived from the symmetry of the solid state space group. However, other workers noted that the space group of Cu_4I_4(acetonitrile)$_2$(p-toluidine)$_2$ could be converted to C2/c with minor changes in the designation of observed and unobserved data [30].

A change of space group for Cu_4I_4(acetonitrile)$_2$(p-toluidine)$_2$ to that of Cu_4I_4(acetonitrile)$_2$(p-chloroaniline)$_2$ leaves open the question of the difference in wavelengths of maximum emission for the two complexes. Thus the focus of the thesis was to prepare complexes of the general type Cu_4I_4(acetonitrile)$_2$(ligand)$_2$ in which the ligand would be a substituted aniline molecule. To this end, syntheses were carried out in acetonitrile as solvent and the stoichiometries of CuI and ligand were controlled in an attempt to prepare as many complexes of this type as possible. Crystals resulting from these synthetic efforts were examined by single crystal X-ray analysis. The emission spectra of complexes identified to be of the type: Cu_4I_4(acetonitrile)$_2$(ligand)$_2$ were measured, *ab initio* calculations of energy levels in the systems with different symmetry elements were carried out, and a correlation of the symmetry of the single crystal motif with the wavelength of maximum emission was sought. This knowledge was sought to gain a better understanding of the luminescent behavior of solid state complexes and to permit an approach to the design of emitting species for use as sensitizers in commercial applications.

CHAPTER II

X - RAY CRYSTALLOGRAPHY

X-ray crystallography studies three-dimensionally crystalline substances by X-ray diffraction. A crystal is a solid which is built up of a regular arrangement of atoms, ions or molecules. This arrangement can be represented by a repeat unit or motif called the unit cell. The unit cell is defined as the smallest, three-dimensional arrangement of atoms that repeats itself throughout the crystal lattice. The geometry of a unit cell can be described by the edges of the unit cell: a, b, and c and the angles between edges: α, β and γ. The relationships between these cell edges and angles determine the crystal system to which the unit cell belongs [31].

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

Another way of categorizing crystal structures is according to the fourteen *Bravais lattices*. These categories include crystal class and face-centering or body-centering.

Atoms or molecules within a unit cell may be related to each other by symmetry elements such as glide planes, screw axes, rotation axes, inversion centers and mirrors. When all possible molecular symmetry operations, crystal classes and centering

When all possible molecular symmetry operations, crystal classes and centering possibilities are taken into consideration, there are 230 discrete structural arrangements allowed. These are known as the 230 space groups. The space group is a fundamental characteristic of a crystal and its structure.

Because the lattice of a crystal is regarded as an infinitely repeating structure, by analogy with the diffraction of light by an optical grating, crystals are capable of diffracting radiation such as X-ray which has a wavelength similar in magnitude to the interatomic separations. The diffraction of a beam of X-ray by a crystal is governed by Bragg's law:

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

where λ is the wavelength of the radiation, θ is the angle of incidence and the angle of diffraction of the X-ray beam with the set of planes diffracting, d is the perpendicular distance between the lattice planes diffracting, and n is the diffraction order. Thus, Bragg's law relates the wavelength of incoming X-ray, the distance between parallel planes of the scattering crystal, and the scattering angles at which various "reflected" beams will be observed and it defines the conditions necessary for diffraction of an X-ray beam of a fixed wavelength by a set of parallel lattice planes of interplanar spacing, d. When Bragg's law is satisfied, the diffracted beams are in phase and enforce each other constructively.

Diffraction patterns created by the diffraction of an X-ray beam by a crystal contain a certain amount of structural information. The X-ray diffraction pattern reveals the interior symmetry of the crystal and allows determination of the unit cell parameters. But the information given by the diffraction pattern is not enough for determination of the three dimensional locations of atoms in the unit cell. This task requires measurement of a complete set of diffraction intensities which depend on the identities and locations of atoms in the unit cell. Two different crystals containing two different compounds may have unit cells of the same size, shape, and symmetry; but the intensities of the diffracted beams will differ.

Using modern diffraction equipment, a photograph of the crystal is taken. The photograph provides a measure of the quality of the crystal. High crystalline quality gives rise to a photograph with many sharp diffraction spots extending well out towards the edges of the film. The photograph shows both horizontal and vertical mirror symmetry about the center of the film. A strong reflection is chosen such that $\chi > 75°$ and $2\theta < 20°$, to adjust the height of the crystal precisely. Fifteen independent reflections are then chosen from the photograph and centered to determine the optimum 2θ, ω, ϕ and χ angles for each reflection [32]. From these data, the unit cell dimensions are determined and refined by least squares procedures. Their accuracy is indicated by the errors (standard deviations) of the unit cell dimensions. If the errors are unacceptably high (>0.003 Å for cell edges or >0.03° for angles) then a fast data scan is needed to locate intense reflections with 2θ values greater than 20° which then replace old reflections of lesser 2θ values. The centering procedure is then repeated to yield a more accurate cell. At this stage the correctness of the cell chosen must be considered. In some cases a cell with greater symmetry may be found using cell vector programs NEWLAT [33] and TRACER [34]. TRACER identifies the reduced primitive cell and may indicate the presence of a cell of higher symmetry.

After the cell is chosen, a set of intensity data is collected so that the diffraction symmetry of the cell generates a complete sphere of data [35]. The minimum diffraction symmetry for a triclinic cell is 1 bar, for a monoclinic system, 2/m, and for an orthorhombic cell, mmm. Thus, it is sufficient to measure 1/8 of the available data for an orthorhombic cell, but 1/2 of the data for a triclinic cell must be measured.

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

The diffraction data is read by a computer program named BATRDN [36] and then reduced by DATRDN [37] which applies four correction factors [35]: for background, polarization, Lorentz effect, and crystal decomposition.

The correction for left and right background is calculated as follows:

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

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

where:

I_{int} = Integrated Intensity

I_{meas} = Measured Intensity

L_{bg} = Left Background

R_{bg} = Right Background

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

The reflection is considered observed if:

$$I_{int} \geq 3\sigma(I_{int}) \tag{4}$$

The measured intensities are observed to be lower than their "true" values due to several factors [38]:

1) Polarization factor ----- the perpendicular and parallel components of the incident beam are diffracted with differing efficiencies. The difference of efficiency depends upon the magnitude of the angle, θ , at which the diffraction is occurring. The unpolarized vector of the X-ray beam has a parallel component (I_{para}) and a perpendicular

component (I_{para}). The perpendicular component of the beam is diffracted with less efficiency at higher 2θ angles.

$$I_{para} = KI_o \qquad (5)$$

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

The scattered intensity of a incident X-ray beam (I) is then obtained by averaging:

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

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

$$P = (1 + \cos^2 2\theta) / 2 \qquad (8)$$

2) Lorentz factor ----- a geometric factor which reflects the fact that reflections measured at differing values of 2θ spend different amounts of time in diffraction position. When the crystal is rotated at a constant speed, reflections with low 2θ spend more time in optimum diffraction geometry than those reflections with high 2θ. The Lorentz factor (L) is given by:

$$L = (\sin 2\theta)^{-1} \qquad (9)$$

The Lorentz and polarization factors are conveniently combined in a single trigonometric expression called Lorentz-polarization factor (LP) which is given by:

$$LP = (1 + \cos^2 2\theta) / 2\sin 2\theta \qquad (10)$$

3) Absorption factor ----- as an X-ray beam passes through a crystal, its intensity is reduced by absorption. The extent of reduction by absorption depends on the path length of the beam through the crystal, the nature of the atoms in the crystal, and the wavelength of the incident X-ray beam. The factor A by which intensity is reduced , is given by:

$$A = (1 / V) \int e^{-\mu L}\, dv \qquad (11)$$

where μ is the linear absorption coefficient, L is the path length through the crystal of a beam diffracted from the volume dv, and V is the volume of the crystal [39].

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

$$D = I_{orig} / I_{ave} \qquad (12)$$

where:

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

I_{ave} = average current intensity of the std. reflection

A general expression for the corrected integrated intensity, I_{corr}, taking into account these factors, is

$$I_{corr} = I_{int} \times (LP)^{-1} \times A^{-1} \times D \qquad (13)$$

where I_{int} is the integrated intensity.

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

$$|F_{hkl}| = K_s (I_{corr})^{1/2} \qquad (14)$$

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

$$\sigma F = (1/2)(k/LP)^{1/2} [N_t + N_{rbg} + N_{lbg} + (0.01 N_{pk})^2] / (N_t - N_{lbg} - N_{rbg})^{1/2} \qquad (15)$$

where:

N_t = no. of counts

N_{lbg} = no. of left background counts

N_{rbg} = no. of right background counts

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

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

$$|F_{hkl}| = [(A_{hkl})^2 + (B_{hkl})^2]^{1/2} \qquad (16)$$

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

$$B_{hkl} = \Sigma f_j \sin 2\pi (hx_j + ky_j + lz_j) \qquad (18)$$

$$F_{hkl} = A_{hkl} + iB_{hkl} = |F_{hkl}| e^{i\alpha(hkl)} \qquad (19)$$

$$\alpha = \tan^{-1} (B/A) \qquad (20)$$

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

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

$$\rho (xyz) = (1/Vc)\sum\sum\sum_{h,k,l} F_{hkl} e^{-i\phi} \qquad (21)$$

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

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

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

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

and Friedel's law:

$$F_{hkl} = F_{-h-k-l} \qquad (22)$$

(21) becomes

$$\rho (xyz) = (2 / V_c) \sum\sum\sum_{h,k,l} |F_{hkl}| \cos [2\pi(hx + ky + lz) - \alpha] \qquad (23)$$

where:

ρ (xyz) = the electron density at some point x y z in the cell

V_c = unit cell volume

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

α = phase angle

Thus, to obtain a three dimensional electron density map, one needs to know amplitudes of the structure factors and their phases. However, only the structure factor, F_{hkl}, may be measured directly from the experiment. The phase, α, is not directly measurable [35]. One must derive α either from values of A and B that are computed from known structures, or by purely analytical methods. The problem of determining the phase angles so that a trial structure can be constructed is known as "the phase problem" in crystallography [31, 35, 40, 41, 42].

Two methods, namely, direct methods and Patterson methods, have been developed to solve the phase problem. The Patterson method consists of evaluating a Fourier series for which only the indices and the $|F_{hkl}|^2$ value of each diffracted intensity are needed; these quantities are directly derivable from the experiment. A function, P (u, v, w), known as the Patterson function, is defined as [40]:

$$P(u, v, w) = 1 / V_c \sum\sum\sum_{k,k,l} |F_{hkl}|^2 \cos 2\pi (hu + kv + lw) \qquad (24)$$

It can also be expressed as:

$$P(u, v, w) = V \iiint \rho(xyz)\, \rho(x+u, y+v, z+w)\, dxdydz \qquad (25)$$

If any two atoms in the unit cell are separated by a vector (u, v, w), then there will be peak in the Patterson map at (u, v, w). Therefore the orientation and length of every interatomic vector in the structure is represented in the Patterson map. This function is always centrosymmetric and defines a map which gives interatomic distances plotted from the origin. Since the height of a Patterson peak is proportional to Z_jZ_k, where Z_j and Z_k are atomic numbers of atoms j and k, respectively, so only vectors formed between heavy atoms (with larger atomic numbers) are clearly visible in the map. Using the general equivalent positions of the space group of the crystal, coordinates of heavy atoms may be derived [34], and thus the method is also called the heavy atom method.

Direct methods, which were developed later than the Patterson method, have now become an important technique of solving crystal structures, because direct methods can be used for structures with and without heavy atoms. The name " direct methods " stems from the fact that the phases of the structure factors are directly derived from the magnitudes of the $|F_{hkl}|^2$. These methods use analytical techniques for deriving an approximate set of phases from which a first approximation to the electron density map can be calculated. Interpretation of this map may then give a suitable trial structure.

The logic and principle of these methods may be understood as follows: The electron density in a real crystal can never be negative anywhere and the electron density consists of discrete spherically symmetric atoms. For centrosymmetric structures, with each atom at x, y, z, matched by an equivalent atom in the structure at -x, -y, -z, the phase angle can only be either 0° or 180°. This can be illustrated by substituting A and B values in (20). In other words, $\cos\alpha = +1$ or -1 and $\sin\alpha = 0$. Therefore, $|F_{hkl}| \cos\alpha = F_{hkl} = +|F_{hkl}|$ or $-|F_{hkl}|$, because of this, the word "sign" is frequently used to speak of the sign of a structure factor, which can either be +1 or -1. In this situation, (23) can be simplified as:

$$\rho (xyz) = (2 / V_c) \sum_{h,k,l}\sum\sum \pm |F_{hkl}| \cos 2\pi (hx + ky + lz) \qquad (26)$$

where the equation takes a positive sign when $\alpha = 0°$, and a negative sign when $\alpha = 180°$ for a given structure factor. Thus, the electron density map may be calculated from (26) when the signs of structure factors are known. The sign determination, therefore, is a key step in getting a trial structure in direct methods. The number of signs for a data set with N reflections is 2N, a very large number. How to determine the signs of a significant number of reflections is a problem that direct methods addresses.

There exist relationships among the signs, which means that signs or relative phases can be determined from a few known phases. These relationships are illustrated by the so-called Sayre equation [42, 43]:

$$s\,(\,h_1, k_1, l_1\,) \cdot s\,(\,h_2, k_2, l_2\,) \approx s\,(\,h_1 + h_2, k_1 + k_2, l_1 + l_2\,) \qquad (27)$$

which is also known as triple product sign relationship, where s is "sign of", $\approx$ means "is probably equal to", s (h, k, l) is $F_{hkl} / | F_{hkl} |$ and is either + or -, and (h_1, k_1, l_1), s (h_2, k_2, l_2), and ($h_1 + h_2, k_1 + k_2, l_1 + l_2$) are reflections with high | E | values. This triplet product sign relationship can be used to expand the number of phases. If two of the signs in the equation are known, the third can be deduced form the equation. For example, if the signs of 802 and 162 are each +1, then 964 is generated by the combination of 802 and 162 and its sign will be positive:

$$s\,(\,964\,) \approx s\,(\,802\,) \cdot s\,(\,162\,) = (\,+1\,) \cdot (\,+1\,) = +1$$

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

$$s\,(\,964\,) \approx s\,(\,900\,) \cdot s\,(\,064\,)$$

$$s\,(\,964\,) \approx s\,(\,113\,) \cdot s\,(\,851\,)$$

The triplet relationship allows determination of only a limited number of signs. To generate more signs, it is necessary to assign symbolic signs (a, b, etc.) to certain reflections and generate the signs of other reflections in terms of these symbols with the hope that eventually the signs of these symbols may become clear. Thus the signs of more reflections can be determined in a symbolic way. It is often possible to derive phases for almost all strong reflections.

The probability concepts associated with these sign relationships are very important, because the higher the probability for a triple product is, the more reliable the sign will be. The probability that a triplet product is positive is [40]

$$P_+(\,hkl\,) = 1/2 + (1/2)\tanh\,[\,(\,\sigma_3/\sigma_2^{3/2}\,)\alpha'] \qquad (28)$$

where α' is given by

$$\alpha' = |\,E_{hkl}\,|\,\sum_{h'k'l'} E\,(\,h', k', l'\,)\,E\,(\,h-h', k-k', l-l'\,) \qquad (29)$$

and σ_n by $\qquad \sigma_n = \Sigma\,Z_j^n \qquad (30)$

and Z_j is the atomic number of the jth atom. $|E_{hkl}|$ is called the normalized structure factor. It is defined as:

$$|E_{hkl}|^2 = |F_{hkl}|^2 / \Sigma\,f^2_i\,. \qquad (31)$$

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

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

After a significant number of phases is known, an E-map, which is an electron density map, is calculated with $|\,E\,|$ values rather than $|\,F\,|$ values (so that atoms are sharper, corresponding to point atoms):

$$\rho\,(\,xyz\,) = (\,2 / V_c\,)\,\Sigma\Sigma\Sigma\;\pm|E_{hkl}|\,\cos 2\pi\,(\,hx + ky + lz\,) \qquad (32)$$

From the E-map, a trial structure can be obtained, but sometimes only part of the structure is revealed.

For noncentrosymmetric structures, additional formulae may be used to derive approximate values for the phase angle. The phase angle can take any value between 0 and 2π. The so-called tangent formula [34, 38]

$$\tan \phi_H \approx \frac{< | E_K || E_{H-K} | \sin (\phi_K + \phi_{H-K}) >_K}{< | E_K || E_{H-K} | \cos (\phi_K + \phi_{H-K}) >_K} \qquad (33)$$

is used extensively to calculate and also to refine phases for noncentrosymmetric structures, where, $H \equiv h, k, l$, $K \equiv h', k', l'$, ϕ is the phase angle of the structure factor, and the brackets refer to an average over all values of K, where $H = (K) + (H - K)$. Just as (27) is the key formula for phase determination in the centric case, the tangent formula is the formula for phase determination in the acentric case.

Whether a structure is centrosymmetric or noncentrosymmetric should be determined at the very beginning of the structure solution. A list of $| E |$ values is prepared using (31). By analyzing of the statistical distribution of $| E |$ values, one can determine if the structure is centrosymmetric or not. This is important if there is an ambiguity in the space group determined from systematically absent reflections. The mean value of $| E |$ is 0.798 for a centrosymmetric structure and 0.886 for a noncentrosymmetric structure.

There are very well developed direct methods computer programs, namely NMULT, MMULT, EMULT, SMULT [44], to accomplish the tasks. When the positions of at least some atoms have been determined by direct or Patterson methods, the correctness of the model is judged by the " residual factor ", R_f, which is defined as:

$$R_f = (\Sigma | | F_{obs} | - | F_{cal} | |) / (\Sigma | F_{obs} |) \qquad (34)$$

A least-squares refinement is performed at this stage to improve atomic positions and obtain a better R factor. The least squares program compares the observed structure amplitudes to the calculated values. Then the atomic parameters of the calculated structure factors are altered so that the least squares fit improves.

The difference Fourier synthesis allows location of missing atoms:

$$\Delta\rho (xyz) = (2 / V_c) \sum\sum\sum_{h,k,l} (| F_{obs} | - | F_{cal} |)\cos [2\pi (hx + ky + lz) - \phi_c] \quad (35)$$

where $$\phi_c = \tan^{-1} [B_c'(hkl) / A_c'(hkl)] \quad (36)$$

$A_c'(hkl)$ and $B_c'(hkl)$ are the real and imaginary components, respectively, of the calculated structure factor, F_{cal}, which can be calculated from (16), (17), (18) with a known structure (a partially known structure, such as a trial structure, or a completely known structure) with atoms j at known positions x_j, y_j, z_j. With an increasing number of atoms found, refinement is repeated. The locations of hydrogens are determined last from the difference Fourier map if the intensity data is good. Otherwise, hydrogen positions are calculated according to specific geometry. As the model approaches completion, the difference between F_{obs} and F_{cal} is expected to be small and R_f is low. For an acceptable solution to a structural problem, the R factor is normally between 3 - 10%.

The thermal vibration of the atom, which is expressed in the temperature factor or thermal parameter, has the effect of spreading the electron cloud over a larger volume. The temperature factor causes the decrease in the atomic scattering factor as 2θ increases. The scattering factor for an atom at rest is given by the expression:

$$\exp [-B_{iso} (\sin^2\theta) / \lambda^2] \quad (37)$$

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

$$\exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl) \qquad (38)$$

where b_{ij} is the individual anisotropic thermal parameter.

When all atoms have been located and the R factor reaches a minimum, the refinement should be considered complete. At this stage, a difference Fourier map phased with final parameters for the refined structure should reveal no fluctuations in electron density greater than those expected on the basis of the estimated precision of the electron density.

Finally, tables of positional parameters, anisotropic thermal parameters, bond distances and angles, and a table showing the final F_{obs} and F_{cal} structure factors are formulated. A projection view of the molecule is prepared showing atoms as ellipsoids of 90% probability. These data contain much information about the structure. The bond type, atomic hybridization and electron location, etc., can be interpreted from bond angles and lengths. Furthermore, molecular conformations can also be considered with analysis of torsion angles. Intermolecular distances can be calculated. These may indicate the presence of hydrogen bonds and warns when two molecules are unusually close (an indication either of an unexpected intermolecular interaction or of an incorrect structure). Analysis of the individual anisotropic thermal parameters of molecules in crystals sometimes reveals patterns of molecular motion, which can frequently be correlated with the shape of the molecule and the nature of its surroundings in the crystal.

CHAPTER III

LUMINESCENCE

Luminescence is a process by which visible radiation is emitted by molecules or atoms that have been excited by the absorption of electromagnetic radiation. The wavelength of the electromagnetic radiation absorbed is characteristic of the particular luminescent material. There are many types of luminescence categorized according to the different input energies which can excite luminescent materials [45]. Photoluminescence uses photons or light, often U.V., for excitation; electroluminescence uses electrical energy input; cathodoluminescence uses cathode rays of electrons to provide energy; chemiluminescence results from energy supplied by a chemical reaction.

The excitation and emission process can be illustrated with Figure 2. A molecule has only discrete energy levels or energy states. When the electrons of a molecule occupy the orbitals of lowest energy, the molecule is said to exist in the ground state. States of higher energy are called excited states. In the ground state each electron is paired with another. Such a state is called a singlet state and given the symbol S. When an energy of a frequency within a normal absorption band of the molecule is absorbed, one of the the paired electrons is raised to an upper excited singlet state, S_1 or S_2. The excited singlet state persists for a finite time of the order of 10^{-8} to 10^{-4} sec. During this time interval any absorbed energy in excess of the lowest vibrational energy level of the first excited state is rapidly dissipated. Dissipation of vibrational energy may involve transfer of energy by intermolecular collisions or by partition of vibrational energy to other modes of rotation and vibration within the molecule until the lowest vibration level of the excited singlet

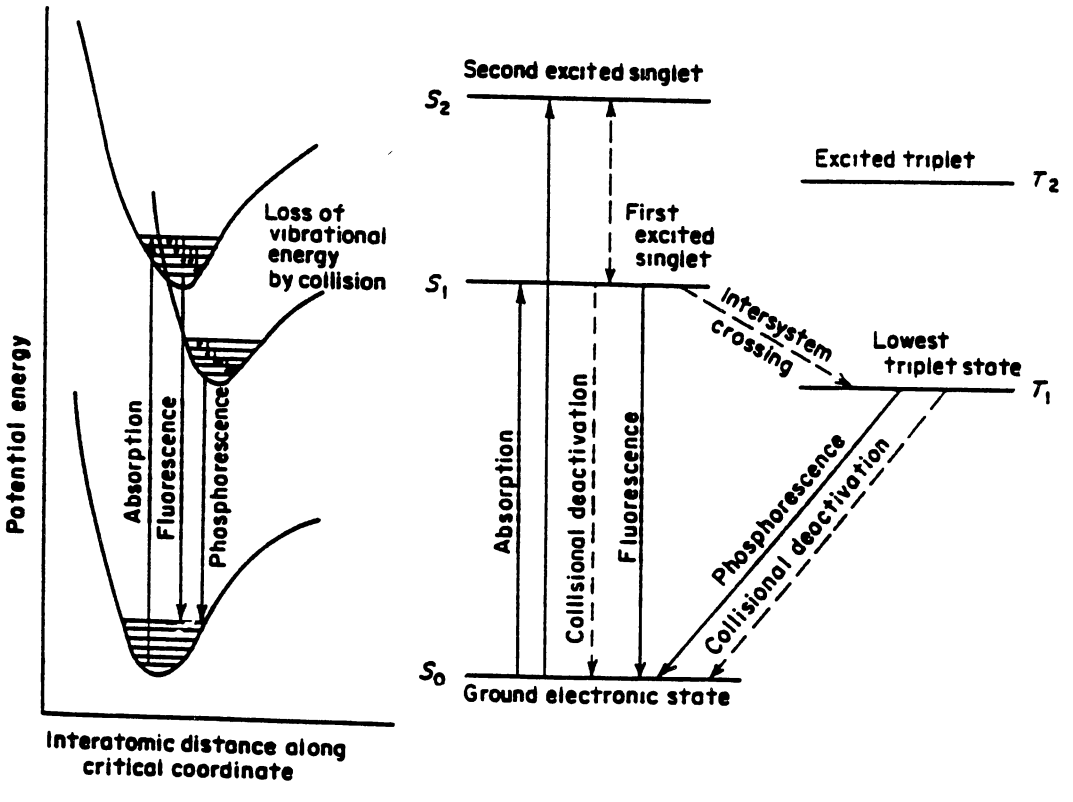


Figure 2. Ground and Excited State Potential Energy Diagram for a Luminescent Center

state S_1 is attained. There are two possible pathways for a molecule to return to the ground state from the lowest vibrational state, S_1. This can occur either by direct return to the ground state or passing through the lowest triplet state, T_1, and then to the ground state. In a triplet state, each electron occupies a different orbital and is aligned with unpaired spins. The emission from the excited singlet state to the ground state is called fluorescence. In fluorescence, the states from which the emission originates and terminates have the same multiplicity (multiplicity is given by the term $2S + 1$ where S is the spin quantum number, multiplicity is 1 for a singlet state, and 3 for a triplet state.). If an emission results from nonradiative decay to an intermediate triplet state, and then radiative decay to the ground state, such an emission is called phosphorescence. In phosphorescence, the multiplicities of the states from which the emission originates and terminates differ.

The time during which a molecule remains in an excited state before it returns spontaneously, with light emission, to a lower state, is called the lifetime of the excited lower energy level. The lifetime of fluorescence is 10^{-8} seconds or less [46]. Therefore, it is impossible for the eye to perceive fluorescence once the source of the excitation has been removed. Phosphorescence persists for a period of time when excitation is discontinued. The lifetime of phosphorescence is usually between 10^{-6} to 100 seconds.

The luminescence of a material is usually studied using a fluorometer which measures the light emitted at right angles to the path of the incident or excitation beam. A typical fluorometer consists of three basic components: a source of radiation, a sample cell, and a detector. A scheme showing the essential components of a fluorometer is indicated in Figure 3 [47].

The radiation source is commonly a mercury or xenon arc lamp; bright and powerful sources of ultra - violet radiation. The mercury lamp has the advantage of giving radiation with very high intensity, however, it has a less continuous spectrum than a

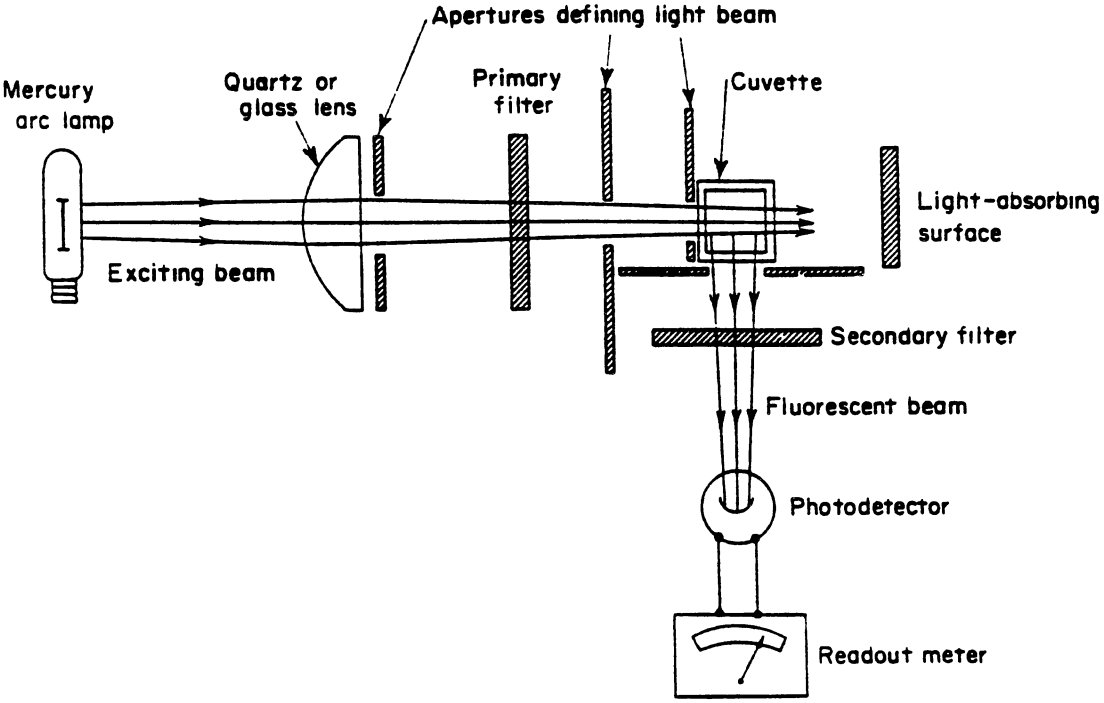


Figure 3. Schematic Diagram of a Typical Fluorometer

xenon arc lamp. A xenon arc lamp gives radiation with lower intensity and produces a small number of lines in the 4000 Å and 6600 - 8000 Å region. These may result in errors in high resolution work but have little effect on low resolution studies. Radiation sources are cooled by water or forced air to avoid overheating.

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

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

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

An experimental arrangement for the determination of an emission spectrum is shown schematically in Figure 4. The output is normally recorded on magnetic media, floppy disk, tape, meter or strip recorder. The data are corrected for irregularities in source lamp intensity, monochromator response and background, then plotted as intensity against wavelength.

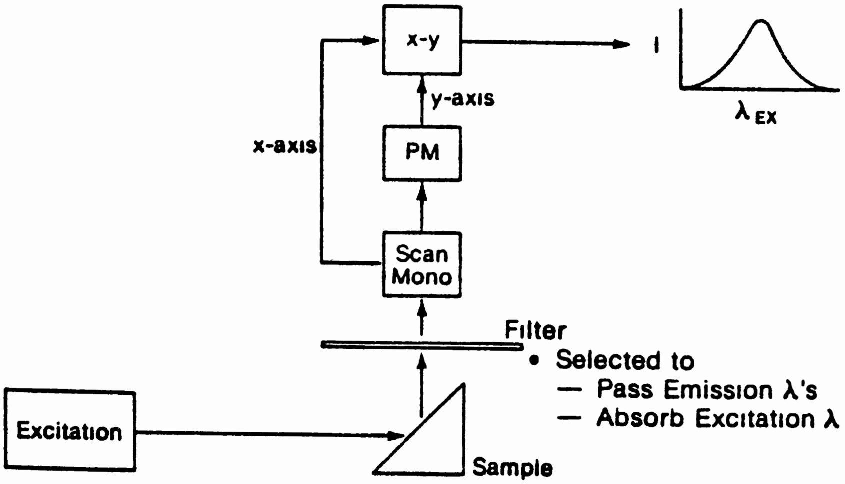


Figure 4. An Experimental Arrangement for Recording the Emission Spectrum of a Phosphor

CHAPTER IV

EXPERIMENTAL

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

Synthesis of the Copper(I) Complexes. $Cu_4I_4(CH_3CN)_2(ligand)_2$.

Cu_4I_4(acetonitrile $)_2$(o-ethylaniline $)_2$:

0.48 g (2.5 m mol) of CuI was dissolved in 30 ml acetonitrile. 5 ml of o-ethylaniline was added to the mixture. The mixture was allowed to react under reflux for four hours, filtered and cooled to room temperature. The filtrate was cooled to about -5°C. Colorless crystals formed. The dry crystals luminesced bright yellow at room temperature. Due to the unstable nature of crystals in the absence of the mother liquor, liquid paraffin was put on the crystals to guard against decomposition. A crystal was mounted on a glass fiber and then coated with glue.

Cu_2I_2 (acetonitrile $)_2$(2-amino-6-methylpyridine $)_2$:

To the solution (0.27 g, 2.5 m mol) of 2-amino-6-methylpyridine in 30 ml acetonitrile, 0.48 g (2.5 m mol) of CuI was added. The resulting mixture was refluxed for four hours and then filtered. The filtrate was allowed to cool to about -5°C. Colorless crystals formed after forty-eight hours. The crystals did not luminesce at room temperature. Liquid paraffin was coated onto the crystal surfaces after separation from the mother liquor. A crystal was sealed in a capillary tube which was pre-saturated with vapor of the mother liquor. The m.p. of crystals was 98-102 °C .

Cu_2I_2 (acetonitrile)$_2$(p-anisidine)$_2$:

0.48 g (2.5 m mol) of CuI and 0.35 g (2.5 m mol) of p-anisidine were added to 30 ml of acetonitrile. The mixture was refluxed for four hours and cooled to room temperature. The solution was filtered. Light yellow cubic crystals formed after the filtrate had been cooled for forty-eight hours. No emission was observed at room temperature, but the crystals luminesced orange at liquid nitrogen temperature. The m.p. of the crystals was 120-128°C. The crystals were unstable in air so a paraffin coating was used to avoid decomposition. A crystal coated with paraffin was mounted on a glass fiber and then coated with epoxy.

Cu_2I_2 (acetonitrile)$_2$(2,6-diaminopyridine)$_2$:

0.28 g (2.5 m mol) of 2,6-diaminopyridine was dissolved in 30 ml acetonitrile and 0.48 g (2.5 m mol) of CuI was added. The resulting solution was refluxed for four hours and allowed to cool. After filtration, light yellow needlelike crystals formed. The crystals did not luminesce under UV light at room temperature. A crystal coated with paraffin was mounted on a glass fiber and then sealed with epoxy. The m.p. of the crystals was 185-192°C.

Cu_4I_4(acetonitrile)$_2$ (6-ethyl-o-toluidine)$_2$:

0.48 g (2.5 m mol) of CuI was dissolved in 30 ml acetonitrile. 5 ml of 6-ethyl-o-toluidine was then added to the mixture. The resulting solution was refluxed for four hours. The solution was filtered. Colorless crystalline plates formed when the filtrate was cooled to about -5°C. Light yellow emission was observed at room temperature. A crystal coated with paraffin was mounted in a capillary tube which was filled with nitrogen gas.

Cu_4I_4 (acetonitrile)$_2$(o-toluidine)$_2$:

0.48 g (2.5 m mol) of CuI was dissolved in 30 ml acetonitrile and 5 ml of o-toluidine was added. The mixture was stirred for twenty-four hours under a nitrogen atmosphere and then filtered. The filtrate was allowed to cool to about -5°C. Colorless needlelike crystals formed. The crystals luminesced orange at room temperature. A crystal coated with paraffin was mounted in a capillary, which was pre-saturated with vapor of mother liquor. The m.p. of crystals was 120-130°C (decomp).

Cu_4I_4 (acetonitrile $)_2$(p- toluidine $)_2$:

To a mixture of 0.48 g(2.5 m mol) of CuI in 30 ml acetonitrile, 0.48 g (5 m mol) of p-toluidine was added with stirring, and the resulting mixture heated under reflux in a nitrogen atmosphere for three hours. The light brown solution was allowed to cool to room temperature under a nitrogen atmosphere and then cooled to -5°C for forty-eight hours whereupon light brown rhombohedral crystals formed. The crystals luminesced bright yellow at room temperature. A crystal coated with paraffin was mounted on a glass fiber and then coated with epoxy.

Cu_4I_4 (acetonitrile $)_2$(2,6-dimethylaniline $)_2$:

5-10 ml 2,6-dimethylaniline was added to a U-tube. One of the two open ends of the tube was sealed with a plastic wrap after nitrogen gas had been used to flush the space over the liquid. 0.48 g (2.5 m mol) of CuI was dissolved in 30 ml acetonitrile and the mixture was filtered. The filtrate was added very slowly by pouring gently down the wall of the other arm of U-tube. Precipitation was observed on the boundary face between two solutions upon the addition of the filtrate. Filtrate was added until the solution was about 5-6 cm high above the boundary line. Nitrogen gas was used to flush air from the space over the liquid level and the opening was sealed. Yellow needlelike crystals were observed after one day. These crystals increased in size with time. The crystals were noticed to luminesce bright yellow at room temperature. A crystal coated with paraffin was mounted on a glass fiber and then sealed with epoxy. The m.p. of crystals was 100-105°C.

Crystallography. Crystals with appropriate dimensions (≤ 1.5 mm in all directions) of all compounds were chosen for X-ray diffraction. The 0.2 mm quartz capillary tubes were used to protect unstable compounds from air and moisture. A Syntex P3 automated diffractometer was utilized with molybdenum radiation. Unit cell dimensions were determined by least-squares refinement of the best angular positions for fifteen independent reflections ($2\theta > 15°$). Data were collected using a θ - 2θ scan mode, a variable scan rate and a maximum 2θ of 60.0°.

Fluorescence. Emission spectra of all compounds were measured using an Oriel modular spectrofluorometer. The sample was prepared as a finely ground powder spread on double-sided tape attached to a 0.5 × 1.5 inch glass plate. A Xe lamp was used as the light source. Measurements were made from 350 - 700 nm at 0.2 nm intervals with a scan speed of 1 nm/sec at temperatures: 10, 25, 50, 75, 125, 175, 225 and 275K. Data were corrected for inhomogeneities of monochromator performance and window transmission before plotted. Intensity scales are in arbitrary units due to lack of standardization of sample preparation.

CHAPTER V

RESULTS AND DISCUSSION

During the course of this research, eight different complexes of copper(I) with iodine and aniline derivatives were prepared (two of them were from pyridine derivatives), six Cu_4I_4 cubes of formula: Cu_4I_4(acetonitrile)$_2$(ligand)$_2$ and two rhombs: $Cu_2I_2(CH_3CN)_2$(2-amino-6-methyl-pyridine)$_2$, Cu_2I_2(2,6-diaminopyridine)$_2$. The preparation of a sufficient group of Cu_4I_4(acetonitrile)$_2$(ligand)$_2$ complexes permitted focus on this group in an effort to correlate structural and emission properties. The preparation of a group of mixed ligand complexes lessened the chances for crystallographic disorder in the unit cell and insured that only mirror and two fold symmetry elements might occur. Threefold axes, 4 bar and centers of symmetry may not occur.

The Cu_4I_4(acetonitrile)$_2$(ligand)$_2$ complexes crystallized in three ways. $Cu_4I_4(CH_3CN)_2$(2,6-dimethylaniline)$_2$, $Cu_4I_4(CH_3CN)_2$(o-ethylaniline)$_2$, $Cu_4I_4(CH_3CN)_2$(o-toluidine)$_2$ crystallized in space group P1 bar with no symmetry element relating atoms of the cubic motif. $Cu_4I_4(CH_3CN)_2$(p-anisidine)$_2$ and $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ crystallized in versions of space group C2/c in which a two fold axis passes through two opposite faces of the cube relating atoms at opposite corners of those faces (Figure 16). $Cu_4I_4(CH_3CN)_2$(6-ethyl-o-toluidine)$_2$ crystallized in the space group Pnam with a mirror plane passing through two opposite edges of the cube. Two copper atoms, two iodide atoms and the atoms of the two CH_3CN ligands lie on the mirror. Two remaining copper atoms and two remaining iodide atoms and the atoms of the 6-ethyl-o-toluidine ligand are paired by the mirror plane.

A tabulation of space group, symmetry within the cubic cluster and bond angles and distances is shown in Table I. Details of $Cu_4I_4(CH_3CN)_2$(p-chloroaniline)$_2$, prepared during earlier work in this laboratory have been included for comparison. Complete crystallographic data and results for all complexes prepared in this study are presented in Tables VII-LI.

Coordination of copper atoms in the Cu_4I_4(acetonitrile)$_2$(ligand)$_2$ complexes is tetrahedral with each copper atom bound to three iodine atoms and the electron pair donating nitrogen atom of a ligand. Cu-I distances average 2.686(6)Å in the complexes. I-Cu-I angles average 112.6(2)° and N-Cu-I angles average 106.1(10)°. As seen in Table I, structural details at copper atoms show only slight deviation from these averages. Cu-Cu distances in the Cu_4I_4(acetonitrile)$_2$(ligand)$_2$ complexes range from 2.682(7) to 2.726(13)Å. While these distances are at the limit of the interactive range suggested by Hoffman [14], they are long compared to the 2.564(12)Å seen in Cu_4I_4(quinoline)$_4$ where Cu···Cu interaction has been postulated. Thus within the group of Cu_4I_4(acetonitrile)$_2$(ligand)$_2$ complexes there are no outstanding crystallographic differences between complexes with and without symmetry elements present in their solid state forms.

Emission spectra for the Cu_4I_4(acetonitrile)$_2$(ligand)$_2$ complexes were measured over the temperature range 10 to 298K. An excitation wavelength of 300 nm was used as previous studies in this laboratory have shown the excitation spectra of copper(I) halide complexes to be broad and featureless. Emission spectra were recorded in the visible range from 350-700 nm using a long pass filter to screen out radiation of the excitation wavelength scattered by the sample. Data were corrected for monochromator response,

TABLE I

COMPARISON OF SPACE GROUP, BOND DISTANCES AND BOND ANGELS FOR 6 COMPLEXES*

Comp. Code	Sym- metry	Space group	Cu···Cu ave.(Å)	Cu - I ave.(Å)	Cu - N ave.(Å)	Cu - I - Cu ave.(°)	I - Cu - I ave.(°)
1	---	P1bar	2.706(8)	2.687(6)	2.11(4)	60.5(2)	112.6(2)
2	---	P1bar	2.707(5)	2.687(4)	2.03(2)	60.5(1)	112.6(1)
3	---	P1bar	2.710(9)	2.691(8)	2.03(4)	60.5(2)	112.6(2)
4	---	P1bar	2.695(3)	2.685(2)	2.02(1)	60.2(1)	112.7(1)
5	2	A2/a	2.716(4)	2.674(4)	2.02(2)	60.6(1)	112.4(1)
6	2	C2/c	2.694(3)	2.686(2)	2.02(1)	60.2(1)	112.8(1)
7	2	C2/c	2.682(7)	2.690(6)	2.06(4)	59.5(2)	113.0(2)
8	m	Pnam	2.726(18)	2.686(13)	1.96(10)	61.0(4)	111.9(4)

Complexes:

1. $Cu_4I_4(CH_3CN)_2$(2,6-dimethylaniline)$_2$
2. $Cu_4I_4(CH_3CN)_2$(o-ethylaniline)$_2$
3. $Cu_4I_4(CH_3CN)_2$(o-toluidine)$_2$
4. $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ -triclinic
5. $Cu_4I_4(CH_3CN)_2$(p-anisidine)$_2$
6. $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ -monoclinic
7. $Cu_4I_4(CH_3CN)_2$(p-chloroaniline)$_2$
8. $Cu_4I_4(CH_3CN)_2$(6-ethyl-o-toluidine)$_2$

* --------------- $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ has been refined in two different space groups: triclinic (4) and monoclinic (6).
The data for $Cu_4I_4(CH_3CN)_2$(p-chloroaniline)$_2$ is taken from the reference [10].

and for inhomogeneities of transmission of the emitted beam at various wavelengths. The wavelengths of maximum emission along with their symmetry are tabulated in Table II. Individual spectra are reproduced in Figures 6-19.

All spectra show an increase of intensity at lower temperatures as compared to room temperature.

MLCT charge transfer between Cu and the acetonitrile ligand is expected to occur in the 400 - 450 nm range as observed by previous workers [10]. All spectra show some evidence of broad but weak intensity in this region. However this emission is not the dominant feature of the spectra. All spectra show a dominant emission band near 570 or near 610 nm.

$Cu_4I_4(CH_3CN)_2$(2,6-dimethylaniline)$_2$ and $Cu_4I_4(CH_3CN)_2$(o-ethylaniline)$_2$ crystallize in space group P1 bar and show emission at 560 - 580 nm both at RT and at low temperature. $Cu_4I_4(CH_3CN)_2$(6-ethyl-o-toluidine)$_2$ crystallizes in space group Pnam with a mirror symmetry element present within the cube and shows maximum emission at 568 nm.

The three complexes which crystallize in the identical space groups A2/a or C2/c offer some confusion: $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ shows a dominant emission at 572 nm at RT and 602 nm at LT, but the compound was previously reported to emit at 584 nm and to show no change in wavelength of maximum emission [10]. $Cu_4I_4(CH_3CN)_2$(p-chloroaniline)$_2$ shows emission at 575 nm in this work compared with 628 nm reported by the same workers [10]. $Cu_4I_4(CH_3CN)_2$(p-anisidine)$_2$ showed only the lower energy emission at 608 nm at both ends of the temperature scale.

Finally, $Cu_4I_4(CH_3CN)_2$(o-toluidine)$_2$ which crystallizes in space group P1 bar, shows only the low energy emission at 630 nm LT and 612 nm at RT.

Inhomogeneities of sample preparation and length of time at low temperature or length of time enduring excitation were explored for the complexes crystallizing in space

TABLE II

CELL DIMENSIONS, SYMMETRY AND MAXIMUM WAVELENGTH FOR COMPLEXES OF $Cu_4I_4(CH_3CN)_2(LIGAND)_2$

Ligand	Cell Dimension	Space Group	Symmetry	Maximum Wavelength
2,6-dimethylaniline	a = 12.449(3)Å b = 14.108(6) c = 10.606(4) α = 73.46(3)° β = 95.00(2) γ = 73.42(3)	P1 bar	none	568(LT & RT)nm
o-ethylaniline	a = 12.224(2)Å b = 14.073(5) c = 12.198(4) α = 114.32(2)° β = 87.85(2) γ = 68.45(2)	P1 bar	none	575(LT & RT)nm
o-toluidine	a = 12.212(3)Å b = 14.599(5) c = 10.245(6) α = 66.18(4)° β = 86.00(4) γ = 72.47(2)	P1 bar	none	630(LT),612(RT)nm
p-toluidine	a = 16.325(7)Å b = 23.293(14) c = 7.576(3) α = 90.0° β = 92.25(3) γ = 90.0	C2/c	$\underline{2}$	602(LT),572(RT)nm

TABLE II (Continued)

p-anisidine	a = 20.032(10)Å b = 7.863(1) c = 18.715(9) α = 90.0° β = 101.56(4) γ = 90.0	A2/a	2	608(LT & RT) nm
p-chloroaniline	a = 15.952(6)Å b = 23.714(11) c = 7.596(3) α = 90.0° β = 92.00(3) γ = 90.0	C2/c	2	575(LT & RT) nm
6-ethyl-o-toluidine	a = 14.976(6)Å b = 21.187(6) c = 12.545(2) α = 90.0° β = 90.0 γ = 90.0	Pnam	m	568(LT & RT) nm

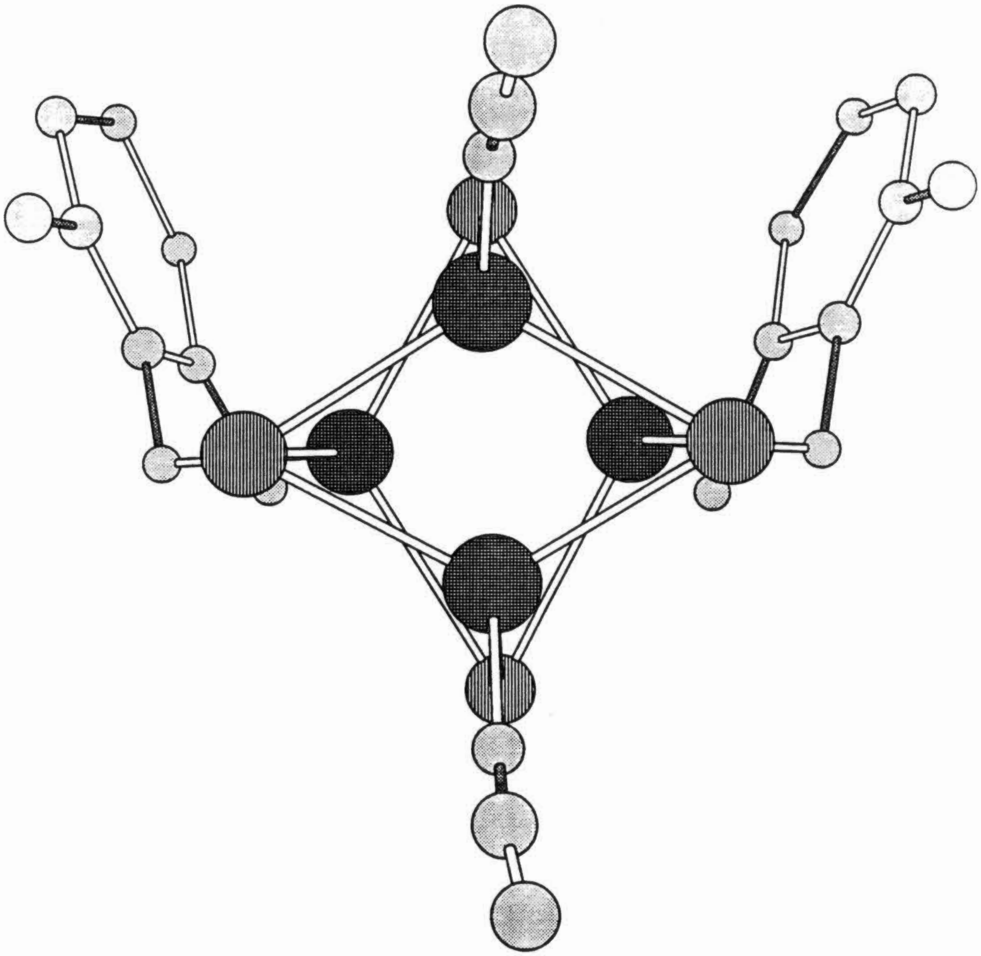


Figure 5. Projection View of $Cu_4I_4(CH_3CN)_2$(2,6-dimethylaniline)$_2$

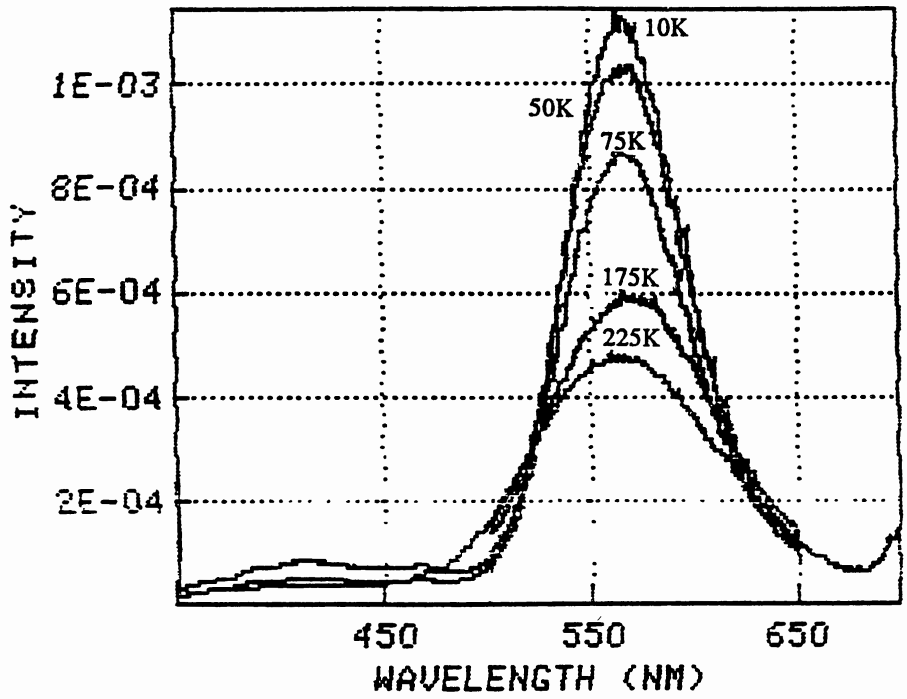


Figure 6. Emission Spectra of $Cu_4I_4(CH_3CN)_2(2,6\text{-dimethylaniline})_2$

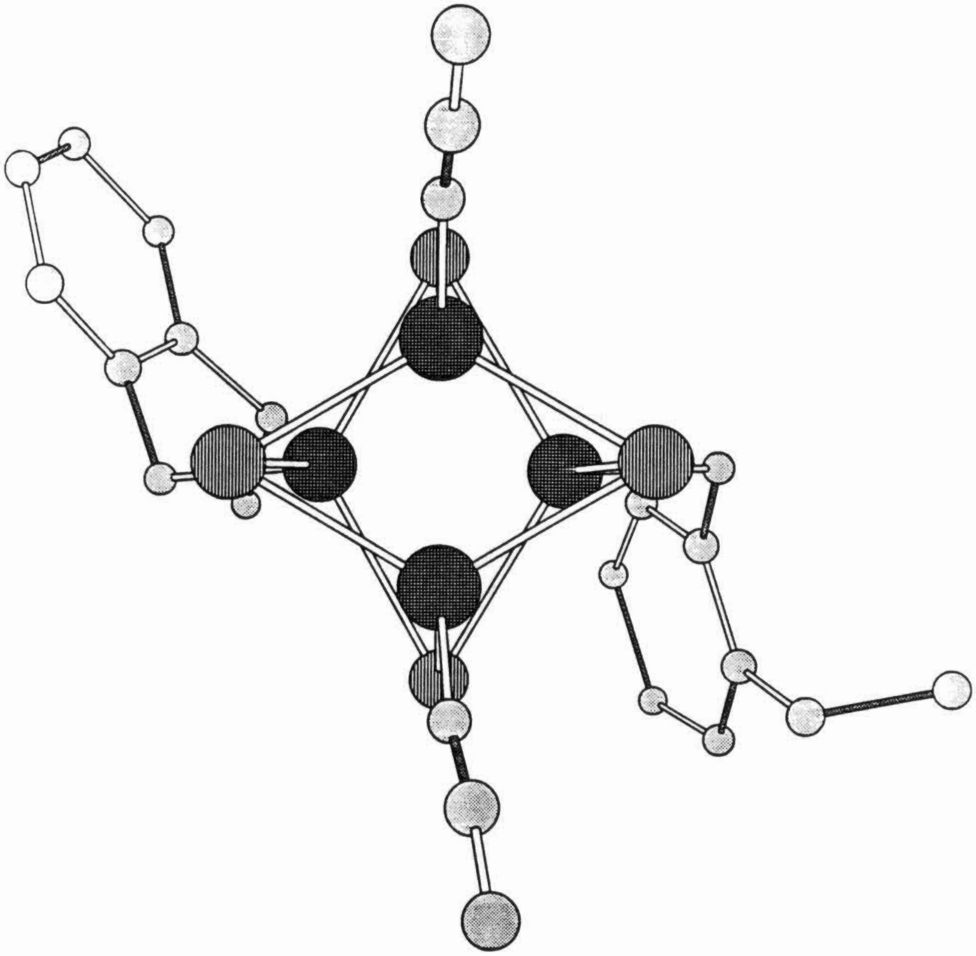


Figure 7. Projection View of $Cu_4I_4(CH_3CN)_2$(o-ethylaniline)$_2$

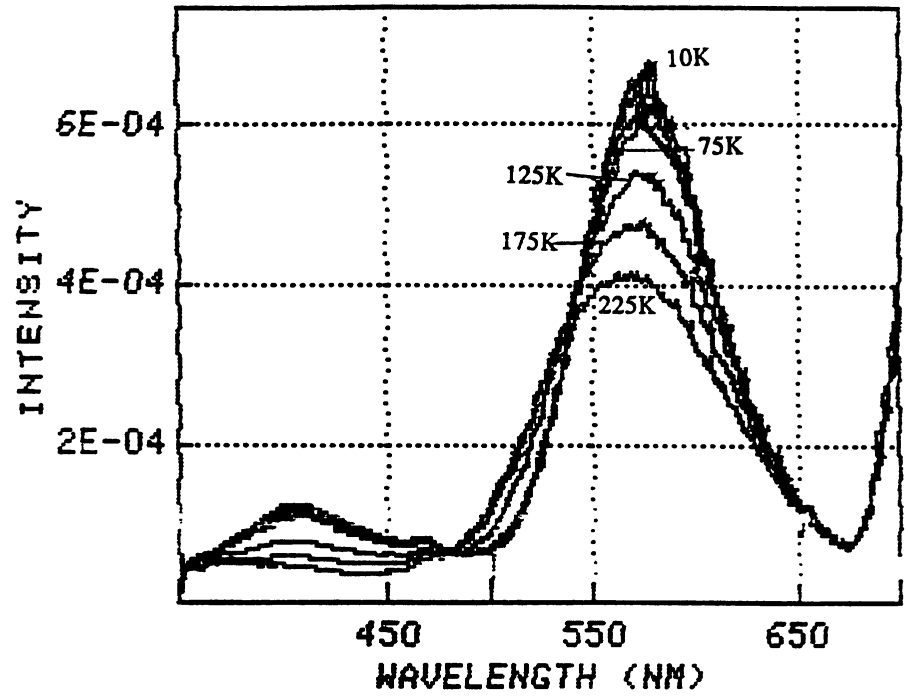


Figure 8. Emission Spectra of $Cu_4I_4(CH_3CN)_2$(o-ethylaniline)$_2$

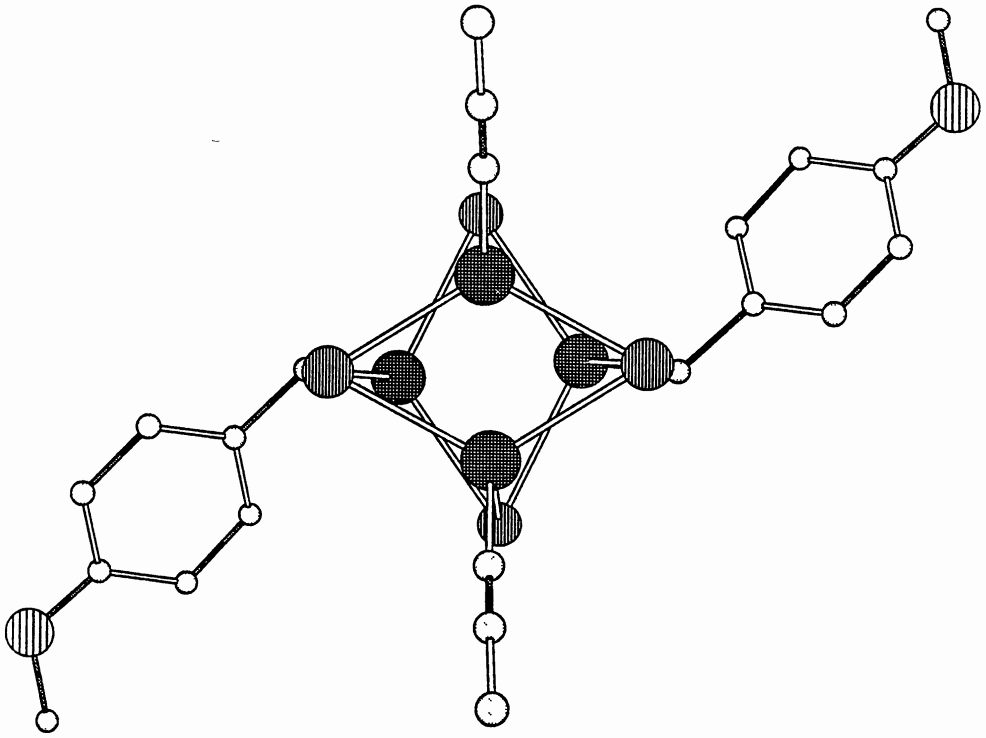


Figure 9. Projection View of $Cu_4I_4(CH_3CN)_2$(p-anisidine)$_2$

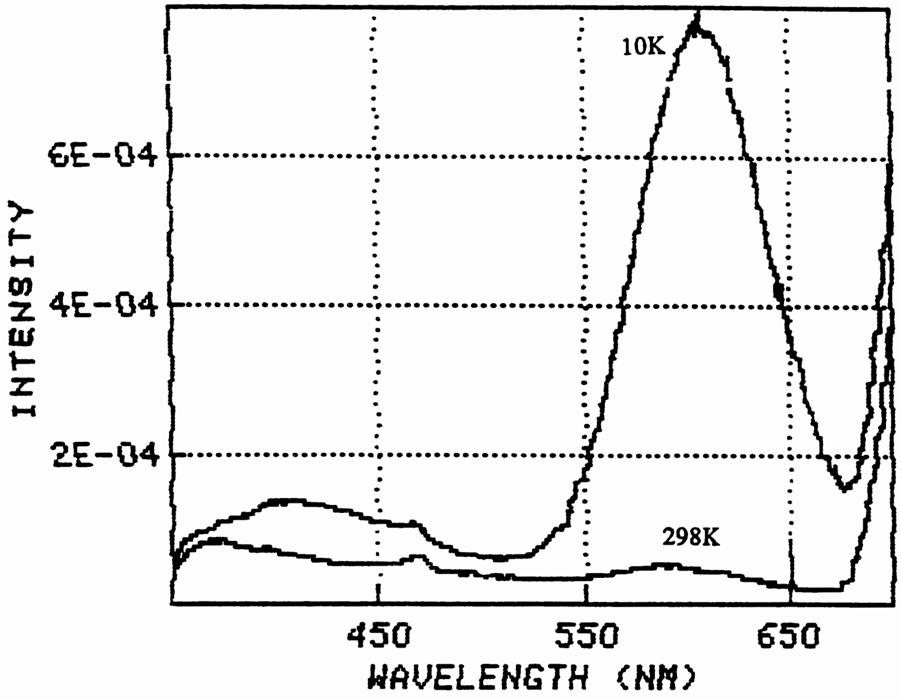


Figure 10. Emission Spectra of $Cu_4I_4(CH_3CN)_2$(p-anisidine)$_2$

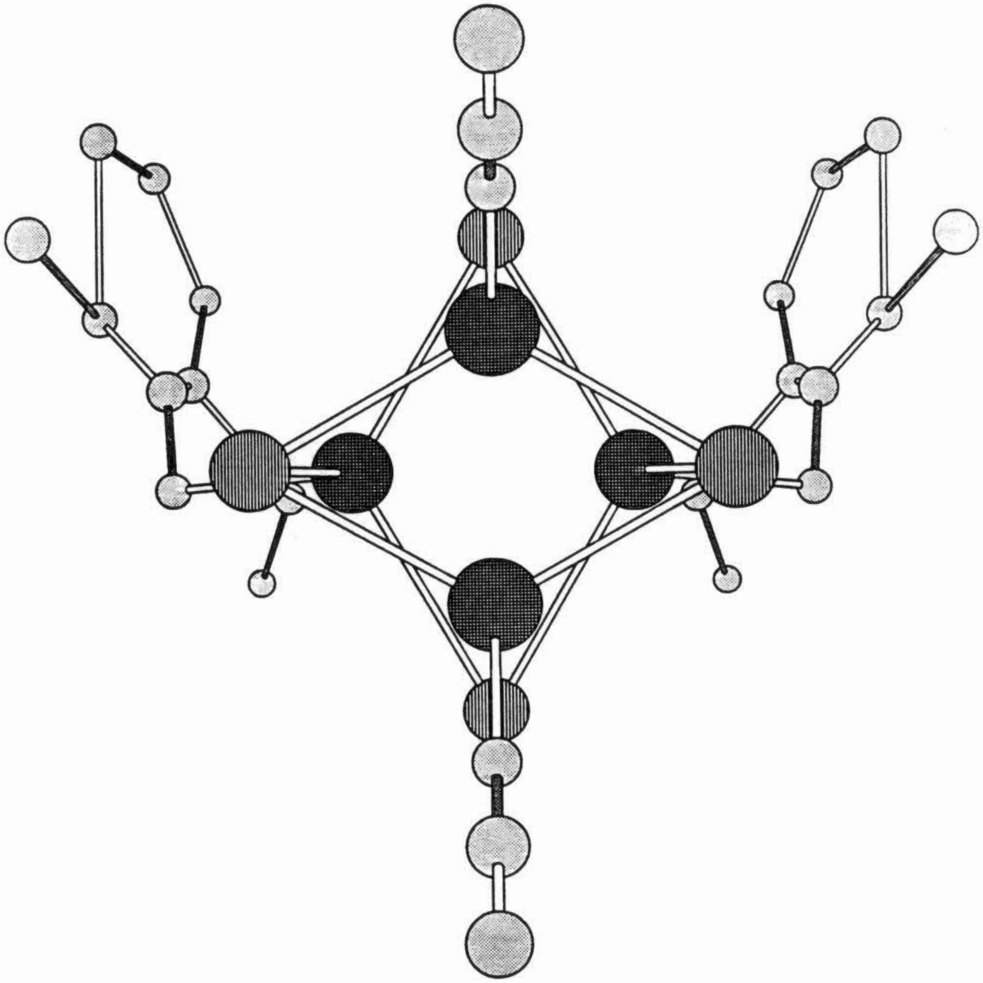


Figure 11. Projection View of $Cu_4I_4(CH_3CN)_2$(6-ethyl-o-toluidine)$_2$

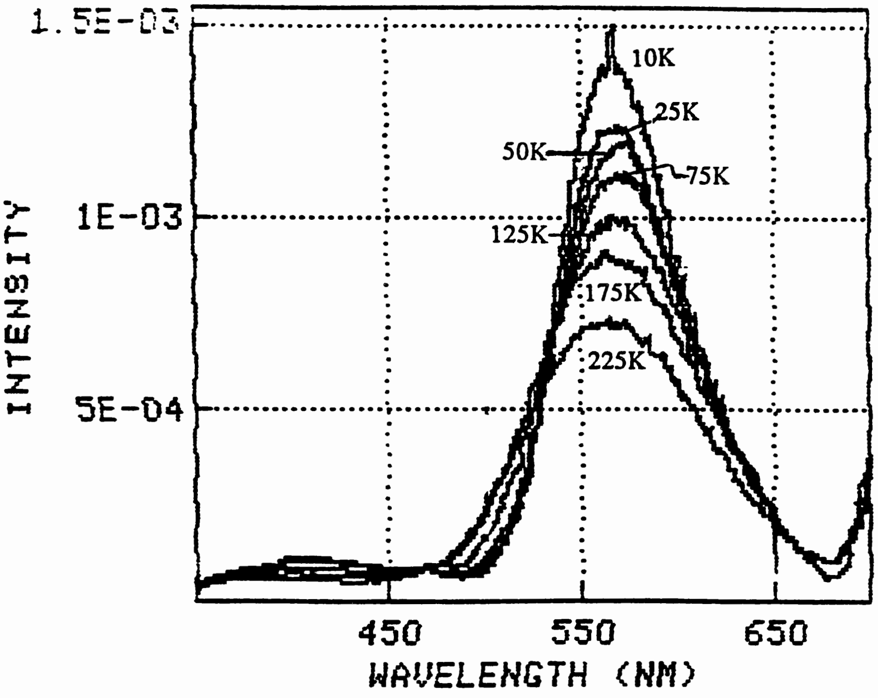


Figure 12. Emission Spectra of $Cu_4I_4(CH_3CN)_2$(6-ethyl-o-toluidine)$_2$

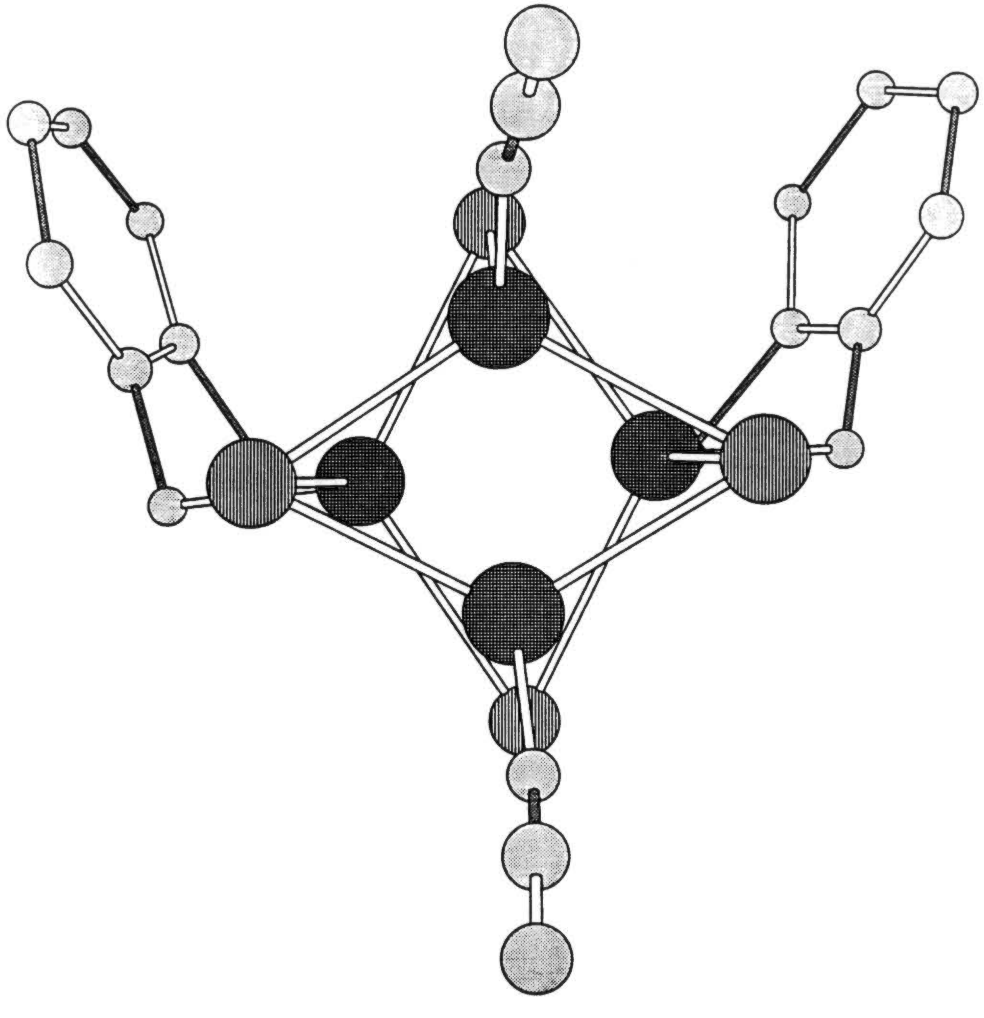


Figure 13. Projection View of $Cu_4I_4(CH_3CN)_2$(o-toluidine)$_2$

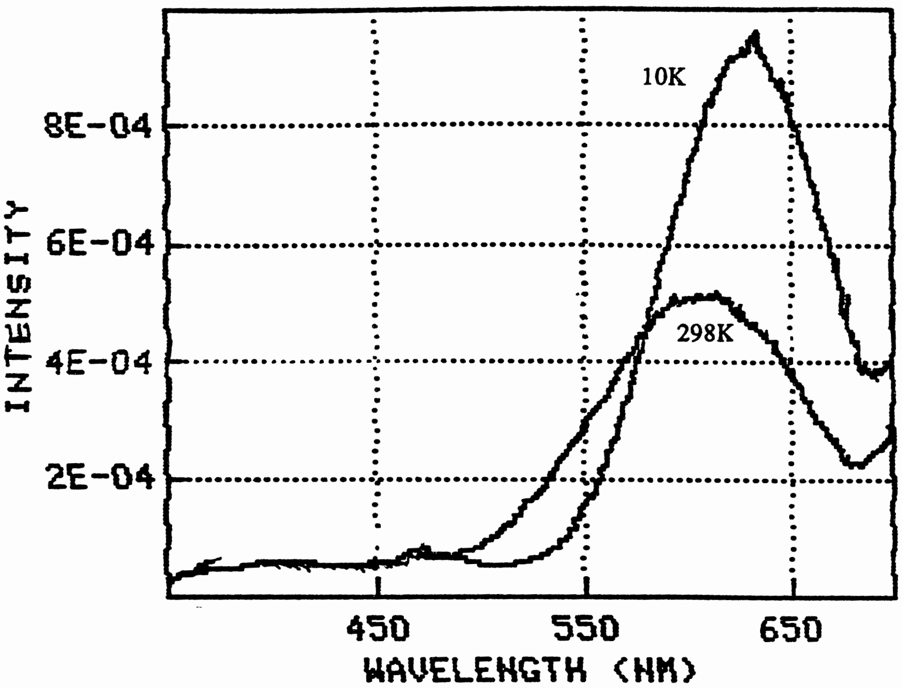


Figure 14. Emission Spectra of $Cu_4I_4(CH_3CN)_2$(o-toluidine)$_2$

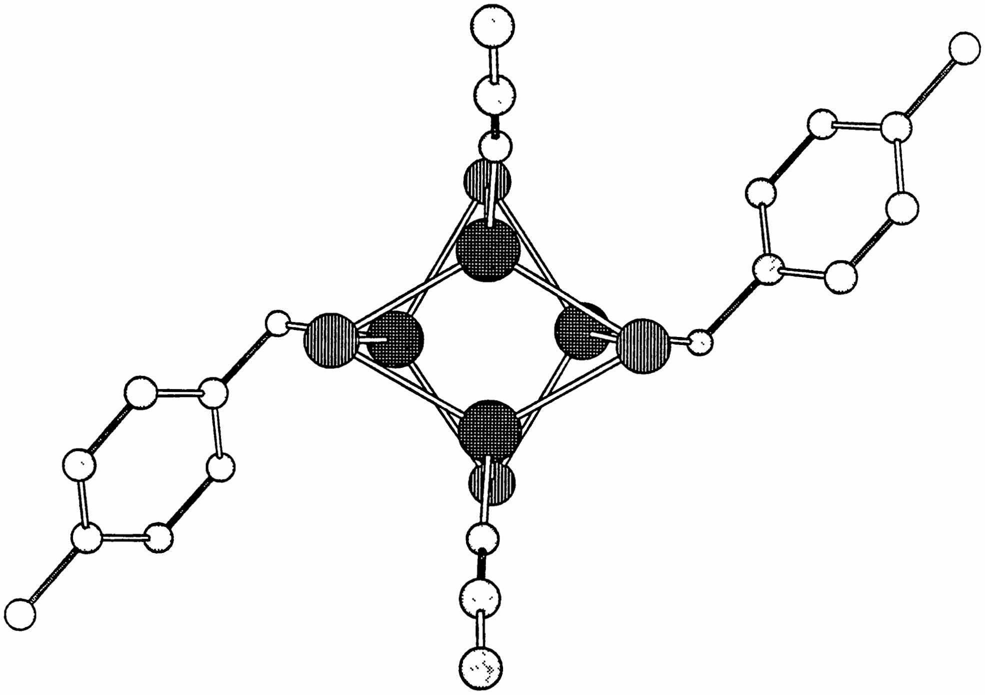


Figure 15. Projection View of $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ -triclinic

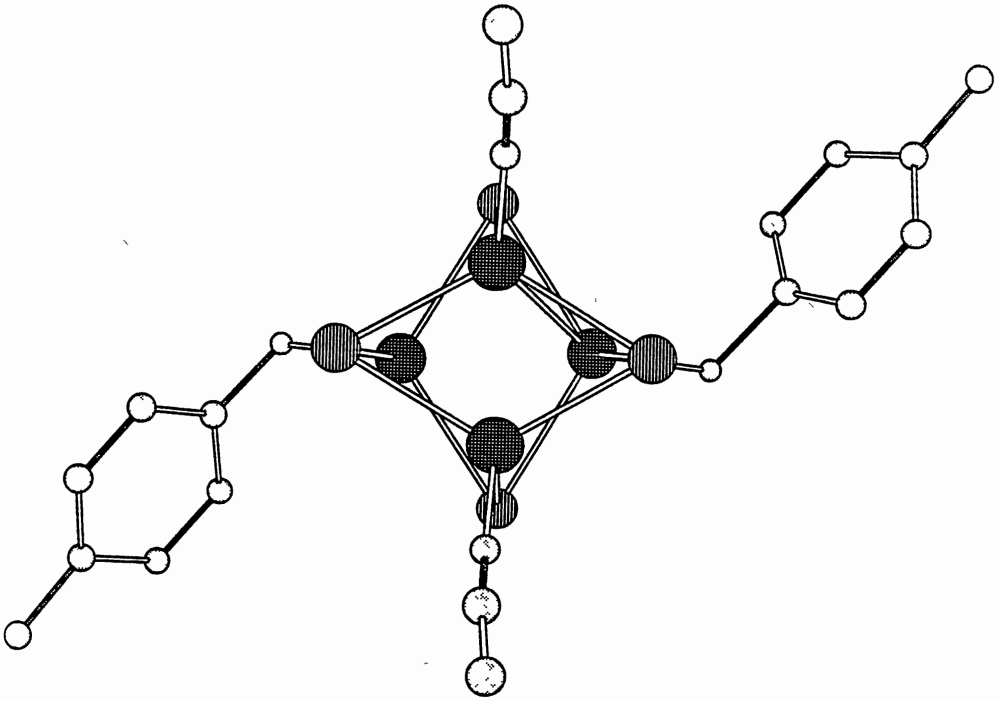


Figure 16. Projection View of $Cu_4I_4(CH_3CN)_2(p\text{-toluidine})_2$ -monoclinic

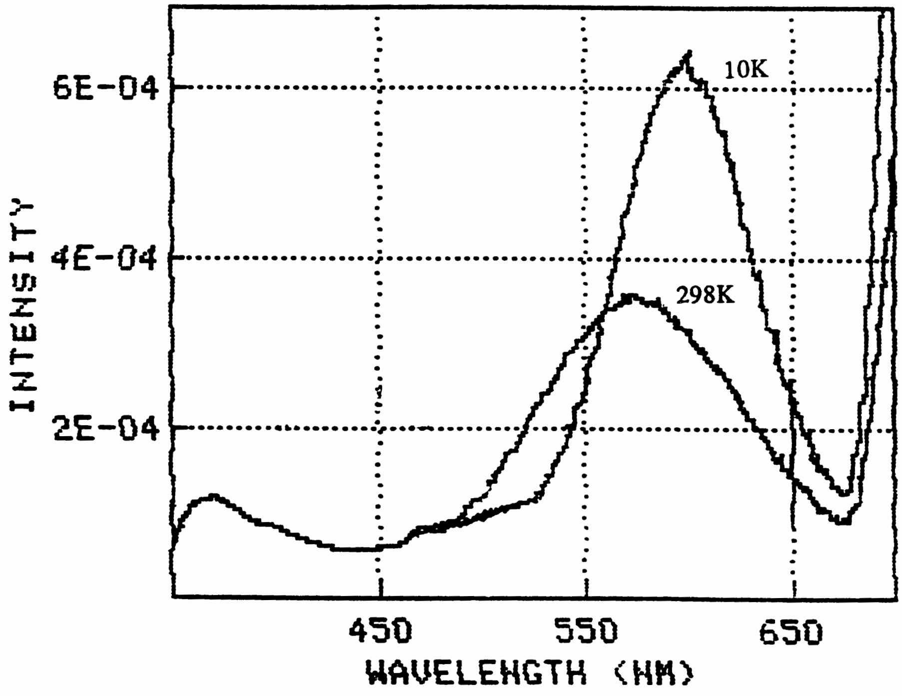


Figure 17. Emission Spectra of $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$

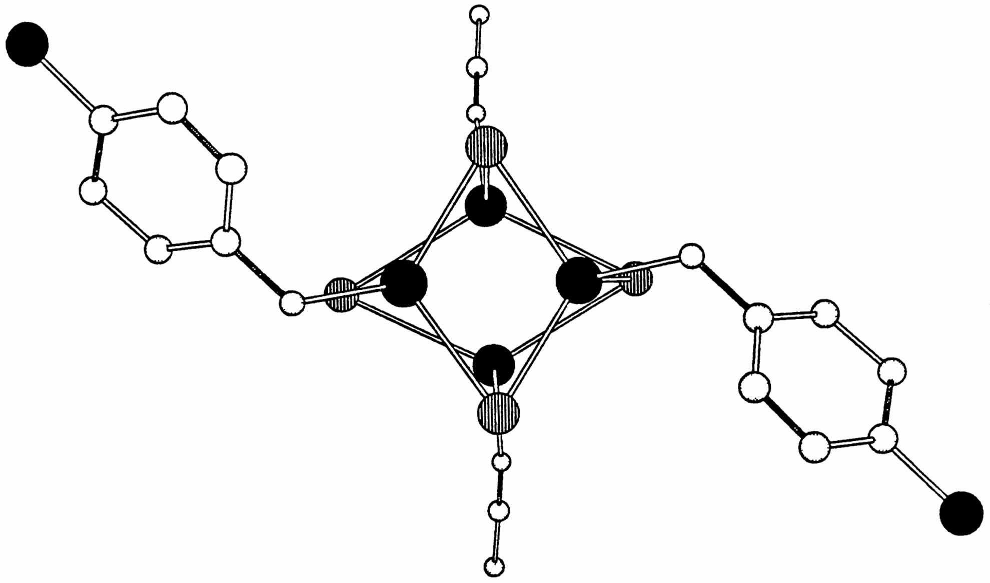


Figure 18. Projection View of $Cu_4I_4(CH_3CN)_2$(p-chloroaniline)$_2$

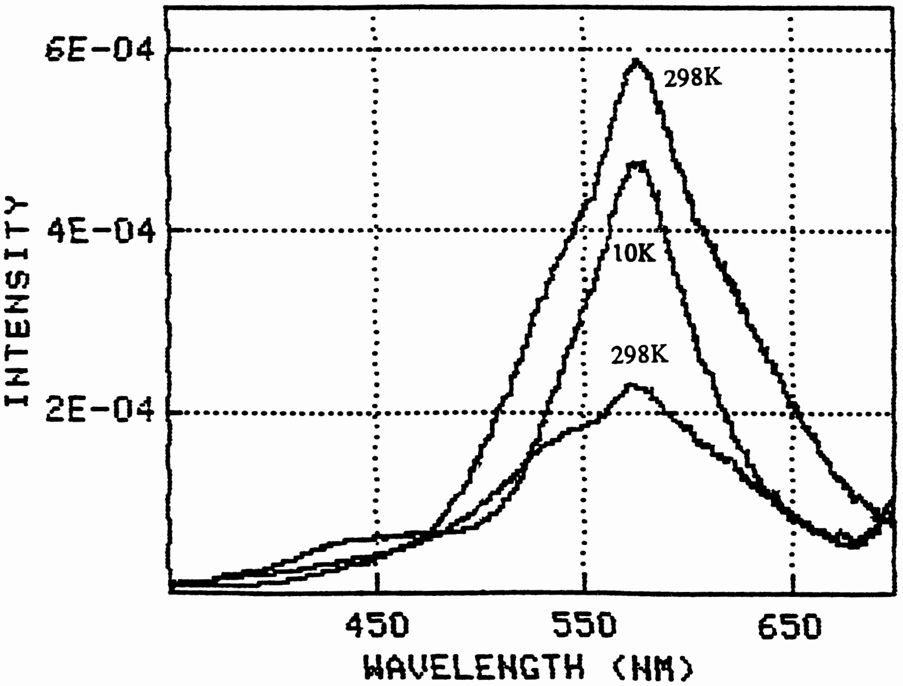


Figure 19. Emission Spectra of $Cu_4I_4(CH_3CN)_2$(p-chloroaniline)$_2$

groups A2/a or C2/c. Emission spectra of samples from several preparations of the same materials were measured. These showed identical emissions. The identities of crystalline samples of these materials were verified by comparison of unit cell dimensions to those of the crystal upon which single crystal X-ray analysis was performed. These materials are too unstable to permit measurement of a powder spectrum on the bulk sample which might be then compared with the powder spectrum calculated from the single crystal results. Crystals ground to prepare the emission sample appear homogeneous to the eye.

Samples of these complexes were placed in the sample chamber which was evacuated. A room temperature spectrum was recorded immediately thereafter. The sample was cooled and spectra were recorded as soon as the temperature reached 10K. The low temperature spectrum was remeasured repeatedly over a 3 - 4 hour period. The sample was warmed to room temperature and the emission at this temperature compared to that of the first measurement. These experiments (as illustrated by Figure 20) served to establish that the sample does not change with time during the experiment. Nor do different samples of the same material show different spectra.

Bao et al [29] used the linear combination of symmetry adapted atomic orbitals to understand the influence of crystallographic symmetry elements upon orbital energy levels. These studies however were carried out on systems which were of the type Cu_4I_4(ligand)$_4$. The cubes studied by these workers included: Cu_4I_4(3-pyrroline)$_4$(I), Cu_4I_4(hexamethyleneimine)$_4$(II), Cu_4I_4(1,2,3,6-tetramethylpyridine)$_4$(III), Cu_4I_4(morpholine)$_4$(IV), Cu_4I_4(3,5-dimethylpiperidine)$_4$(V), Cu_4I_4(piperidine)$_4$(VI). Symmetry data along with maximum wavelengths observed are summarized in Table III.

These workers explained that (IV), which is belong to the C_2 point group, emits at a longer wavelength than do (I), (II), (III), because in the case with a twofold symmetry element the energy differences between HOMO and LUMO were reduced using symmetry adapted combinations of the orbitals as compared to cases without

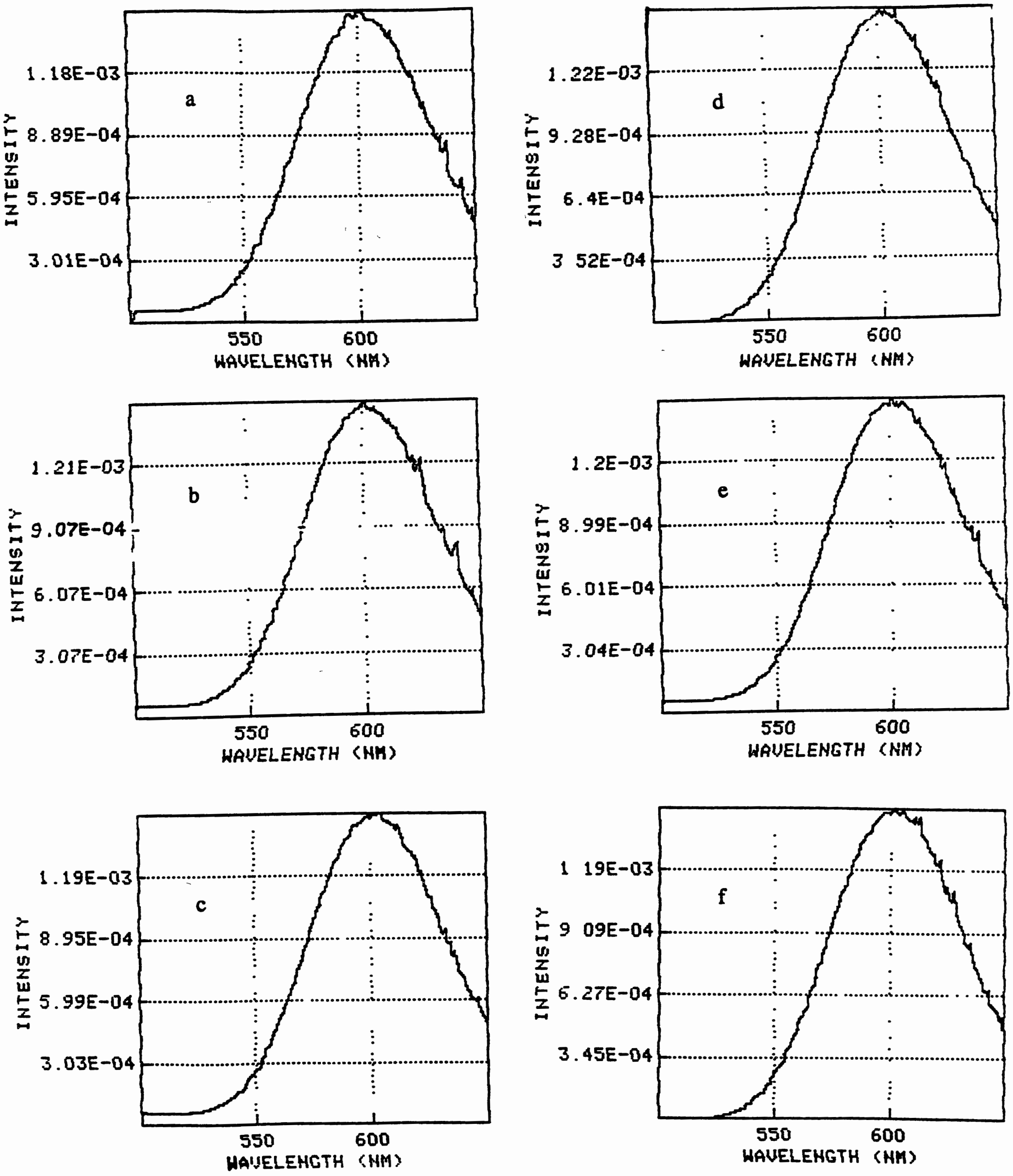


Figure 20. Emission Spectra of $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ Measured with Time at 10K
a --- start b --- 30 min later c --- 1.5 hr later
d --- 3 hr later e --- 5.5 hr later f --- 7.5 hr later

symmetry. Therefore, emission appears at longer wavelength. Compound (V) has two mirror planes and belongs to the C_{2v} point group. The dual emission was explained by a phase change occuring in the crystal as the temperature was lowered. The change in wavelength of maximum emission suggests that the molecule loses two mirrors at low temperature and changes to symmetry C_2. The emission at RT of this compound was discussed by these workers. Transition between the HOMO and LUMO is not allowed in this case because the triple product of ground state, excited state and operator is zero. The emission must originate from transition between lowest antibonding orbital to HOMO from which excitation took place. Therefore the compound emits in higher energy than (IV). Compound (VI) belongs to point group S_4 and again transition between HOMO and LUMO is forbidden based on the rules as mentioned earlier. Emission took place between the lowest antibonding orbital and the HOMO, thus appears at considerably higher energy than (IV).

TABLE III
SOME CUBIC CLUSTERS $Cu_4I_4(LIGAND)_4$ AND THEIR MAXIMUM EMISSION WAVELENGTHS [29]

Compound	Space Group	Symmetry	Maximum Wavelength (nm)
I	P1 bar	None	630
II	P1 bar	None	580
III	P1 bar	None	620
IV	B2/b	2	640 - 680
V	$P4_2$/nmc	2m	650(LT), 610(RT)
VI	$P4_2$/n	S_4	580

These studies suffer from the limitation of orbital combination to one per atom at a time and from the need for assignment of the relative atomic energy levels. In particular the assignment of the energies of the Cu orbitals relative to those of the I is not necessarily obvious.

Ab initio calculations were carried out using Gaussian 90 and the LANL1N basis set with pseudopotentials used to reduce the number of electron considered to 68. The final crystallographic coordinates for $Cu_4I_4(CH_3CN)_2$(2,6-dimethylaniline)$_2$ (no symmetry element), $Cu_4I_4(CH_3CN)_2$(6-ethyl-o-toluidine)$_2$ (mirror symmetry element) and $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ (2-fold symmetry element) were used as input data. In each case coordinates for Cu, I and CH_3CN groups were included as determined but the aniline derivative ligand was replaced by a NH_3 group with the nitrogen atom placed in the crystallographically determined position and hydrogen atom positions calculated using N-H distances of 0.97 and idealized geometry.

The results of the calculations (Tables IV-VI) show the HOMO orbital in each case to be dominated by iodine p orbitals. The LUMO orbital is dominated by p orbitals on copper. There is no significant presence of acetonitrile ligand orbitals in either HOMO or LUMO levels. Therefore, metal to ligand charge transfer interactions are not involved in emission from these complexes.This observation correlates with the expectation for earlier work, that Cu to acetonitrile excitation will result in emission near 429 nm.

The C_1, C_2 and mirror symmetry elements do not impose selection rules upon transitions between HOMO and excited state orbitals unlike C_i symmetry. The energy differences between HOMO and LUMO states for the three calculations are not interpretably different. Nor are the energies of the levels themselves calculated with a precision suitable for interpretation.

Therefore the question of the observed similarities of emission in the nonsymmetry and mirror symmetry case and the differences observed in emission from

TABLE IV

RESULTS OF *ab initio* CALCULATIONS FOR COMPOUND $Cu_4I_4(CH_3CN)_2$(2,6-dimethylaniline)$_2$

				HOMO	LUMO					HOMO	LUMO
				68	69						
EIGENVALUES --				-0.30197	0.19186	53	9	N	1S	0.00734	0.05268
1	1	I	1S	-0.00347	-0.17435	54			2S	-0.03743	-0.34451
2			2PX	0.44628	0.02311	55			2PX	0.04387	0.03457
3			2PY	0.31385	-0.02807	56			2PY	-0.01448	-0.01459
4			2PZ	-0.10520	0.26169	57			2PZ	0.04580	0.13303
5	2	I	1S	0.00293	-0.26037	58	10	N	1S	0.00774	0 04606
6			2PX	0.17902	-0.33159	59			2S	-0.03956	-0.29962
7			2PY	0.18915	-0.31362	60			2PX	0.03398	0.00595
8			2PZ	-0.02532	0.03178	61			2PY	-0.00827	0.00790
9	3	I	1S	-0.00177	-0.17853	62			2PZ	-0.05542	-0.12448
10			2PX	0.43778	-0.02511	63	11	N	1S	0.00597	-0.00090
11			2PY	0.31288	0.03119	64			2S	-0.03320	0.01043
12			2PZ	-0.01987	-0.27003	65			2PX	0.00190	-0.02556
13	4	I	1S	0.00380	-0.25051	66			2PY	0.03136	-0.00275
14			2PX	0.52608	-0.06395	67			2PZ	-0.00156	0.01280
15			2PY	0.16634	0.43372	68	12	N	1S	-0.01930	-0.00151
16			2PZ	-0.07028	0.00082	69			2S	0.10631	0.01677
17	5	Cu	1S	0.00340	0.33794	70			2PX	0.07241	-0.00038
18			2PX	-0.00884	0.58743	71			2PY	0.03188	0.03072
19			2PY	0.00842	-0.19857	72			2PZ	-0.00389	-0.00296
20			2PZ	0.01062	-0.01802	73	13	C	1S	-0.00231	-0.00065
21			3D 0	0.01254	-0.00964	74			2S	0.00521	0.00216
22			3D+1	0.04805	0.01432	75			2PX	0.02365	0.08839
23			3D-1	-0.13644	-0.00129	76			2PY	0.00062	0.02843
24			3D+2	-0.02764	-0.02895	77			2PZ	-0.00313	-0.01926
25			3D-2	0.07034	0.02481	78	14	C	1S	0.00048	-0.00549
26	6	Cu	1S	0.00494	0.34068	79			2S	-0.00085	0.03136
27			2PX	-0.00228	0.51197	80			2PX	-0.00701	0.02102
28			2PY	0.00944	-0.18296	81			2PY	0.00021	0.00731
29			2PZ	-0.00582	-0.06084	82			2PZ	0.00103	-0.00379
30			3D 0	0.03909	-0.00839	83	15	C	1S	0.00674	0.00004
31			3D+1	-0.02454	-0.00644	84			2S	-0.02093	0.00331
32			3D-1	0.11105	-0.00968	85			2PX	-0.02655	0.01239
33			3D+2	-0.01261	-0.03219	86			2PY	0.02834	-0.13524
34			3D-2	0.09879	0.02087	87			2PZ	-0.00707	0.00420
35	7	Cu	1S	0.01011	0.26281	88	16	C	1S	-0.00180	-0.00134
36			2PX	-0.04040	-0.32660	89			2S	0.00627	0.00812
37			2PY	-0.01871	-0.35016	90			2PX	0.01200	0.00433
38			2PZ	0.00684	0.06800	91			2PY	-0.00431	-0.02194
39			3D 0	-0.19723	0.04966	92			2PZ	0.00149	0.00036
40			3D+1	-0.04644	0.00928	93	17	H	1S	0.01359	-0.00634
41			3D-1	0.01802	-0.00703	94	18	H	1S	0.00550	0.04062
42			3D+2	0.09956	0.00888	95	19	H	1S	-0.00008	0.03355
43			3D-2	-0.00341	0.00320	96	20	H	1S	0.01211	-0.00654
44	8	Cu	1S	-0.03215	0.28364	97	21	H	1S	0.00118	0.03438
45			2PX	0.02307	-0.01566	98	22	H	1S	0.00622	0.03711
46			2PY	-0.01697	0.52841	99	23	H	1S	0.00599	0.02416
47			2PZ	-0.00923	-0.02856	100	24	H	1S	0.00487	0.01519
48			3D 0	0.09267	0.04633	101	25	H	1S	-0.00957	-0.04602
49			3D+1	0.01257	0.01055	102	26	H	1S	-0.01086	0.03914
50			3D-1	-0.00541	-0.00355	103	27	H	1S	0.00133	-0.02057
51			3D+2	-0.04276	-0.00445	104	28	H	1S	0.00325	-0.01936
52			3D-2	-0.08314	-0.00694						

TABLE V

RESULTS OF *ab initio* CALCULATIONS FOR COMPOUND $Cu_4I_4(CH_3CN)_2$(6-ethyl-o-toluidine$)_2$

				HOMO	LUMO
				68	69
EIGENVALUES --				-0.29617	0.19220
1	1	I	1S	0.00061	0.16581
2			2PX	0.00932	0.01193
3			2PY	0.50556	0.04103
4			2PZ	0.05241	-0.28249
5	2	I	1S	0.00301	0.22648
6			2PX	0.10894	0.37359
7			2PY	0.41557	-0.23643
8			2PZ	0.00000	0.00000
9	3	I	1S	-0.00143	0.19562
10			2PX	0.03096	-0.34632
11			2PY	0.50344	-0.23307
12			2PZ	0.00000	0.00000
13	4	Cu	1S	-0.00031	-0.26471
14			2PX	-0.00480	0.00774
15			2PY	-0.01604	0.62266
16			2PZ	-0.00191	-0.03547
17			3D 0	-0.05778	-0.00015
18			3D+1	-0.02639	-0.00912
19			3D-1	0.14832	0.01694
20			3D+2	-0.10995	-0.03635
21			3D-2	-0.00894	0.00188
22	5	Cu	1S	0.01348	-0.30467
23			2PX	-0.00947	-0.53932
24			2PY	0.00555	-0.15736
25			2PZ	0.00000	0.00000
26			3D 0	0.07253	-0.05361
27			3D+1	0.00000	0.00000
28			3D-1	0.00000	0.00000
29			3D+2	0.08466	0.00041
30			3D-2	-0.11791	-0.00095
31	6	Cu	1S	0.01831	-0.31480
32			2PX	0.01817	0.45928
33			2PY	-0.00869	-0.26131
34			2PZ	0.00000	0.00000
35			3D 0	0.07359	-0.05382
36			3D+1	0.00000	0.00000
37			3D-1	0.00000	0.00000
38			3D+2	0.08299	-0.00422
39			3D-2	0.13850	-0.00132
40	7	N	1S	-0.01459	-0.04774
41			2S	0.07516	0.31730
42			2PX	-0.00335	-0.01178
43			2PY	0.07824	0.00110
44			2PZ	-0.09778	-0.11419
45	8	N	1S	0.01086	0.00398
46			2S	-0.06102	-0.03720
47			2PX	-0.02243	-0.02236
48			2PY	0.03543	-0.01127
49			2PZ	0.00000	0.00000
50	9	N	1S	0.01468	-0.00336
51			2S	-0.08017	0.01281
52			2PX	0.02944	0.04410
53			2PY	0.04586	-0.05570
54			2PZ	0.00000	0.00000
55	10	C	1S	-0.00423	-0.00037
56			2S	0.01388	-0.00533
57			2PX	0.01162	0.12512
58			2PY	-0.01115	0.07507
59			2PZ	0.00000	0.00000
60	11	C	1S	0.00109	0.00399
61			2S	-0.00467	-0.02301
62			2PX	-0.00610	0.00439
63			2PY	0.00762	0.01884
64			2PZ	0.00000	0.00000
65	12	C	1S	-0.00590	[illegible]
66			2S	0.02213	-0.02748
67			2PX	-0.02675	-0.13825
68			2PY	-0.00512	0.13117
69			2PZ	0.00000	0.00000
70	13	C	1S	0.00139	0.00111
71			2S	-0.00498	-0.00686
72			2PX	0.00952	-0.01528
73			2PY	0.00571	0.00790
74			2PZ	0.00000	0.00000
75	14	I	1S	0.00061	0.16581
76			2PX	0.00932	[illegible]
77			2PY	0.50556	0.04103
78			2PZ	-0.05241	0.28249
79	15	Cu	1S	-0.00031	-0.26471
80			2PX	-0.00480	0.00774
81			2PY	-0.01604	0.62266
82			2PZ	0.00191	0.03547
83			3D 0	-0.05778	-0.00015
84			3D+1	0.02639	0.00912
85			3D-1	-0.14832	-0.01694
86			3D+2	-0.10995	-0.03635
87			3D-2	-0.00894	0.00188
88	16	N	1S	-0.01459	-0.04774
89			2S	0.07516	0.31730
90			2PX	-0.00335	-0.01178
91			2PY	0.07824	0.00110
92			2PZ	0.09778	0.11419
93	17	H	1S	-0.00918	-0.03366
94	18	H	1S	-0.02429	0.01255
95	19	H	1S	-0.00652	-0.03962
96	20	H	1S	-0.00918	-0.03366
97	21	H	1S	-0.02429	0.01255
98	22	H	1S	-0.00652	-0.03962
99	23	H	1S	0.00061	-0.02089
100	24	H	1S	0.00173	0.01257
101	25	H	1S	0.00173	0.01257
102	26	H	1S	-0.00242	-0.05101
103	27	H	1S	0.00361	0.02622
104	28	H	1S	0.00361	0.02622

TABLE VI

RESULTS OF *ab initio* CALCULATIONS FOR COMPOUND $Cu_4I_4(CH_3CN)_2$(p-toluidine

				HOMO	LUMO
				68 (B)	69 (A)
EIGENVALUES --				-0 29769	0 20319
1	1	I	1S	-0 00093	-0 12481
2			2PX	0.13556	-0 00304
3			2PY	0.35841	0 34196
4			2PZ	-0 01558	0.27831
5	2	I	1S	0 00529	-0.21971
6			2PX	0.23626	-0 27487
7			2PY	0.53181	0 12385
8			2PZ	-0 03429	-0 10958
9	3	Cu	1S	0 00405	0 25675
10			2PX	-0 01310	-0 37047
11			2PY	-0 02331	-0.38618
12			2PZ	0 00561	-0 04155
13			3D 0	-0 02696	0 00856
14			3D+1	-0 03927	-0 01857
15			3D-1	-0 10386	0 02972
16			3D+2	-0 06958	0 01103
17			3D-2	0 16984	-0 02891
18	4	Cu	1S	0 01336	0 21062
19			2PX	0 00286	0 62934
20			2PY	0 01393	-0 08281
21			2PZ	0 00391	-0.32805
22			3D 0	0 08060	0 01384
23			3D+1	0 03581	0 01997
24			3D-1	0 04980	-0 02207
25			3D+2	-0 08984	0 00662
26			3D-2	-0 03012	-0 03737
27	5	N	1S	-0 00935	0 03979
28			2S	0.04741	-0 26171
29			2PX	0.07028	-0 05644
30			2PY	0 00076	0 06108
31			2PZ	0 05065	-0 06447
32	6	N	1S	0 01415	-0 00464
33			2S	-0 07860	0 03833
34			2PX	0 00392	0 07211
35			2PY	0 04505	0 01830
36			2PZ	0.03114	-0 00765
37	7	C	1S	-0.00535	0 00040
38			2S	0 01769	0 00281
39			2PX	0 00432	-0 19729
40			2PY	-0 00331	-0 05158
41			2PZ	-0.02366	0 04518
42	8	C	1S	0 00128	-0 00677
43			2S	-0 00483	0 04411
44			2PX	-0 00120	-0 02235
45			2PY	0 00508	-0 01816
46			2PZ	0 00820	-0 00817
47	9	Cu	1S	-0 00405	0 25675
48			2PX	-0 01310	0 37047
49			2PY	-0 02331	0 38618
50			2PZ	-0 00561	-0 04155
51			3D 0	0 02696	0 00856
52			3D+1	-0 03927	0 01857
53			3D-1	-0 10386	-0 02972
54			3D+2	0 06958	0 01103
55			3D-2	-0 16984	-0 02891
56	10	Cu	1S	-0 01336	0 21062
57			2PX	0 00286	-0 62934
58			2PY	0 01393	0 08281
59			2PZ	-0 00391	-0 32805
60			3D 0	-0 08060	0 01384
61			3D+1	0 03581	-0 01997
62			3D-1	0 04980	0 02207
63			3D+2	0 08984	0 00662
64			3D-2	0 03012	-0 03737
65	11	I	1S	0 00093	-0 12481
66			2PX	0 13556	0 00304
67			2PY	0 35841	-0 34196
68			2PZ	0 01558	0 27831
69	12	I	1S	-0 00529	-0.21971
70			2PX	0 23626	0 27487
71			2PY	0 53181	-0 12385
72			2PZ	0 03429	-0 10958
73	13	N	1S	0.00935	0.03979
74			2S	-0 04741	-0 26171
75			2PX	0 07028	0 05644
76			2PY	0.00076	-0 06108
77			2PZ	-0 05065	-0 06447
78	14	N	1S	-0 01415	-0 00464
79			2S	0 07860	0 03833
80			2PX	0 00392	-0 07211
81			2PY	0 04505	-0 01830
82			2PZ	-0 03114	-0 00765
83	15	C	1S	0 00535	0 00040
84			2S	-0 01769	0 00281
85			2PX	0 00432	0 19729
86			2PY	-0 00331	0 05158
87			2PZ	0 02366	0 04518
88	16	C	1S	-0 00128	-0 00677
89			2S	0 00483	0 04411
90			2PX	-0 00120	0 02235
91			2PY	0 00508	0 01816
92			2PZ	-0.00820	-0 00817
93	17	H	1S	-0 02191	-0 00735
94	18	H	1S	0 00050	0 04115
95	19	H	1S	-0 00506	0 02104
96	20	H	1S	0 02191	-0 00735
97	21	H	1S	-0 00050	0 04115
98	22	H	1S	0 00506	0 02104
99	23	H	1S	-0 00116	-0 01585
100	24	H	1S	0 00478	-0 03848
101	25	H	1S	0 00019	0 05434
102	26	H	1S	0 00116	-0 01585
103	27	H	1S	-0 00478	-0 03848
104	28	H	1S	-0 00019	0 05434

complexes with crystallographic two fold symmetry axes has not been answered by the *ab initio* approach. An understanding of the influence of crystallographic symmetry upon emission wavelength therefore must consider other factors:

1. The X-ray crystallography has been performed at room temperature. Emission measurements were recorded in the 10 - 298 K range. The nonsymmetric and mirror symmetry examples tend to show emission at 570 nm. The two fold complexes show a marked tendency to change emission characteristics as temperature is lowered. They show both 570 and 610-630 nm emission and several appear to show both types. The question of a structural phase change occuring between 298 and 10K for those complexes with two fold axes is thus raised. The complex of mirror symmetry behaves as a nonsymmetrical complex at low temperatures.

2. The experimental evidence suggests that the more parameters fixed by the symmetry element present, the lower the emission energy. Thus clusters with no symmetry element present emit at higher energy than those with two fold axes in which x and z parameters are correlated by the presence of a two fold axis parallel to the y axis. The low temperature structure appears to manifest higher symmetry than the room temperature one. Thus the two fold axis is apparently joined by other restrictions at lower temperatures leaving the complex to diffract as a more highly symmetrical motif at low temperatures. However symmetry elements which fit more than two atomic parameters are not possible in $Cu_4I_4(CH_3CN)_2(ligand)_2$ complexes.

3. Samples were measured by lowering the temperature to 10 K and then measuring successive spectra with warming of the sample chamber. The sample was thus present in an evacuated chamber for 1.5 hours before measurement began. When spectra were measured at room temperature under vacuum prior to cooling, the original spectra was normally higher in intensity, (although maximum emission wavelength was unchanged) than that of the sample which had undergone the cooling and rewarming

procedure. This suggests that sample decomposition was occuring. Copper iodide acetonitrile complexes are unstable, losing acetonitrile in air. The instability of these complexes did not allow control of identity of bulk sample by observation of powder diffraction spectra before and after emission measurements and comparison of these spectra with powder spectra calculated from the single crystal data. The wavelengths of emission observed appear too systematic to arise from decomposition alone.

Thus this study has considered a group of $Cu_4I_4(CH_3CN)_2(ligand)_2$ complexes and has found emission at 570 and or 620 nm which may be only partially correlated with symmetry elements present within the complexes in room temperature single crystal X-ray results. These complexes, in concert with those of previous work, show iodide to copper excitation and reemission which is independent of the nature of the organic ligands attached to copper. As a group these complexes show two different solid state emission mechanisms which appear influenced by temperature and other unknown factors.

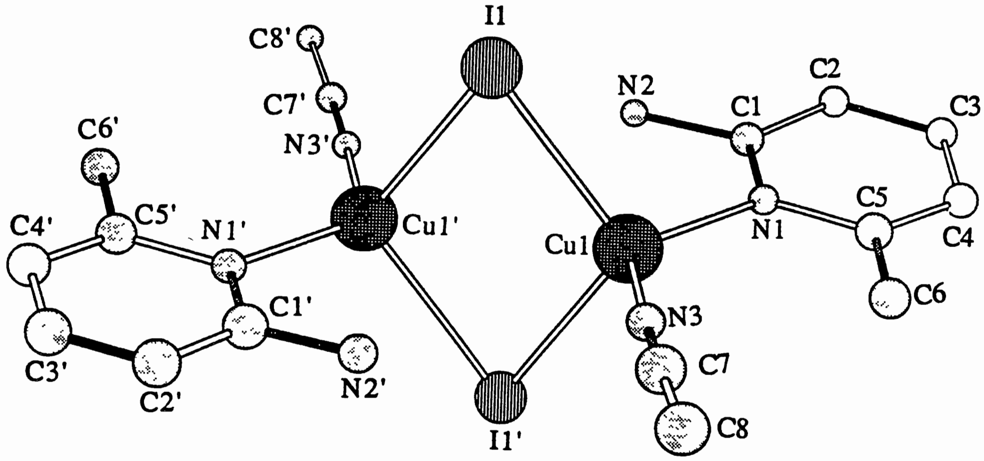


Figure 21. Projection View of $Cu_2I_2(CH_3CN)$(2-amino-6-methyl-pyridine)

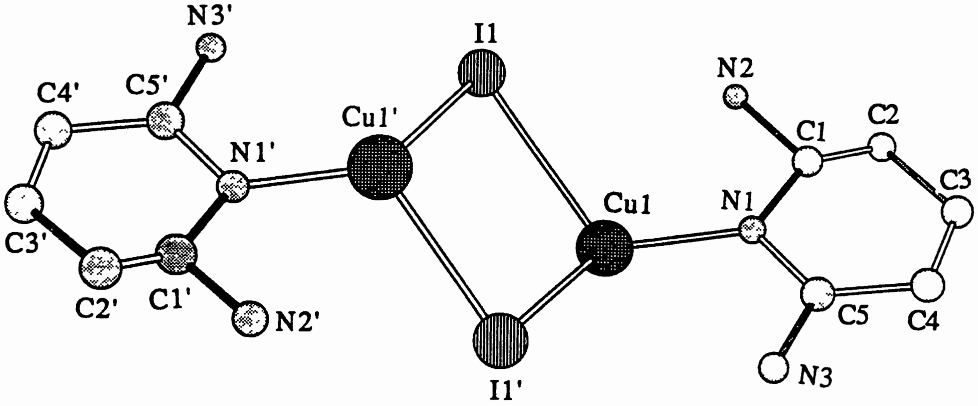


Figure 22. Projection View of Cu_2I_2(2,6-diamino-pyridine)$_2$

TABLE VII

CRYSTAL DATA FOR $Cu_4I_4(CH_3CN)_2$(2,6-dimethylaniline)$_2$

Formula	$Cu_4I_4C_{20}H_{28}N_4$
MWT	1086.3
a	12.449(3) Å
b	14.108(6)
c	10.606(4)
α	73.46(3)°
β	95.00(2)
γ	73.42(3)
V	1682.3(10) $Å^3$
F (000)	1008
μMoK_α	61.51 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.144 g cm^{-3}
Z	2
Meas. Refl.	8648
Obs. Refl.	2617
R	8.0 %
Space Group	P1 bar
Octants Meas.	±h, k, ±l

TABLE VIII

POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(2,6-dimethylaniline)$_2$

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.0014 (2)	0.3414 (2)	0.2726 (2)
I2	-0.1433 (2)	0.1817 (2)	0.0333 (3)
I3	-0.3706 (2)	0.3512 (2)	0.2554 (3)
I4	-0.2606 (2)	0.5361 (2)	-0.0883 (3)
Cu1	-0.0912 (4)	0.3526 (4)	0.0256 (5)
Cu2	-0.3046 (4)	0.3543 (4)	0.0203 (5)
Cu3	-0.2204 (5)	0.4495 (4)	0.1761 (5)
Cu4	-0.1516 (5)	0.2405 (4)	0.2501 (5)
N11	0.045 (3)	0.358 (2)	-0.083 (3)
N21	-0.459 (3)	0.373 (2)	-0.106 (3)
N31	-0.254 (4)	0.567 (3)	0.273 (4)
N41	-0.119 (3)	0.129 (3)	0.430 (4)
C11	0.080 (3)	0.275 (3)	-0.136 (3)
C12	0.156 (4)	0.182 (3)	-0.066 (4)
C13	0.195 (5)	0.103 (4)	-0.105 (5)
C14	0.141 (5)	0.114 (4)	-0.237 (7)
C15	0.065 (5)	0.210 (4)	-0.325 (4)
C16	0.030 (4)	0.293 (4)	-0.272 (5)
C17	-0.054 (5)	0.389 (5)	-0.352 (5)
C18	0.204 (4)	0.169 (4)	0.067 (6)
C21	-0.450 (3)	0.284 (3)	-0.165 (4)
C22	-0.408 (4)	0.299 (4)	-0.288 (4)
C23	-0.400 (4)	0.220 (4)	-0.342 (4)
C24	-0.426 (4)	0.139 (3)	-0.272 (6)
C25	-0.462 (5)	0.120 (4)	-0.152 (4)
C26	-0.470 (4)	0.196 (3)	-0.108 (4)
C27	-0.500 (6)	0.182 (4)	0.027 (6)
C28	-0.398 (6)	0.411 (7)	-0.364 (6)

TABLE VIII (Continued)

C31	-0.271 (5)	0.621 (4)	0.321 (6)
C32	-0.316 (11)	0.686 (6)	0.359 (13)
C41	-0.114 (4)	0.090 (4)	0.537 (4)
C42	-0.108 (5)	0.039 (5)	0.672 (7)

TABLE IX

HYDROGEN POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(2,6-dimethylaniline)$_2$

ATOM	X	Y	Z
H131	0.2610	0.0354	-0.0461
H141	0.1555	0.0517	-0.2714
H151	0.0369	0.2197	-0.4192
H171	-0.1209	0.4066	-0.3056
H172	-0.0230	0.4493	-0.3584
H173	-0.0934	0.4086	-0.4463
H181	0.2424	0.2238	0.0689
H182	0.1427	0.1842	0.1223
H183	0.2606	0.1036	0.1257
H231	-0.3728	0.2247	-0.4306
H241	-0.4171	0.0836	-0.3161
H251	-0.4831	0.0561	-0.1070
H271	-0.4369	0.1855	0.0913
H272	-0.5679	0.2410	0.0272
H273	-0.5156	0.1187	0.0761
H281	-0.4719	0.4670	-0.3803
H282	-0.3450	0.4277	-0.3014
H283	-0.3695	0.4257	-0.4475
H321	-0.3744	0.6762	0.3917
H322	-0.2480	0.6284	0.4736
H323	-0.3157	0.7329	0.4407
H421	-0.1891	0.0386	0.6544
H422	-0.0626	-0.0321	0.6628
H423	-0.1048	-0.0033	0.7678

TABLE X

ANISOTROPIC THERMAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(2,6-dimethylaniline)$_2$

ATOM	U11	U22	U33	U12	U13	U23
I1	47 (2)	65 (2)	34 (1)	-21 (1)	5 (1)	-22 (1)
I2	54 (2)	41 (2)	54 (2)	-13 (1)	9 (1)	-25 (1)
I3	52 (2)	49 (2)	38 (1)	-18 (1)	21 (1)	-18 (1)
I4	52 (1)	37 (1)	43 (1)	-16 (1)	6 (1)	-11 (1)
Cu1	52 (3)	55 (3)	47 (3)	-20 (3)	20 (2)	-26 (3)
Cu2	51 (3)	59 (3)	46 (3)	-21 (3)	6 (2)	-28 (3)
Cu3	58 (4)	54 (3)	55 (3)	-20 (3)	15 (3)	-30 (3)
Cu4	72 (4)	53 (3)	40 (3)	-16 (3)	6 (3)	- 12 (3)
N11	5 (2)	4 (2)	4 (2)	-2 (2)	2 (2)	-2 (2)
N21	4 (2)	6 (2)	4 (2)	- 1 (2)	0 (2)	-3 (2)
N31	8 (3)	8 (3)	7 (3)	-2 (3)	0 (2)	- 3 (2)
N41	7 (3)	6 (3)	6 (3)	-3 (2)	0 (2)	0 (2)
C11	5 (2)	6 (2)	3 (2)	- 3 (2)	1 (2)	-2 (2)
C12	6 (3)	4 (2)	2 (2)	-2 (2)	0 (2)	-1 (2)
C13	12 (5)	7 (4)	6 (3)	-4 (3)	4 (3)	-4 (3)
C14	11 (5)	6 (3)	18 (7)	-4 (4)	9 (5)	-7 (4)
C15	12 (4)	8 (4)	5 (3)	-6 (3)	4 (3)	-6 (3)
C16	5 (3)	6 (3)	11 (4)	-2 (3)	5 (3)	1 (3)
C17	8 (4)	14 (6)	5 (3)	-4 (4)	0 (3)	-3 (3)
C18	3 (3)	5 (3)	13 (5)	1 (2)	3 (3)	3 (3)
C21	3 (2)	5 (2)	4 (2)	0 (2)	0 (2)	-2 (2)
C22	7 (3)	7 (3)	2 (2)	-3 (3)	0 (2)	-2 (2)
C23	8 (4)	9 (4)	4 (3)	0 (3)	0 (2)	-4 (3)
C24	6 (3)	5 (3)	11 (4)	-1 (2)	-2 (3)	-4 (3)
C25	12 (4)	6 (3)	5 (3)	-3 (3)	3 (3)	-4 (2)
C26	7 (3)	6 (3)	3 (2)	-2 (2)	3 (2)	-2 (2)
C27	14 (6)	4 (3)	11 (5)	-4 (3)	5 (4)	0 (3)
C28	10 (5)	24 (9)	6 (4)	-4 (6)	4 (4)	-5 (5)

TABLE X (Continued)

C31	9 (4)	10 (4)	11 (4)	-2 (3)	3 (3)	10 (4)
C32	48 (16)	12 (6)	50 (17)	-7 (8)	42 (15)	17 (9)
C41	5 (3)	6 (3)	4 (3)	1 (2)	-1 (2)	1 (3)
C42	9 (5)	9 (5)	11 (5)	3 (4)	4 (4)	1 (4)

Anisotropic thermal parameters in the form:

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

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

TABLE XI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR Cu$_4$I$_4$(CH$_3$CN)$_2$(2,6-dimethylaniline)$_2$

I1 - Cu1	2.711 (6)	Cu1 - I1 - Cu3	60.7 (2)
I1 - Cu3	2.686 (6)	Cu1 - I1 - Cu4	61.0 (2)
I1 - Cu4	2.715 (8)	Cu1 - I2 - Cu2	60.0 (2)
I2 - Cu1	2.651 (7)	Cu1 - I2 - Cu4	62.5 (2)
I2 - Cu2	2.636 (6)	Cu1 - I4 - Cu2	58.4 (2)
I2 - Cu4	2.658 (7)	Cu1 - I4 - Cu3	61.3 (2)
I3 - Cu2	2.685 (6)	Cu2 - I2 - Cu4	61.7 (2)
I3 - Cu3	2.687 (7)	Cu2 - I3 - Cu4	60.0 (2)
I3 - Cu4	2.742 (7)	Cu2 - I3 - Cu3	60.8 (2)
I4 - Cu1	2.695 (5)	Cu2 - I4 - Cu3	60.7 (2)
I4 - Cu2	2.726 (7)	Cu3 - I1 - Cu4	59.4 (2)
I4 - Cu3	2.657 (6)	Cu3 - I3 - Cu4	59.1 (2)
Cu1 - N11	2.14 (4)	I1 - Cu1 - N11	103.0 (10)
Cu2 - N21	2.15 (3)	I2 - Cu1 - N11	108.9 (10)
Cu3 - N31	2.15 (5)	I4 - Cu1 - N11	107.0 (7)
Cu4 - N41	2.02 (4)	I2 - Cu2 - N21	110.7 (10)
N11 - C11	1.41 (6)	I3 - Cu2 - N21	102.7 (9)
C11 - C12	1.33 (5)	I4 - Cu2 - N21	103.8 (9)
C12 - C13	1.29 (7)	I1 - Cu3 - N31	103.1 (12)
C12 - C18	1.42 (7)	I3 - Cu3 - N31	102.0 (14)
C13 - C14	1.44 (9)	I4 - Cu3 - N31	111.0 (10)
C14 - C15	1.42 (6)	I1 - Cu4 - N41	104.2 (14)
C15 - C16	1.40 (8)	I2 - Cu4 - N41	118.5 (14)
C16 - C17	1.43 (6)	I3 - Cu4 - N41	98.0 (12)
C16 - C11	1.45 (7)	Cu1 - N11 - C11	114 (3)
N21 - C21	1.54 (6)	N11 - C11 - C12	123 (4)
C21 - C22	1.43 (6)	N11 - C11 - C16	118 (3)
C22 - C23	1.38 (8)	C11 - C12 - C13	128 (4)

TABLE XI (Continued)

C23 - C24	1.31 (8)	C12 - C13 - C14	115 (4)
C24 - C25	1.36 (8)	C13 - C14 - C15	122 (6)
C26 - C27	1.48 (8)	C14 - C15 - C16	117 (5)
C26 - C21	1.31 (6)	C15 - C16 - C17	120 (5)
C22 - C28	1.60 (10)	C15 - C16 - C11	118 (4)
N31 - C31	1.02 (9)	C17 - C16 - C11	122 (5)
C31 - C32	1.15 (13)	C16 - C11 - C12	119 (4)
N41 - C41	1.10 (6)	C11 - C12 - C18	117 (4)
C41 - C42	1.39 (8)	C13 - C12 - C18	115 (4)
Cu1 ··· Cu2	2.645 (8)	Cu2 - N21 - C21	114 (2)
Cu1 ··· Cu3	2.728 (8)	N21 - C21 - C22	114 (4)
Cu1 ··· Cu4	2.754 (8)	N21 - C21 - C26	125 (4)
Cu2 ··· Cu3	2.720 (10)	C21 - C22 - C23	115 (4)
Cu2 ··· Cu4	2.714 (7)	C22 - C23 - C24	116 (5)
Cu3 ··· Cu4	2.678 (8)	C23 - C24 - C25	130 (6)
		C24 - C25 - C26	111 (5)
		C25 - C26 - C27	116 (5)
		C25 - C26 - C21	128 (5)
		C27 - C26 - C21	117 (5)
		C26 - C21 - C22	120 (4)
		C21 - C22 - C28	119 (5)
		C23 - C22 - C28	125 (4)
		Cu3 - N31 - C31	177 (5)
		N31 - C31 - C32	164 (9)
		Cu4 - N41 - C41	162 (4)
		N41 - C41 - C42	179 (7)
		I1 - Cu1 - I2	111.0 (2)
		I1 - Cu1 - I4	109.8 (2)

TABLE XI (Continued)

	I1 - Cu3 - I3	116.9 (2)
	I1 - Cu3 - I4	111.7 (2)
	I1 - Cu4 - I2	110.7 (2)
	I1 - Cu4 - I3	114.1 (2)
	I2 - Cu1 - I4	116.3 (2)
	I2 - Cu2 - I3	113.4 (2)
	I2 - Cu2 - I4	115.7 (2)
	I2 - Cu4 - I3	110.9 (2)
	I3 - Cu2 - I4	109.2 (2)
	I3 - Cu3 - I4	111.3 (2)

TABLE XII

CRYSTAL DATA FOR $Cu_4I_4(CH_3CN)_2$(o-ethylaniline)$_2$

Formula	$Cu_4I_4C_{20}H_{28}N_4$
MWT	1086.3
a	12.224(2) Å
b	14.073(5)
c	12.198(4)
α	114.32(2)°
β	87.85(2)
γ	68.45(2)
V	1734.0(8) Å^3
F (000)	1008
μMoK_α	59.68 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.080 g cm^{-3}
Z	2
Meas. Refl.	10054
Obs. Refl.	4557
R	7.4 %
Space Group	P1 bar
Octants Meas.	$\pm$h, k, $\pm$l

TABLE XIII

POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(o-ethylaniline)$_2$

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.1043 (1)	0.1467 (1)	0.1921 (1)
I2	0.0594 (1)	0.0809 (1)	-0.1872 (1)
I3	0.2400 (1)	0.3092 (1)	-0.0072 (1)
I4	-0.1492 (1)	0.4338 (1)	0.1384 (1)
Cu1	-0.0473 (3)	0.2089 (2)	0.0549 (3)
Cu2	0.1956 (3)	0.1283 (2)	-0.0231 (3)
Cu3	0.0362 (3)	0.2967 (2)	-0.0653 (3)
Cu4	0.0733 (3)	0.3370 (2)	0.1683 (3)
N1	-0.177 (2)	0.151 (1)	0.073 (2)
N2	0.357 (2)	0.005 (2)	-0.085 (2)
N3	-0.017 (2)	0.374 (1)	-0.182 (2)
N4	0.101 (2)	0.438 (2)	0.324 (2)
C11	-0.291 (2)	0.237 (2)	0.152 (2)
C12	-0.377 (2)	0.299 (2)	0.102 (3)
C13	-0.478 (5)	0.386 (5)	0.175 (5)
C14	-0.513 (5)	0.420 (4)	0.296 (8)
C15	-0.430 (4)	0.364 (3)	0.348 (3)
C16	-0.311 (3)	0.269 (3)	0.278 (2)
C17	-0.355 (3)	0.274 (4)	-0.024 (3)
C18	-0.373 (5)	0.200 (7)	-0.106 (4)
C21	0.451 (2)	-0.066 (2)	-0.140 (2)
C22	0.577 (2)	-0.164 (3)	-0.204 (3)
C31	-0.066 (2)	0.316 (2)	-0.277 (2)
C32	0.001 (2)	0.230 (2)	-0.390 (2)
C33	-0.045 (2)	0.172 (2)	-0.477 (2)
C34	-0.157 (3)	0.192 (3)	-0.453 (2)
C35	-0.233 (3)	0.284 (3)	-0.338 (3)
C36	-0.180 (2)	0.341 (2)	-0.255 (2)

TABLE XIII (Continued)

C37	0.136 (3)	0.198 (3)	-0.415 (3)
C38	0.172 (6)	0.275 (5)	-0.463 (4)
C41	0.126 (2)	0.493 (2)	0.406 (2)
C42	0.164 (3)	0.559 (2)	0.514 (2)

TABLE XIV

HYDROGEN POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(o-ethylaniline)$_2$

ATOM	X	Y	Z
H11	-0.1462	0.0966	0.1063
H12	-0.1906	0.1122	-0.0081
H13	-0.5368	0.4253	0.1328
H14	-0.5875	0.4876	0.3514
H15	-0.4540	0.3829	0.4393
H16	-0.2474	0.2269	0.3145
H31	0.0540	0.3769	-0.2201
H32	-0.0767	0.4534	-0.1327
H33	0.0082	0.1137	-0.5608
H34	-0.1869	0.1417	-0.5164
H35	-0.3179	0.3022	-0.3238
H36	-0.2286	0.4033	-0.1771
H171	-0.4017	0.3479	-0.0309
H172	-0.2672	0.2615	-0.0496
H371	0.1648	0.2057	-0.3367
H372	0.1792	0.1165	-0.4746

TABLE XV

ANISOTROPIC THERMAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(o-ethylaniline)$_2$

ATOM	U11	U22	U33	U12	U13	U23
I1	679 (10)	523 (8)	398 (7)	-289 (8)	-157 (7)	279 (6)
I2	729 (10)	414 (7)	344 (7)	-278 (7)	-145 (7)	177 (6)
I3	558 (9)	553 (9)	554 (9)	-307 (7)	-109 (7)	293 (7)
I4	562 (9)	408 (7)	491 (8)	-182 (7)	-54 (7)	206 (6)
Cu1	568 (18)	526 (16)	570 (18)	-270 (14)	-86 (14)	278 (14)
Cu2	550 (18)	524 (16)	510 (17)	-163 (14)	-74 (14)	248 (14)
Cu3	826 (22)	555 (17)	454 (16)	-348(16)	-241 (15)	326 (14)
Cu4	767 (21)	544 (17)	414 (16)	-345 (16)	-155 (15)	191 (13)
N1	5 (1)	4 (1)	5 (1)	-2 (1)	-1 (1)	2 (1)
N2	4 (1)	6 (1)	7 (1)	-1 (1)	-2 (1)	4 (1)
N3	7 (1)	4 (1)	3 (1)	-2 (1)	-1 (1)	2 (1)
N4	8 (1)	8 (1)	4 (1)	-5 (1)	-2 (1)	3 (1)
C11	4 (1)	5 (1)	7 (2)	-2 (1)	0 (1)	2 (1)
C12	5 (2)	6 (2)	11 (2)	-2 (1)	3 (2)	4 (2)
C13	8 (3)	10 (4)	20 (6)	0 (2)	-4 (4)	2 (4)
C14	14 (5)	9 (4)	48 (13)	-6 (4)	-11 (7)	12 (6)
C15	21 (4)	16 (4)	7 (2)	-16 (4)	8 (2)	-6 (2)
C16	8 (2)	10 (2)	4 (1)	-5 (2)	0 (1)	2 (1)
C17	12 (3)	16 (4)	8 (2)	-5 (3)	-6 (2)	7 (2)
C18	15 (5)	56 (12)	8 (3)	6 (6)	-2 (3)	15 (6)
C21	7 (2)	6 (2)	5 (1)	-4 (1)	-3 (1)	3 (1)
C22	6 (2)	10 (2)	8 (2)	-2 (2)	0 (1)	1 (2)
C31	7 (2)	4 (1)	4 (1)	-2 (1)	-2 (1)	3 (1)
C32	6 (2)	6 (1)	4 (1)	-2 (1)	-2 (1)	3 (1)
C33	7 (2)	9 (2)	6 (2)	-4 (2)	-2 (1)	2 (2)
C34	16 (3)	10 (2)	6 (2)	-10 (2)	-5 (2)	4 (2)
C35	8 (2)	12 (3)	13 (3)	-7 (2)	-5 (2)	8 (2)
C36	6 (2)	7 (2)	8 (2)	-3 (1)	-3 (2)	3 (1)

TABLE XV (Continued)

C37	15 (3)	8 (2)	7 (2)	-1 (2)	-1 (2)	4 (2)
C38	38 (8)	23 (5)	10 (3)	-23 (6)	-4 (4)	10 (4)
C41	6 (2)	5 (1)	5 (1)	-2 (1)	-1 (1)	2 (1)
C42	10 (2)	7 (2)	5 (1)	-4 (2)	-4 (2)	0 (1)

Anisotropic thermal parameters in the form:

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

$\times 10^4$ for I, Cu; $\times 10^2$ for C, N.

TABLE XVI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $Cu_4I_4(CH_3CN)_2$(o-ethylaniline)$_2$

I1 - Cu1	2.690 (4)	Cu1 - I1 - Cu2	61.0 (1)
I1 - Cu2	2.683 (4)	Cu1 - I1 - Cu4	60.5 (1)
I1 - Cu4	2.701 (4)	Cu1 - I2 - Cu3	59.2 (1)
I2 - Cu1	2.694 (3)	Cu1 - I2 - Cu2	61.0 (1)
I2 - Cu2	2.680 (4)	Cu1 - I4 - Cu3	59.2 (1)
I2 - Cu3	2.670 (4)	Cu1 - I4 - Cu4	61.5 (1)
I3 - Cu2	2.726 (5)	Cu2 - I1 - Cu4	59.6 (1)
I3 - Cu3	2.663 (4)	Cu2 - I3 - Cu3	60.4 (1)
I3 - Cu4	2.698 (4)	Cu2 - I3 - Cu4	59.2 (1)
I4 - Cu1	2.638 (4)	Cu2 - I2 - Cu3	60.9 (1)
I4 - Cu3	2.728 (3)	Cu3 - I4 - Cu4	61.3 (1)
I4 - Cu4	2.674 (4)	Cu3 - I3 - Cu4	61.8 (1)
Cu1 - N1	2.08 (2)	I1 - Cu1 - I2	110.5 (1)
Cu2 - N2	1.94 (2)	I1 - Cu1 - I4	111.8 (1)
Cu3 - N3	2.12 (2)	I1 - Cu2 - I2	111.1 (1)
Cu4 - N4	1.98 (2)	I1 - Cu2 - I3	115.5 (1)
N1 - C11	1.42 (2)	I1 - Cu4 - I3	115.9 (1)
C11 - C12	1.43 (4)	I1 - Cu4 - I4	110.4 (2)
C12 - C13	1.31 (5)	I2 - Cu1 - I4	116.7 (2)
C13 - C14	1.35 (11)	I2 - Cu2 - I3	110.7 (1)
C14 - C15	1.39 (10)	I2 - Cu3 - I3	113.0 (1)
C15 - C16	1.47 (4)	I2 - Cu3 - I4	114.5 (2)
C16 - C11	1.40 (4)	I3 - Cu3 - I4	110.1 (1)
C12 - C17	1.42 (5)	I3 - Cu4 - I4	110.7 (1)
C17 - C18	1.21 (8)	Cu1 - N1 - C11	115 (2)
N2 - C21	1.14 (3)	N1 - C11 - C12	119 (2)
C21 - C22	1.53 (3)	N1 - C11 - C16	120 (2)
N3 - C31	1.40 (3)	C11 - C12 - C13	120 (4)

TABLE XVI (Continued)

C31 - C32	1.36 (2)	C12 - C13 - C14	125 (6)
C32 - C33	1.33 (4)	C13 - C14 - C15	116 (4)
C33 - C34	1.29 (5)	C14 - C15 - C16	124 (4)
C34 - C35	1.42 (4)	C15 - C16 - C11	113 (3)
C35 - C36	1.36 (5)	C16 - C11 - C12	121 (2)
C36 - C31	1.29 (4)	C11 - C12 - C17	122 (2)
C32 - C37	1.52 (5)	C12 - C17 - C18	124 (6)
C37 - C38	1.60 (9)	C13 - C12 - C17	118 (4)
N41 - C41	1.12 (3)	Cu2 - N2 - C21	168 (3)
C41 - C42	1.46 (4)	N2 - C21 - C22	175 (3)
Cu1 ··· Cu2	2.726 (4)	Cu3 - N3 - C31	114 (2)
Cu1 ··· Cu3	2.650 (6)	N3 - C31 - C32	124 (2)
Cu1 ··· Cu4	2.717 (5)	N3 - C31 - C36	119 (2)
Cu2 ··· Cu3	2.714 (5)	C31 - C32 - C33	123 (2)
Cu2 ··· Cu4	2.678 (3)	C32 - C33 - C34	120 (2)
Cu3 ··· Cu4	2.755 (5)	C33 - C34 - C35	119 (3)
I1 - Cu1 - N1	103.8 (6)	C34 - C35 - C36	117 (3)
I2 - Cu1 - N1	102.8 (5)	C35 - C36 - C31	123 (2)
I4 - Cu1 - N1	110.0 (4)	C36 - C31- C32	117 (2)
I2 - Cu3 - N3	106.7 (5)	C31 - C32 - C37	117 (2)
I3 - Cu3 - N3	109.2 (6)	C32 - C37 - C38	114 (3)
I4 - Cu3 - N3	102.6 (4)	C33 - C32 - C37	119 (2)
I1 - Cu2 - N2	107.4 (8)	Cu4 - N4 - C41	174 (2)
I2 - Cu2 - N2	109.8 (6)	N4 - C41 - C42	177 (3)
I3 - Cu2 - N2	101.6 (8)	I1 - Cu4 - N4	104.2 (8)
I3 - Cu4 - N4	103.3 (8)	I4 - Cu4 - N4	111.9 (6)

TABLE XVII

CRYSTAL DATA FOR $Cu_4I_4(CH_3CN)_2$(p-anisidine)$_2$

Formula	$Cu_2I_2C_9H_{12}N_2O$
MWT	545.1
a	20.032(10) Å
b	7.863(1)
c	18.715(9)
α	90.0°
β	101.56(4)
γ	90.0
V	2888.0(2) Å^3
F (000)	2016
μMoK_α	71.72 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.507 g cm^{-3}
Z	8
Meas. Refl.	6985
Obs. Refl.	1516
R	5.5 %
Space Group	A2/a
Octants Meas.	±h, k, l

TABLE XVIII

POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(p-anisidine)$_2$

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.8602 (1)	0.5683 (2)	0.4800 (1)
I2	0.7060 (1)	0.1860 (2)	0.3785 (1)
Cu1	0.8117 (1)	0.2603 (4)	0.4837 (2)
Cu2	0.7255 (2)	0.5109 (4)	0.4273 (2)
O1	1.010 (1)	0.014 (2)	0.244 (1)
N1	0.880 (1)	0.066 (2)	0.481 (1)
N2	0.700 (1)	0.666 (2)	0.343 (1)
C11	0.914 (1)	0.053 (2)	0.420 (1)
C12	0.976 (1)	0.132 (3)	0.420 (1)
C13	1.006 (1)	0.118 (3)	0.360 (1)
C14	0.976 (1)	0.018 (3)	0.300 (1)
C15	0.913 (1)	-0.058 (3)	0.300 (1)
C16	0.885 (1)	-0.050 (3)	0.361 (1)
C17	0.977 (1)	-0.060 (3)	0.177 (1)
C21	0.684 (1)	0.748 (3)	0.294 (1)
C22	0.662 (1)	0.858 (3)	0.230 (1)

TABLE XIX

HYDROGEN POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(p-anisidine)$_2$

ATOM	X	Y	Z
H11	0.9159	0.0725	0.5253
H12	0.8560	-0.0433	0.4833
H121	0.9992	0.1987	0.4632
H131	1.0488	0.1776	0.3588
H151	0.8890	-0.1172	0.2560
H161	0.8646	-0.0451	0.4050
H171	0.9645	-0.1775	0.1863
H172	0.9342	0.0028	0.1593
H173	1.0004	-0.0645	0.1364
H221	0.6261	0.7755	0.2085
H222	0.6398	0.9388	0.2589
H223	0.6467	0.9320	0.1868

TABLE XX

ANISOTROPIC THERMAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(p-anisidine)$_2$

ATOM	U11	U22	U33	U12	U13	U23
I1	570 (10)	475 (9)	491 (9)	-190 (8)	57 (7)	80 (7)
I2	500 (9)	423 (8)	339 (6)	-25 (7)	72 (6)	-96 (6)
Cu1	45 (1)	44 (2)	54 (2)	8 (1)	15 (1)	2 (1)
Cu2	67 (2)	51 (2)	47 (2)	7 (2)	2 (1)	10 (1)
O1	4 (1)	6 (1)	5 (1)	0 (1)	1 (1)	0 (1)
N1	5 (1)	5 (1)	3 (1)	1 (1)	1 (1)	1 (1)
N2	7 (1)	3 (1)	5 (1)	-1 (1)	1 (1)	2 (1)
C11	4 (1)	3 (1)	5 (1)	2 (1)	1 (1)	1 (1)
C12	4 (1)	3 (1)	5 (1)	1 (1)	1 (1)	0 (1)
C13	4 (1)	3 (1)	5 (1)	0 (1)	2 (1)	1 (1)
C14	5 (1)	5 (1)	4 (1)	0 (1)	2 (1)	1 (1)
C15	3 (1)	5 (1)	3 (1)	0 (1)	-1 (1)	0 (1)
C16	4 (1)	4 (1)	4 (1)	2 (1)	1 (1)	2 (1)
C17	7 (2)	5 (1)	5 (1)	0 (1)	2 (1)	-1 (1)
C21	4 (1)	3 (1)	5 (1)	1 (1)	1 (1)	1 (1)
C22	5 (1)	5 (1)	3 (1)	1 (1)	1 (1)	0 (1)

Anisotropic thermal parameters in the form:

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

x 10^4 for I, x 10^3 for Cu, x 10^2 for C, N.

TABLE XXI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $Cu_4I_4(CH_3CN)_2(p\text{-anisidine})_2$

I1 - Cu1	2.615 (3)	Cu1 - I1 - Cu2	60.6 (1)
I1 - Cu2	2.717 (4)	Cu1 - I2 - Cu2	60.2 (1)
I2 - Cu1	2.650 (3)	I1 - Cu1 - I2	115.5 (2)
I2 - Cu2	2.715 (4)	I1 - Cu2 - I2	110.1 (1)
Cu1 - N1	2.06 (2)	I1 - Cu1 - N1	115.7 (5)
Cu2 - N2	1.98 (2)	I2 - Cu1 - N1	104.7 (5)
N1 - C11	1.44 (3)	I1 - Cu2 - N2	105.6 (6)
C11 - C12	1.39 (3)	I2 - Cu2 - N2	108.4 (5)
C11 - C16	1.40 (3)	Cu1 - N1 - C11	119.7 (13)
C12 - C13	1.37 (3)	Cu2 - N2 - C21	177.2 (18)
C13 - C14	1.39 (3)	N1 - C11 - C12	123 (2)
C14 - C15	1.38 (3)	N1 - C11 - C16	118 (2)
C14 - O1	1.38 (3)	C11 - C12 - C13	120 (2)
C15 - C16	1.38 (3)	C12 - C13 - C14	121 (2)
N2 - C21	1.11 (3)	C13 - C14 - C15	120 (2)
C21 - C22	1.48 (3)	C13 - C14 - O1	115 (2)
O1 - C17	1.42 (3)	C14 - O1 - C17	118 (2)
Cu1 ··· Cu1'	2.661 (4)	O1 - C14 - C15	125 (2)
Cu1 ··· Cu2	2.691 (4)	C14 - C15 - C16	119 (2)
Cu2 ··· Cu2'	2.701 (4)	C15 - C16 - C11	121 (2)
Cu1 ··· Cu2'	2.777 (4)	C16 - C11 - C12	119 (2)
Cu1' ··· Cu2	2.777 (4)	N2 - C21 - C22	177 (2)
Cu1' ··· Cu2'	2.691 (4)	Cu1 - I1 - Cu2'	62.8 (1)
		Cu1 - I2 - Cu1'	59.2 (1)
		Cu1 - I2' - Cu1'	59.2 (1)
		Cu1 - I2' - Cu2'	61.2 (1)
		Cu2 - I1 - Cu2'	59.7 (1)
		Cu2 - I2 - Cu1'	61.2 (1)

TABLE XXI (Continued)

Cu2 - I1' - Cu1'	62.8 (1)
Cu2 - I1' - Cu2'	59.7 (1)
Cu1' - I1' - Cu2'	60.6 (1)
Cu1' - I2' - Cu2'	60.2 (1)
I1 - Cu1 - I2'	110.0 (1)
I1 - Cu2 - I1'	116.7 (1)
I1 - Cu2' - I1'	116.7 (1)
I1 - Cu2' - I2'	107.8 (1)
I2 - Cu1 - I2'	114.7 (1)
I2 - Cu2 - I1'	107.7 (1)
I2 - Cu1' - I1'	110.0 (1)
I2 - Cu1' - I2'	114.7 (1)
I1' - Cu1' - I2'	115.5 (1)
I1' - Cu2' - I2'	110.1 (1)

Symmetry operation:

' = 1.5-x, y, 1-z.

TABLE XXII

CRYSTAL DATA FOR $Cu_4I_4(CH_3CN)_2$(6-ethyl-o-toluidine)$_2$

Formula	$Cu_3I_3C_{13}H_{19}N_3$
MWT	788.7
a	14.976(6) Å
b	21.187(6)
c	12.545(2)
α	90.0°
β	90.0
γ	90.0
V	3980.7(2) Å^3
F (000)	2912
μMoK_α	77.94 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.631 g cm^{-3}
Z	8
Meas. Refl.	5973
Obs. Refl.	682
R	8.1 %
Space Group	Pnam
Octants Meas.	h, k, l

TABLE XXIII

POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(6-ethyl-o-toluidine)$_2$

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.3158 (4)	0.0330 (2)	0.5660 (5)
I2	0.4250 (7)	0.1912 (4)	0.7500
I3	0.5632 (6)	0.0007 (3)	0.7500
Cu1	0.4651 (7)	0.0865 (4)	0.6432 (9)
Cu2	0.3043 (12)	0.0994 (8)	0.7500
Cu3	0.3859 (11)	-0.0108 (6)	0.7500
N1	0.536 (4)	0.104 (2)	0.508 (7)
N2	0.184 (10)	0.128 (7)	0.750
N3	0.358 (7)	-0.101 (4)	0.750
C11	0.546 (8)	0.158 (5)	0.504 (7)
C12	0.613 (9)	0.186 (4)	0.522 (8)
C13	0.667 (10)	0.249 (6)	0.533 (9)
C14	0.620 (6)	0.294 (3)	0.496 (7)
C15	0.527 (7)	0.279 (7)	0.454 (8)
C16	0.595 (7)	0.213 (4)	0.454 (8)
C17	0.694 (6)	0.158 (5)	0.596 (6)
C18	0.790 (5)	0.150 (4)	0.574 (10)
C19	0.414 (3)	0.188 (3)	0.399 (4)
C21	0.109 (11)	0.130 (8)	0.750
C22	0.000 (8)	0.136 (8)	0.750
C31	0.330 (9)	-0.154 (6)	0.750
C32	0.296 (10)	-0.216 (6)	0.750

TABLE XXIV

HYDROGEN POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2(6\text{-ethyl-o-toluidine})_2$

ATOM	X	Y	Z
H131	0.7213	0.2797	0.5862
H141	0.6276	0.3473	0.4694
H151	0.4993	0.3099	0.3856
H171	0.6947	0.1435	0.6705
H172	0.6977	0.1088	0.5587
H181	0.8086	0.1689	0.5098
H182	0.8056	0.2036	0.6216
H183	0.8356	0.1325	0.6143
H191	0.4209	0.1636	0.3627
H192	0.3812	0.1867	0.4731
H193	0.3772	0.2306	0.3726
H221	0.0078	0.1660	0.8131
H222	-0.0591	0.1365	0.7500
H321	0.3412	-0.2282	0.6869
H322	0.2857	-0.2648	0.7500

TABLE XXV

ANISOTROPIC THERMAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(6-ethyl-o-toluidine)$_2$

ATOM	U11	U22	U33	U12	U13	U23
I1	78 (4)	53 (3)	69 (4)	-1 (3)	-11 (4)	-7 (4)
I2	106 (8)	37 (5)	84 (7)	1 (6)	0	0
I3	67 (6)	43 (5)	70 (5)	11 (5)	0	0
Cu1	82 (8)	48 (6)	65 (8)	-6 (6)	10 (8)	4 (6)
Cu2	62 (12)	74 (12)	122 (17)	16 (10)	0	0
Cu3	91 (13)	36 (9)	83 (12)	-4 (9)	0	0
N1	8 (5)	1 (3)	17 (8)	-2 (4)	7 (6)	0 (4)
N2	16 (13)	16 (13)	3 (6)	-10 (13)	0	0
N3	10 (8)	0 (4)	10 (9)	-2 (6)	0	0
C11	44	59	20	46	-17	23
C12	25 (16)	7 (7)	9 (8)	11 (9)	11 (10)	8 (6)
C13	22 (15)	15 (11)	11 (10)	0 (11)	-3 (12)	-5 (10)
C14	22	7	18	-6	17	-6
C15	12 (9)	26 (15)	8 (8)	9 (10)	6 (8)	14 (10)
C16	21 (13)	1 (4)	7 (8)	-2 (6)	6 (8)	1 (5)
C17	21	22	12	-14	3	1
C18	10	17	46	-1	5	16
C19	6	13	11	-2	-3	2
C21	10 (13)	10 (12)	5 (10)	-7 (12)	0	0
C22	4 (11)	13 (14)	26 (22)	7 (9)	0	0
C31	11 (13)	6 (9)	5 (8)	4 (9)	0	0
C32	11 (13)	6 (9)	18 (17)	-8 (10)	0	0

Anisotropic thermal parameters in the form:

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

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

TABLE XXVI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $Cu_4I_4(CH_3CN)_2$(6-ethyl-o-toluidine)$_2$

I1 - Cu1	2.689 (12)	Cu1 - I1 - Cu2	61.7 (4)
I1 - Cu2	2.709 (11)	Cu1 - I2 - Cu2	62.8 (4)
I1 - Cu3	2.700 (10)	Cu1 - I1 - Cu3	60.8 (4)
I2 - Cu2	2.656 (19)	Cu1 - I3 - Cu3	61.2 (4)
I2 - Cu1'	2.660 (12)	Cu2 - I1 - Cu3	58.3 (4)
I2 - Cu1	2.660 (12)	Cu2 - I2 - Cu1'	62.8 (4)
I3 - Cu3	2.667 (19)	Cu2 - I1' - Cu3	58.2 (4)
I3 - Cu1'	2.693 (12)	Cu2 - I1' - Cu1'	61.7 (4)
I3 - Cu1	2.694 (12)	Cu3 - I3 - Cu1'	61.2 (4)
I1' - Cu2	2.709 (11)	Cu3 - I1' - Cu1'	60.8 (4)
I1' - Cu3	2.700 (10)	I1 - Cu1 - I2	110.2 (4)
I1' - Cu1'	2.689 (12)	I1 - Cu1 - I3	110.4 (4)
Cu1 ··· Cu2	2.769 (19)	I1 - Cu2 - I2	109.7 (4)
Cu1 ··· Cu3	2.729 (16)	I2 - Cu2 - I1'	109.7 (4)
Cu2 ··· Cu3	2.633 (22)	I2 - Cu1' - I3	115.8 (4)
Cu2 ··· Cu1'	2.769 (19)	I2 - Cu1' - I1'	110.2 (4)
Cu3 ··· Cu1'	2.729 (16)	I3 - Cu1' - I2	115.8 (4)
Cu1 - N1	2.04 (8)	I3 - Cu1' - I1'	110.4 (4)
Cu2 - N2	1.90 (15)	I1 - Cu3 - I3	110.8 (4)
Cu3 - N3	1.95 (8)	I2 - Cu1 - I3	115.8 (4)
N1 - C11	1.15 (12)	I1 - Cu1 - N1	102.1 (20)
C11 - C12	1.19 (16)	I2 - Cu1 - N1	112.9 (16)
C12 - C13	1.56 (17)	I3 - Cu1 - N1	104.4 (18)
C13 - C14	1.28 (16)	I2 - Cu2 - N2	114.4 (44)
C14 - C15	1.51 (14)	I1 - Cu2 - N2	103.0 (21)
C15 - C16	1.47 (16)	I1 - Cu3 - N3	104.5 (15)

TABLE XXVI (Continued)

C16 - C11	1.54 (14)	I3 - Cu3 - N3	107.8 (30)
C16 - C19	1.50 (12)	Cu1 - N1 - C11	106 (7)
C12 - C17	1.64 (14)	N1 - C11 - C12	128 (11)
C17 - C18	1.48 (11)	N1 - C11 - C16	135 (10)
N3 - C31	1.19 (16)	C11 - C12 - C13	153 (12)
C31 - C32	1.41 (19)	C11 - C12 - C17	122 (9)
N2 - C21	1.13 (22)	C12 - C13 - C14	108 (11)
C21 - C22	1.63 (20)	C13 - C14 - C15	119 (10)
		C14 - C15 - C16	119 (10)
		C15 - C16 - C11	124 (9)
		C15 - C16 - C19	126 (8)
		C13 - C12 - C17	82 (8)
		C11 - C16 - C19	109 (7)
		C12 - C17 - C18	131 (8)
		Cu2 - N2 - C21	164 (14)
		N2 - C21 - C22	178 (17)
		Cu3 - N3 - C31	172 (10)
		N3 - C31 - C32	179 (14)

Symmetry operation:
' = x, y, 1.5-z.

TABLE XXVII

CRYSTAL DATA FOR $Cu_4I_4(CH_3CN)_2$(o-toluidine)$_2$

Formula	$Cu_4I_4C_{18}H_{24}N_4$
MWT	1058.2
a	12.212(3) Å
b	14.599(5)
c	10.245(6)
α	66.18(4)°
β	86.00(4)
γ	72.47(2)
V	1590.5(13) $Å^3$
F (000)	976
μMoK_α	65.03 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.209 g cm^{-3}
Z	2
Meas. Refl.	4173
Obs. Refl.	1461
R	6.1 %
Space Group	P1 bar
Octants Meas.	±h, k, ±l

TABLE XXVIII

POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(o-toluidine)$_2$

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.3772 (3)	0.1572 (2)	0.6220 (3)
I2	0.1580 (3)	0.3128 (2)	0.2202 (3)
I3	0.2644 (2)	-0.0397 (2)	0.4593 (3)
I4	-0.0056 (3)	0.1714 (2)	0.6159 (3)
Cu1	0.3164 (5)	0.1446 (4)	0.3886 (6)
Cu2	0.0965 (5)	0.1445 (4)	0.3891 (6)
Cu3	0.2178 (5)	0.0582 (5)	0.6404 (6)
Cu4	0.1595 (5)	0.2674 (4)	0.4966 (7)
N11	0.465 (3)	0.128 (3)	0.282 (4)
N22	-0.035 (3)	0.129 (3)	0.288 (4)
N33	0.248 (3)	-0.046 (3)	0.839 (4)
N44	0.873 (4)	0.616 (3)	0.435 (4)
C11	0.465 (3)	0.203 (4)	0.142 (5)
C12	0.505 (4)	0.282 (4)	0.138 (5)
C13	0.505 (8)	0.360 (6)	0.001 (8)
C14	0.449 (5)	0.359 (5)	-0.094 (10)
C15	0.410 (5)	0.280 (5)	-0.096 (6)
C16	0.422 (4)	0.199 (4)	0.038 (4)
C17	0.369 (5)	0.112 (5)	0.052 (6)
C21	-0.078 (4)	0.220 (4)	0.144 (7)
C22	-0.163 (5)	0.306 (4)	0.168 (7)
C23	-0.195 (7)	0.399 (5)	0.028 (11)
C24	-0.152 (7)	0.384 (6)	-0.076 (10)
C25	-0.076 (6)	0.307 (6)	-0.087 (6)
C26	-0.036 (7)	0.226 (5)	0.032 (7)
C27	0.055 (6)	0.127 (10)	0.026 (7)
C31	0.256 (4)	-0.096 (4)	0.953 (5)
C32	0.264 (5)	-0.159 (4)	1.101 (7)

TABLE XXVIII (Continued)

C41	0.875 (5)	0.564 (3)	0.378 (6)
C42	0.883 (6)	0.510 (5)	0.288 (10)

TABLE XXIX

HYDROGEN POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(o-toluidine)$_2$

ATOM	X	Y	Z
H11	0.4871	0.0570	0.2759
H12	0.5291	0.1231	0.3410
H21	-0.1033	0.1286	0.3531
H22	-0.0130	0.0615	0.2825
H121	0.5378	0.2893	0.2159
H131	0.5370	0.4197	-0.0214
H151	0.3718	0.2847	-0.1858
H161	0.3876	0.1389	0.0416
H171	0.4351	0.0472	0.0898
H172	0.3153	0.1088	0.1274
H173	0.3291	0.1045	-0.0263
H221	-0.2090	0.3066	0.2568
H231	-0.2450	0.4696	-0.0008
H251	-0.0275	0.2949	-0.1730
H261	0.0394	0.1475	0.0326
H271	0.1326	0.1143	0.0943
H272	0.0372	0.0633	0.0857
H273	0.1095	0.1038	-0.0487
H321	0.3371	-0.2195	1.0885
H322	0.3201	-0.1198	1.1231
H323	0.2897	-0.2087	1.2106
H421	0.9561	0.5113	0.2661
H422	0.8863	0.4463	0.3844
H423	0.8814	0.4645	0.2414

TABLE XXX

ANISOTROPIC THERMAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(o-toluidine)$_2$

ATOM	U11	U22	U33	U12	U13	U23
I1	61 (2)	54 (2)	56 (2)	-17 (2)	-5 (2)	-23 (2)
I2	58 (2)	42 (2)	54 (2)	-11 (2)	4 (2)	-4 (2)
I3	46 (2)	38 (2)	57 (2)	-12 (2)	3 (2)	-16 (2)
I4	55 (2)	61 (2)	56 (2)	-18 (2)	12 (2)	-26 (2)
Cu1	48 (4)	56 (4)	56 (4)	-9 (3)	7 (3)	-15 (3)
Cu2	51 (4)	56 (4)	50 (4)	-18 (3)	-3 (3)	-8 (3)
Cu3	70 (4)	61 (4)	47 (4)	-17 (3)	-1 (3)	-10 (3)
Cu4	74 (5)	50 (4)	77 (5)	-6 (3)	0 (4)	-29 (4)
N11	5 (2)	4 (2)	4 (2)	0 (2)	0 (2)	0 (2)
N22	4 (2)	6 (2)	5 (2)	-3 (2)	-1 (2)	-1 (2)
N33	6 (3)	4 (2)	6 (3)	-1 (2)	1 (2)	0 (2)
N44	13 (4)	4 (3)	9 (3)	-4 (3)	3 (3)	-2 (2)
C11	4 (3)	6 (3)	5 (3)	-3 (2)	0 (2)	-4 (3)
C12	7 (4)	4(3)	4 (3)	1 (3)	2 (3)	1 (2)
C13	19 (8)	15 (7)	14 (7)	15 (7)	6 (6)	-7 (6)
C14	2 (3)	6 (4)	26 (11)	1 (3)	2 (4)	-6 (5)
C15	10 (5)	14 (6)	4 (4)	-2 (4)	0 (3)	-7 (4)
C16	7 (4)	7(4)	3 (3)	-3 (3)	5 (2)	-2 (3)
C17	10 (5)	11 (5)	6 (4)	-3 (4)	0 (3)	-3 (4)
C21	1 (3)	6 (4)	10 (5)	-1 (2)	-1 (3)	0 (4)
C22	8 (4)	4 (3)	14 (6)	-1 (3)	-4 (4)	2 (3)
C23	11 (6)	2 (4)	24 (11)	-1 (3)	-4 (6)	-2 (5)
C24	12 (7)	12 (6)	24 (11)	-5 (5)	-2 (6)	-11 (7)
C25	20 (7)	19 (7)	4 (4)	-17 (6)	3 (4)	-7 (4)
C26	12 (6)	12 (6)	5 (5)	-5 (5)	0 (4)	-3 (5)
C27	5 (4)	43 (16)	7 (5)	0 (7)	0 (4)	0 (8)
C31	7 (4)	7 (3)	6 (3)	-4 (3)	3(3)	-3 (3)
C32	13 (6)	6 (4)	9 (5)	2 (4)	-5 (4)	-1 (4)

TABLE XXX (Continued)

C41	14 (5)	1 (2)	12 (5)	0 (3)	2 (4)	-3 (3)
C42	16 (6)	6 (4)	30 (10)	1 (4)	-5 (6)	-13 (6)

Anisotropic thermal parameters in the form:

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

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

TABLE XXXI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $Cu_4I_4(CH_3CN)_2(o\text{-toluidine})_2$

I1 - Cu1	2.645 (8)	Cu1 - I1 - Cu3	61.7 (2)
I1 - Cu3	2.709 (9)	Cu1 - I1 - Cu4	60.4 (2)
I1 - Cu4	2.746 (7)	Cu1 - I2 - Cu2	60.9 (2)
I2 - Cu1	2.633 (5)	Cu1 - I2 - Cu4	62.0 (2)
I2 - Cu2	2.663 (7)	Cu1 - I3 - Cu2	59.1 (2)
I2 - Cu4	2.635 (8)	Cu1 - I3 - Cu3	60.5 (2)
I3 - Cu1	2.749 (8)	Cu2 - I2 - Cu4	62.6 (2)
I3 - Cu2	2.697 (6)	Cu2 - I3 - Cu3	59.6 (2)
I3 - Cu3	2.704 (9)	Cu2 - I4 - Cu3	59.9 (2)
I4 - Cu2	2.673 (7)	Cu2 - I4 - Cu4	61.1 (2)
I4 - Cu3	2.699 (7)	Cu3 - I1 - Cu4	59.0 (2)
I4 - Cu4	2.738 (8)	Cu3 - I4 - Cu4	59.2 (2)
Cu1 - N11	2.06 (4)	I1 - Cu1 - N11	104.2 (12)
Cu2 - N22	2.09 (4)	I2 - Cu1 - N11	108.6 (8)
Cu3 - N33	1.96 (3)	I3 - Cu1 - N11	104.9 (12)
Cu4 - N44	2.01 (5)	I2 - Cu2 - N22	110.4 (9)
N11 - C11	1.40 (5)	I3 - Cu2 - N22	104.8 (10)
C11 - C12	1.38 (8)	I4 - Cu2 - N22	101.9 (10)
C12 - C13	1.40 (8)	I1 - Cu3 - N33	101.0 (14)
C13 - C14	1.22 (14)	I3 - Cu3 - N33	110.1 (13)
C14 - C15	1.38 (12)	I4 - Cu3 - N33	106.1 (11)
C15 - C16	1.39 (6)	I1 - Cu4 - N44	98.6 (13)
C16 - C17	1.55 (9)	I2 - Cu4 - N44	119.6 (11)
C16 - C11	1.26 (8)	I4 - Cu4 - N44	103.2 (13)
N22 - C21	1.52 (6)	Cu1 - N11 - C11	118 (2)
C21 - C22	1.46 (8)	N11 - C11 - C12	113 (5)
C22 - C23	1.50 (9)	N11 - C11 - C16	121 (5)
C23 - C24	1.23 (15)	C11 - C12 - C13	115 (6)

TABLE XXXI (Continued)

C24 - C25	1.26 (12)	C12 - C13 - C14	116 (9)
C25 - C26	1.30 (8)	C13 - C14 - C15	130 (7)
C26 - C27	1.56 (14)	C14 - C15 - C16	112 (6)
C26 - C21	1.20 (10)	C15 - C16 - C17	117 (5)
N33 - C31	1.09 (6)	C15 - C16 - C11	120 (6)
C31 - C32	1.41 (7)	C16 - C11 - C12	126 (4)
N44 - C41	1.14 (8)	C17 - C16 - C11	123 (4)
C41 - C42	1.40 (12)	Cu2 - N22 - C21	113 (3)
Cu1 ··· Cu2	2.685 (9)	N22 - C21 - C22	109 (5)
Cu1 ··· Cu3	2.747 (8)	N22 - C21 - C26	125 (5)
Cu1 ··· Cu4	2.711 (9)	C21 - C22 - C23	108 (6)
Cu2 ··· Cu3	2.683 (8)	C22 - C23 - C24	115 (6)
Cu2 ··· Cu4	2.751 (11)	C23 - C24 - C25	132 (8)
Cu3 ··· Cu4	2.685 (8)	C24 - C25 - C26	116 (7)
		C25 - C26 - C27	119 (7)
		C25 - C26 - C21	122 (7)
		C26 - C21 - C22	125 (5)
		C27 - C26 - C21	118 (5)
		Cu3 - N33 - C31	173 (4)
		N33 - C31 - C32	178 (5)
		Cu4 - N44 - C41	167 (4)
		N44 - C41 - C42	171 (6)
		I1 - Cu1 - I2	114.0 (3)
		I1 - Cu1 - I3	110.0 (2)
		I1 - Cu3 - I3	109.4 (2)
		I1 - Cu3 - I4	117.4 (3)
		I1 - Cu4 - I2	110.7 (2)
		I1 - Cu4 - I4	114.8 (2)

TABLE XXXI (Continued)

I2 - Cu1 - I3	114.1 (3)
I2 - Cu2 - I3	114.9 (3)
I2 - Cu2 - I4	110.7 (3)
I2 - Cu4 - I4	109.6 (3)
I3 - Cu2 - I4	113.1 (2)
I3 - Cu3 - I4	112.0 (3)

TABLE XXXII

CRYSTAL DATA FOR $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ -triclinic

Formula	$Cu_4I_4C_{18}H_{24}N_4$
MWT	1058.2
a	14.236(5) Å
b	7.576(2)
c	14.227(6)
α	88.60(3)°
β	70.00(3)
γ	91.19(3)
V	1440.6(9) $Å^3$
F (000)	976
μMoK_α	71.80 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.439 g cm^{-3}
Z	2
Meas. Refl.	3793
Obs. Refl.	3088
R	4.3 %
Space Group	P1 bar
Octants Meas.	±h, k, ±l

TABLE XXXIII

POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$-triclinic

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.3191 (1)	0.4587 (1)	1.0006 (1)
I2	0.5005 (1)	0.0415 (1)	0.8192 (1)
I3	0.3750 (1)	0.4658 (1)	0.6744 (1)
I4	0.1744 (1)	0.0345 (1)	0.8749 (1)
Cu1	0.4438 (1)	0.3722 (2)	0.8162 (1)
Cu2	0.3164 (1)	0.1283 (2)	0.9435 (1)
Cu3	0.2430 (1)	0.3749 (2)	0.8529 (2)
Cu4	0.3525 (2)	0.1257 (2)	0.7430 (1)
N1	0.564 (1)	0.548 (1)	0.799 (1)
N2	0.300 (1)	-0.050 (1)	1.063 (1)
N3	0.121 (1)	0.510 (2)	0.872 (1)
N4	0.370 (1)	-0.008 (2)	0.624 (1)
C11	0.647 (1)	0.544 (1)	0.710 (1)
C12	0.726 (1)	0.429 (2)	0.705 (1)
C13	0.807 (1)	0.418 (2)	0.617 (1)
C14	0.811 (1)	0.517 (2)	0.532 (1)
C15	0.733 (1)	0.630 (2)	0.537 (1)
C16	0.652 (1)	0.646 (2)	0.625 (1)
C17	0.894 (1)	0.503 (2)	0.433 (1)
C21	0.210 (1)	-0.042 (1)	1.150 (1)
C22	0.205 (1)	0.069 (2)	1.225 (1)
C23	0.120 (1)	0.081 (2)	1.304 (1)
C24	0.031 (1)	-0.021 (2)	1.310 (1)
C25	0.040 (1)	-0.136 (2)	1.232 (1)
C26	0.126 (1)	-0.146 (2)	1.153 (1)
C27	-0.074 (1)	-0.008 (2)	1.394 (2)
C31	0.054 (1)	0.584 (2)	0.870 (1)
C32	-0.031 (1)	0.684 (2)	0.870 (2)

TABLE XXXIII (Continued)

C41	0.373 (1)	-0.082 (2)	0.554 (1)
C42	0.369 (1)	-0.174 (2)	0.470 (1)

TABLE XXXIV

HYDROGEN POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ -triclinic

ATOM	X	Y	Z
H11	0.5578	0.5758	0.8626
H12	0.5545	0.6812	0.7856
H21	0.2865	-0.1861	1.0403
H22	0.3527	-0.0578	1.0855
H121	0.7297	0.4100	0.7758
H131	0.8715	0.3491	0.6251
H151	0.7389	0.6792	0.4677
H161	0.6000	0.7739	0.6404
H171	0.8869	0.3758	0.3785
H172	0.8773	0.5280	0.3646
H173	0.9559	0.4669	0.4417
H221	0.2751	0.1511	1.2044
H231	0.1365	0.1387	1.3609
H251	-0.0200	-0.2163	1.2592
H261	0.1307	-0.1983	1.0832
H271	-0.0740	0.1180	1.4361
H272	-0.0771	-0.1087	1.4521
H273	-0.0338	0.0192	1.3765
H321	-0.0151	0.6038	0.8361
H322	0.0200	0.7498	0.7953
H323	-0.0869	0.6287	0.8981
H421	0.3546	-0.2892	0.4625
H422	0.4200	-0.1648	0.4192
H423	0.3000	-0.2147	0.4605

TABLE XXXV

ANISOTROPIC THERMAL PARAMETERS FOR
$Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ -triclinic

ATOM	U11	U22	U33	U12	U13	U23
I1	510 (5)	420 (4)	522 (5)	68 (4)	-199 (4)	-142 (4)
I2	468 (5)	424 (4)	556 (5)	176 (4)	-195 (4)	-28 (4)
I3	842 (7)	590 (6)	671 (6)	6 (5)	-460 (6)	167 (5)
I4	595 (6)	590 (6)	917 (7)	-126 (5)	-458 (6)	33 (5)
Cu1	472 (9)	468 (9)	583 (10)	-16 (7)	-219 (8)	32 (8)
Cu2	513 (9)	465 (9)	542 (10)	0 (7)	- 225 (8)	61 (7)
Cu3	562 (11)	647 (12)	959 (14)	242 (9)	-359 (10)	4 (10)
Cu4	917 (14)	632 (12)	611 (11)	28 (10)	-363 (10)	-196 (9)
N1	56 (6)	34 (5)	40 (6)	4 (5)	-13 (5)	-7 (4)
N2	48 (6)	38 (6)	70 (7)	12 (5)	-36 (6)	1 (5)
N3	60 (8)	62 (8)	102 (10)	17 (6)	-37 (7)	0 (7)
N4	92 (10)	76 (9)	63 (8)	12 (7)	-37 (7)	-30 (7)
C11	59 (8)	29 (6)	48 (7)	-4 (6)	-26 (6)	-6 (5)
C12	72 (9)	37 (7)	70 (9)	-2 (6)	-52 (8)	3 (6)
C13	39 (7)	57 (8)	68 (9)	-5 (6)	-8 (7)	9 (7)
C14	58 (9)	42 (8)	71 (10)	-16 (6)	-12 (8)	4 (7)
C15	76 (10)	41 (7)	50 (8)	-8 (7)	-24 (8)	14 (6)
C16	61 (8)	32 (7)	66 (9)	-4 (6)	-25 (8)	2 (6)
C17	83 (12)	86 (12)	76 (11)	16 (10)	2 (10)	-15 (10)
C21	45 (7)	33 (6)	41 (7)	10 (5)	-14 (6)	5 (6)
C22	46 (8)	49 (8)	45 (8)	1 (6)	-13 (6)	11 (6)
C23	85 (11)	53 (8)	58 (9)	0 (8)	-37 (9)	2 (7)
C24	51 (8)	53 (8)	52 (8)	7 (6)	-2 (6)	6 (6)
C25	56 (9)	46 (8)	71 (10)	-10 (6)	-29 (8)	21 (7)
C26	49 (8)	40 (7)	55 (8)	-5 (6)	-25 (7)	9 (6)
C27	79 (12)	99 (14)	118 (16)	6 (11)	50 (11)	50 (12)
C31	33 (7)	43 (7)	71 (9)	16 (6)	-14 (6)	11 (6)
C32	42 (8)	78 (11)	142 (16)	9 (8)	-20 (10)	31 (11)

TABLE XXXV (Continued)

C41	60 (9)	58 (9)	57 (8)	-6 (7)	-28 (7)	11 (7)
C42	98 (12)	86 (12)	53 (9)	-24 (10)	-14 (9)	-36 (8)

Anisotropic thermal parameters in the form:

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

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

TABLE XXXVI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ -triclinic

I1 - Cu1	2.722 (2)	Cu1 - I1 - Cu2	60.93 (4)
I1 - Cu2	2.654 (2)	Cu1 - I2 - Cu2	61.01 (5)
I1 - Cu3	2.755 (3)	Cu1 - I1 - Cu3	59.65 (6)
I2 - Cu1	2.652 (2)	Cu1 - I2 - Cu4	59.32 (6)
I2 - Cu2	2.718 (2)	Cu1 - I3 - Cu3	62.24 (7)
I2 - Cu4	2.758 (3)	Cu1 - I3 - Cu4	60.41 (6)
I3 - Cu1	2.615 (2)	Cu2 - I4 - Cu3	60.08 (6)
I3 - Cu3	2.656 (2)	Cu2 - I4 - Cu4	62.12 (7)
I3 - Cu4	2.706 (2)	Cu2 - I1 - Cu3	59.13 (6)
I4 - Cu2	2.620 (2)	Cu2 - I2 - Cu4	59.57 (6)
I4 - Cu3	2.711 (2)	Cu3 - I3 - Cu4	59.31 (6)
I4 - Cu4	2.652 (2)	Cu3 - I4 - Cu4	59.29 (6)
Cu1 - N1	2.09 (1)	I1 - Cu1 - N1	100.1 (2)
Cu2 - N2	2.09 (1)	I2 - Cu1 - N1	110.3 (3)
Cu3 - N3	1.98 (1)	I3 - Cu1 - N1	105.0 (3)
Cu4 - N4	1.93 (1)	I1 - Cu2 - N2	110.7 (3)
N1 - C11	1.40 (1)	I2 - Cu2 - N2	99.9 (2)
C11 - C12	1.42 (2)	I4 - Cu2 - N2	104.4 (3)
C12 - C13	1.39 (2)	I1 - Cu3 - N3	108.8 (4)
C13 - C14	1.39 (2)	I3 - Cu3 - N3	108.3 (4)
C14 - C15	1.39 (2)	I4 - Cu3 - N3	103.1 (4)
C15 - C16	1.39 (2)	I2 - Cu4 - N4	108.9 (4)
C14 - C17	1.50 (2)	I3 - Cu4 - N4	103.7 (4)
C16 - C11	1.40 (2)	I4 - Cu4 - N4	107.5 (4)
N2 - C21	1.44 (1)	Cu1 - N1 - C11	118 (1)
C21 - C22	1.36 (2)	N1 - C11 - C12	120 (1)
C22 - C23	1.34 (2)	N1 - C11 - C16	122 (1)
C23 - C24	1.45 (2)	C11 - C12 - C13	121 (1)

TABLE XXXVI (Continued)

C24 - C25	1.39 (2)	C12 - C13 - C14	120 (1)
C25 - C26	1.35 (2)	C13 - C14 - C15	119 (1)
C26 - C21	1.41 (2)	C13 - C14 - C17	122 (1)
C24 - C27	1.58 (2)	C14 - C15 - C16	122 (1)
N3 - C31	1.12 (2)	C15 - C14 - C17	119 (1)
C31 - C32	1.44 (2)	C15 - C16 - C11	120 (1)
N4 - C41	1.15 (2)	C16 - C11 - C12	118 (1)
C41 - C42	1.42 (2)	Cu2 - N2 - C21	118 (1)
Cu1 ··· Cu2	2.726 (2)	N2 - C21 - C22	121 (1)
Cu1 ··· Cu3	2.724 (3)	N2 - C21 - C26	118 (1)
Cu1 ··· Cu4	2.679 (3)	C21 - C22 - C23	121 (1)
Cu2 ··· Cu3	2.670 (3)	C22 - C23 - C24	121 (1)
Cu2 ··· Cu4	2.720 (3)	C23 - C24 - C25	116 (1)
Cu3 ··· Cu4	2.653 (3)	C23 - C24 - C27	125 (1)
		C24 - C25 - C26	123 (1)
		C25 - C24 - C27	119 (1)
		C25 - C26 - C21	119 (1)
		C26 - C21 - C22	120 (1)
		Cu3 - N3 - C31	171 (1)
		N3 - C31 - C32	178 (2)
		Cu4 - N4 - C41	174 (1)
		N4 - C41 - C42	176 (2)
		I1 - Cu1 - I2	110.46 (6)
		I1 - Cu1 - I3	112.25 (7)
		I1 - Cu2 - I2	110.55 (6)
		I1 - Cu2 - I4	117.34 (7)
		I1 - Cu3 - I3	109.98 (8)
		I1 - Cu3 - I4	111.02 (8)

TABLE XXXVI (Continued)

	I2 - Cu1 - I3	117.17 (7)
	I2 - Cu2 - I4	112.29 (7)
	I2 - Cu4 - I3	110.70 (8)
	I2 - Cu4 - I4	110.03 (7)
	I3 - Cu3 - I4	115.28 (8)
	I3 - Cu4 - I4	115.56 (8)

TABLE XXXVII

CRYSTAL DATA FOR $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ -monoclinic

Formula	$Cu_2I_2C_9H_{12}N_2$
MWT	529.11
a	16.325 (7) Å
b	23.293 (14)
c	7.576 (3)
α	90.0°
β	92.25 (3)
γ	90.0
V	2878.4 (23) $Å^3$
F (000)	1952
μMoK_α	71.87 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.441 g cm^{-3}
Z	8
Meas. Refl.	2038
Obs. Refl.	1691
R	4.7 %
Space Group	C2/c
Octants Meas.	±h, k, l

TABLE XXXVIII

POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2(p\text{-toluidine})_2$-monoclinic

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.39971 (7)	0.22534 (4)	0.53433 (14)
I2	0.59073 (6)	0.09008 (3)	0.54151 (11)
Cu1	0.4362 (1)	0.1201 (1)	0.6278 (2)
Cu2	0.5548 (1)	0.2021 (1)	0.6256 (3)
N1	0.3676 (7)	0.0686 (4)	0.4494 (13)
N2	0.6235 (9)	0.2533 (6)	0.4922 (18)
C11	0.2807 (8)	0.0703 (5)	0.4566 (15)
C12	0.2396 (10)	0.0347 (5)	0.5683 (19)
C13	0.1566 (10)	0.0383 (6)	0.5811 (19)
C14	0.1091 (10)	0.0790 (6)	0.4792 (19)
C15	0.1536 (10)	0.1145 (6)	0.3683 (19)
C16	0.2374 (10)	0.1108 (6)	0.3541 (18)
C17	0.0210 (13)	0.0889 (9)	0.4990 (25)
C21	0.6591 (10)	0.2873 (6)	0.4190 (20)
C22	0.6983 (11)	0.3306 (7)	0.3154 (24)

TABLE XXXIX

HYDROGEN POSITIONAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ -monoclinic

ATOM	X	Y	Z
H11	0.3802	0.0811	0.3252
H12	0.3950	0.0368	0.5590
H121	0.2800	0.0040	0.6353
H131	0.1277	-0.0005	0.6496
H151	0.1027	0.1428	0.3390
H161	0.2879	0.1407	0.3008
H171	0.0132	0.0797	0.6438
H172	-0.0084	0.0613	0.3916
H173	0.0034	0.1180	0.6173
H221	0.7600	0.3417	0.3774
H222	0.6738	0.3803	0.3082
H223	0.7000	0.3592	0.4372

TABLE XL

ANISOTROPIC THERMAL PARAMETERS FOR $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ -monoclinic

ATOM	U11	U22	U33	U12	U13	U23
I1	863 (9)	460 (6)	607 (7)	132 (5)	-121 (6)	114 (4)
I2	494 (6)	498 (5)	426 (5)	22 (4)	110 (5)	-95 (4)
Cu1	528 (13)	476 (10)	475 (10)	-16 (7)	-53 (10)	-18 (8)
Cu2	777 (17)	629 (12)	648 (12)	-184 (10)	115 (13)	178 (10)
N1	57 (9)	52 (6)	34 (6)	15 (5)	5 (6)	1 (5)
N2	90 (12)	70 (9)	70 (9)	-21 (8)	14 (10)	16 (8)
C11	50 (10)	42 (7)	27 (6)	4 (6)	2 (7)	-8 (6)
C12	64 (12)	36 (7)	53 (8)	6 (6)	-11 (9)	-5 (6)
C13	52 (12)	71 (10)	47 (8)	-15 (8)	-19 (9)	-1 (7)
C14	44 (11)	84 (11)	40 (8)	-1 (7)	-16 (9)	-9 (8)
C15	71 (13)	59 (9)	48 (9)	5 (8)	-3 (10)	-1 (7)
C16	69 (12)	50 (8)	41 (8)	5 (7)	2 (9)	-5 (7)
C17	54 (13)	194 (22)	60 (12)	24 (12)	-3 (13)	-30 (12)
C21	63 (11)	52 (8)	52 (9)	-9 (7)	4 (10)	8 (7)
C22	85 (15)	70 (10)	88 (12)	-41(9)	3 (12)	14 (9)

Anisotropic thermal parameters in the form:

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

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

TABLE XLI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $Cu_4I_4(CH_3CN)_2$(p-toluidine)$_2$ -monoclinic

I1 - Cu1	2.614 (2)	Cu1 - I1 - Cu2	62.18 (6)
I1 - Cu2	2.654 (3)	Cu1 - I2 - Cu2	59.58 (6)
I2 - Cu1	2.722 (2)	I1 - Cu1 - I2	112.27 (7)
I2 - Cu2	2.754 (2)	I1 - Cu2 - I2	110.02 (7)
Cu1 - N1	2.10 (1)	I1 - Cu1 - N1	104.6 (3)
N1 - C11	1.42 (2)	I2 - Cu1 - N1	100.1 (3)
C11 - C12	1.38 (2)	I1 - Cu2 - N2	107.6 (4)
C12 - C13	1.36 (2)	I2 - Cu2 - N2	109.2 (4)
C13 - C14	1.43 (2)	Cu1 - N1 - C11	118 (1)
C14 - C15	1.40 (2)	N1 - C11 - C12	121 (1)
C15 - C16	1.38 (2)	N1 - C11 - C16	119 (1)
C16 - C11	1.40 (2)	C11 - C12 - C13	121 (1)
C14 - C17	1.47 (3)	C12 - C13 - C14	121 (1)
Cu2 - N2	1.95 (1)	C13 - C14 - C15	116 (1)
N2 - C21	1.14 (2)	C14 - C15 - C16	123 (1)
C21 - C22	1.44 (2)	C13 - C14 - C17	124 (1)
Cu1 ··· Cu2	2.721 (3)	C15 - C14 - C17	120 (1)
Cu1 ··· Cu2'	2.672 (3)	C15 - C16 - C11	119 (1)
Cu1' ··· Cu2	2.672 (3)	C16 - C11 - C12	120 (1)
Cu1' ··· Cu2'	2.719 (3)	Cu2 - N2 - C21	174 (1)
Cu1 ··· Cu1'	2.732 (3)	N2 - C21 - C22	175 (2)
Cu2 ··· Cu2'	2.648 (3)	Cu1 - I1 - Cu2'	60.24 (6)
		Cu1 - I2' - Cu1'	61.07 (6)
		Cu1 - I2' - Cu2'	59.18 (6)
		Cu1 - I2 - Cu1'	61.07 (6)
		Cu2 - I1 - Cu2'	59.18 (6)
		Cu2 - I1' - Cu2'	59.21 (6)
		Cu2 - I1' - Cu1'	60.24 (6)

TABLE XLI (Continued)

Cu2 - I2 - Cu1'	59.18 (6)
Cu1' - I1' - Cu2'	62.18 (6)
Cu1' - I2' - Cu2'	59.54 (6)
I1 - Cu1 - I2'	117.28 (7)
I1 - Cu2 - I1'	115.48 (8)
I1 - Cu2' - I1'	115.52 (8)
I1 - Cu2' - I2'	110.86 (7)
I2 - Cu1' - I2'	110.40 (7)
I2 - Cu1 - I2'	110.40 (7)
I2 - Cu2 - I1'	110.89 (7)
I2 - Cu1' - I1'	117.28 (7)
I1' - Cu1' - I2'	112.27 (7)
I1' - Cu2' - I2'	110.05 (7)

Symmetry operation:

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

TABLE XLII

CRYSTAL DATA FOR $Cu_2I_2(CH_3CN)_2$(2-amino-6-methyl-pyridine)$_2$

Formula	$(CuIC_8H_{11}N_3)_n$
MWT	339.6
a	7.768(3) Å
b	19.483(5)
c	7.342(2)
α	90.0°
β	102.58(3)
γ	90.0
V	1084.4(6) Å^3
F (000)	648
μMoK_α	47.98 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.080 cm^{-3}
Z	4
Meas. Refl.	1409
Obs. Refl.	1130
R	5.0 %
Space Group	$P2_1/a$
Octants Meas.	$\pm$h, k, l

TABLE XLIII

POSITIONAL PARAMETERS FOR $Cu_2I_2(CH_3CN)_2$(2-amino-6-methyl-pyridine)$_2$

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.21397 (10)	0.05732 (4)	0.91162 (11)
Cu1	-0.1187 (2)	0.0678 (1)	0.9682 (2)
N1	-0.117 (1)	0.1432 (1)	1.166 (1)
N2	0.063 (1)	0.0757 (5)	1.389 (1)
N3	-0.269 (1)	0.0697 (5)	0.708 (2)
C1	-0.032 (1)	0.1352 (6)	1.342 (2)
C2	-0.032 (2)	0.1840 (6)	1.480 (2)
C3	-0.119 (2)	0.2440 (6)	1.432 (2)
C4	-0.204 (2)	0.2549 (6)	1.247 (2)
C5	-0.205 (2)	0.2053 (7)	1.117 (2)
C6	-0.302 (2)	0.2123 (7)	0.918 (2)
C7	-0.350 (2)	0.0750 (6)	0.559 (2)
C8	-0.453 (2)	0.0830 (7)	0.373 (2)

TABLE XLIV

HYDROGEN POSITIONAL PARAMETERS FOR $Cu_2I_2(CH_3CN)_2$(2-amino-6-methyl-pyridine)$_2$

ATOM	X	Y	Z
H2	0.0437	0.1756	1.6136
H3	-0.1137	0.2872	1.5254
H4	-0.2808	0.3028	1.1938
H11	0.0422	0.0423	1.2895
H12	0.0929	0.0617	1.5331
H21	0.2796	0.2203	-0.3501
H61	-0.3326	0.2543	0.8503
H62	-0.1851	0.2102	0.8235
H63	-0.3978	0.1663	0.8824
H81	-0.4153	0.0488	0.2911
H82	-0.5605	0.0758	0.3761
H83	-0.4305	0.1384	0.3148

TABLE XLV

ANISOTROPIC THERMAL PARAMETERS FOR $Cu_2I_2(CH_3CN)$(2-amino-6-methyl-pyridine)

ATOM	U11	U22	U33	U12	U13	U23
I1	516 (6)	297 (5)	353 (5)	-3 (4)	18 (4)	7 (4)
CU1	706 (12)	400 (10)	304 (9)	40 (8)	-15 (8)	-40 (7)
N1	39 (5)	25 (5)	25 (5)	0 (4)	1 (4)	3 (4)
N2	61 (7)	35 (6)	32 (6)	14 (5)	-2 (5)	-1 (4)
N3	59 (9)	34 (6)	38 (7)	0 (5)	6 (6)	0 (5)
C1	41 (7)	24 (6)	32 (7)	-2 (5)	12 (6)	4 (5)
C2	55 (8)	28 (7)	29 (6)	-3 (6)	6 (6)	1 (5)
C3	68 (9)	25 (7)	46 (8)	-3 (6)	18 (7)	-6 (6)
C4	57 (8)	34 (8)	42 (8)	3 (6)	14 (6)	-2 (6)
C5	48 (8)	37 (8)	39 (7)	2 (6)	11 (6)	0 (6)
C6	82 (11)	33 (8)	70 (10)	23 (7)	0 (8)	24 (7)
C7	51 (8)	24 (7)	35 (8)	-2 (6)	4 (6)	0 (5)
C8	53 (8)	48 (8)	39 (8)	-3 (6)	2 (6)	0 (6)

Anisotropic thermal parameters in the form:

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

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

TABLE XLVI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $Cu_2I_2(CH_3CN)$(2-amino-6-methyl-pyridine)

I1 - Cu1	2.713 (2)	Cu1 - I1 - Cu1'	71.6 (5)
I1 - Cu1'	2.746 (2)	I1 - Cu1 - I1'	108.4 (6)
Cu1 - Cu1'	3.195 (2)	I1 - Cu1 - N1	107.6 (3)
Cu1 - N1	2.065 (9)	I1 - Cu1 - N3	103.4 (4)
Cu1 - N3	2.008 (10)	N1 - Cu1 - N3	124.6 (4)
N1 - C1	1.32 (1)	I1' - Cu1 - N1	55.7 (1)
N1 - C5	1.40 (2)	I1' - Cu1 - N3	100.4 (3)
C7 - C8	1.44 (2)	I1 - Cu1' - I1'	108.4 (6)
C1 - C2	1.39 (2)	Cu1 - N1 - C1	122 (1)
C1 - N2	1.37 (1)	Cu1 - N1 - C5	120 (1)
C2 - C3	1.36 (2)	Cu1 - N3 - C7	175 (1)
C4 - C5	1.36 (2)	N1 - C1 - C2	123 (1)
C5 - C6	1.50 (2)	N2 - C1 - C2	118 (1)
N3 - C7	1.14 (2)	C1 - C2 - C3	118 (1)
		C2 - C3 - C4	119 (1)
		C3 - C4 - C5	120 (1)
		C4 - C5 - N1	120 (1)
		N1 - C5 - C6	116 (1)
		N3 - C7 - C8	179 (1)

symmetry operation:

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

TABLE XLVII

CRYSTAL DATA FOR Cu_2I_2(2,6-diamino-pyridine)$_2$

Formula	$(CuIC_5H_7N_3)_n$
MWT	299.58
a	15.432(7) Å
b	11.890(6)
c	4.277(2)
α	90.0°
β	97.82(3)
γ	90.0
V	777.5(6) $Å^3$
F (000)	560
μMoK_α	66.74 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.559 g cm^{-3}
Z	4
Meas. Refl.	2261
Obs. Refl.	468
R	9.3 %
Space Group	$P2_1/a$
Octants Meas.	±h, k, l

TABLE XLVIII

POSITIONAL PARAMETERS FOR Cu_2I_2(2,6-diamino-pyridine)$_2$

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.4824 (3)	0.1480 (4)	0.2822 (11)
Cu1	0.4143 (6)	0.0431 (8)	0.7480 (22)
N1	0.291 (4)	0.019 (4)	0.760 (12)
N2	0.319 (4)	-0.128 (5)	1.092 (12)
N3	0.259 (6)	0.172 (6)	0.431 (15)
C1	0.250 (6)	-0.058 (6)	0.927 (16)
C2	0.194 (12)	-0.075 (9)	1.084 (52)
C3	0.118 (7)	-0.005 (6)	0.799 (24)
C4	0.136 (5)	0.077 (8)	0.632 (20)
C5	0.229 (6)	0.090 (7)	0.612 (18)

TABLE XLIX

HYDROGEN POSITIONAL PARAMETERS FOR Cu_2I_2(2,6-diamino-pyridine)$_2$

ATOM	X	Y	Z
H21	0.1418	-0.1419	1.0717
H31	0.0450	-0.0247	0.7926
H41	0.0892	0.1277	0.5213

TABLE L

ANISOTROPIC THERMAL PARAMETERS FOR Cu_2I_2(2,6-diamino-pyridine)$_2$

ATOM	U11	U22	U33	U12	U13	U23
I1	36 (2)	29 (2)	32 (2)	4 (3)	5 (2)	-1 (3)
Cu1	37 (7)	45 (6)	48 (6)	-10 (5)	6 (5)	0 (5)
N1	4 (4)	0 (3)	2 (3)	-1 (3)	0 (3)	0 (2)
N2	4 (4)	3 (4)	3 (3)	2 (3)	-1 (3)	2 (3)
N3	16 (8)	3 (6)	4 (4)	-7 (5)	-4 (5)	2 (4)
C1	6 (5)	3 (5)	3 (4)	-1 (4)	-1 (4)	-2 (3)
C2	25 (22)	2 (7)	49 (34)	-7 (10)	37 (27)	-9 (12)
C3	10 (8)	0 (4)	9 (7)	0 (5)	6 (6)	0 (4)
C4	2 (4)	8 (7)	5 (5)	0 (5)	2 (4)	-4 (5)
C5	6 (6)	4 (5)	3 (4)	-2 (5)	2 (4)	-3 (4)

Anisotropic thermal parameters in the form:

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

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

TABLE LI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR Cu_2I_2(2,6-diamino-pyridine)$_2$

I1 - Cu1	2.683 (11)	Cu1 - I1 - Cu1'	86.5 (3)
I1 - Cu1'	2.789 (11)	I1 - Cu1 - I1'	93.5 (3)
Cu1 - Cu1'	3.751 (13)	I1 - Cu1 - N1	125.2 (16)
Cu1 - N1	1.93 (6)	Cu1 - N1 - C1	130 (5)
N1 - C1	1.36 (10)	Cu1 - N1 - C5	121 (5)
N1 - C5	1.37 (10)	N1 - C1 - C2	147 (9)
C5 - N3	1.36 (11)	N2 - C1 - C2	99 (9)
C1 - C2	1.18 (22)	C1 - C2 - C3	90 (13)
C1 - N2	1.45 (9)	C2 - C3 - C4	125 (9)
C2 - C3	1.78 (20)	C3 - C4 - C5	114 (8)
C4 - C5	1.47 (12)	C4 - C5 - N3	121 (8)
C5 - N3	1.36 (11)	C4 - C5 - N1	122 (7)
		N1 - C5 - N3	116 (8)

Symmetry operation:

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

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VITA

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