I. CORRELATION OF STRUCTURAL DETAILS AND EMISSION PROPERTIES OF COPPER(I)IODIDE COMPLEXES WITH ALIPHATIC AMINES

II. COPPER(I) HALIDE π COMPLEXES

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INTRODUCTION

Two areas of investigation are involved in this study. The major emphasis is placed upon establishing a correlation between structural details as determined by single crystal X-ray analysis and emission properties of copper(I) iodide complexes with aliphatic nitrogen bases. The second area of interest is the synthesis and X-ray structural characterization of copper(I) halide π complexes.

Copper(I) iodide aliphatic amine complexes are of interest because they lack the possibility of ligand centered solid state emission (metal - ligand charge transfer and ligand - ligand charge transfer). Therefore, attention can be focused on the mechanisms of solid state emission originating from metal centered electron transitions (single metal excitation and metal - metal charge transfer). This investigation was intended to provide knowledge of how the molecular structures of copper(I) iodide complexes influence their solid state emission properties and thus an idea of how to design materials for practical application such as fluorescent/phosphorescent sensitizers for photoconductors (1, 2).

Luminescent behavior of copper(I) halides and their complexes was discovered by J. T. Randall in 1939 (3,4). He reported that this luminescence was temperature dependent in many cases, i.e. the solid state emission changed color when the temperature was lowered to 77 K. In the 1970's, several investigators were actively interested in the emission properties of Cu(I) halide complexes. H. D. Hardt was one of the primary investigators in this area, reporting numerous examples of luminescent copper(I) halide complexes (5 - 13). Since this early work, many luminescent copper(I) halide complexes have been examined.

So far, most of the single crystal structural investigation of copper(I) halide complexes with nitrogen donor ligands has focused on those complexes with unsaturated nitrogen bases such as pyridine, quinoline and their derivatives (14, 15). Only limited numbers of single crystal structures of copper(I) halide complexed with saturated nitrogen donor ligands were previously known because of the difficulty in obtaining single crystals of suitable quality due to the air and moisture sensitivity of the complexes (16 - 20).

In this work, copper(I) iodide complexes with aliphatic amines were synthesized and structurally characterized by single crystal X-ray diffraction. These complexes crystallize in different motifs such as cube ($Cu_4I_4L_4$), rhombohedron ($Cu_2I_2L_4$) and polymeric chain ($(CuIL_2)_n$). The solid state emission spectra of a series of cubic and rhombohedral complexes were measured by exciting the compound at $\lambda = 300$ nm at temperatures ranging from 10 K to 298 K. The emission properties of these compounds in the range 350-700 nm are discussed in terms of their structural details.

The second area of study is the synthesis and single crystal X-ray examination of copper(I) halide π complexes with donors such as cyclooctadiene and norbornene. These complexes are stable to air and moisture. No solid state emission of copper(I) halide π complexes was found upon excitation with UV light in the temperature range, 10 K to 298 K.

PART I

CORRELATION OF STRUCTURAL DETAILS AND EMISSION PROPERTIES OF COPPER(I)IODIDE COMPLEXES WITH ALIPHATIC AMINES

CHAPTER I

INTRODUCTION AND HISTORICAL

Luminescence of copper(I) halides was first reported by J. T. Randall in 1938 (3, 4). He found that, in many cases, the luminescence of these materials was temperature dependent, i.e. the visible color of the emission changed between room temperature and 77 K. In the 1970's, H. D. Hardt and co-workers prepared a great number of copper(I) halide Lewis base complexes (5 - 13), mainly with pyridine derivatives, whose emission, as observed by eye, was temperature dependent. He termed this phenomenon " fluorescence thermochromism" (6, 7). On examining the temperature dependent emission in a more quantitative manner with a low temperature fluorometer, he found that there were two different phenomena responsible for the change in color of emission with temperature: (a) a shift of the λ_{max} and (b) an intensity change of λ_{max} with temperature.

The first attempt at an explanation of temperature dependent luminescence involving a shift of λ_{max} was made by Weber and Hardt (12). They compared the powder diffraction patterns of the formate, acetate, propionate, and butyrate salts of copper(I) and found all of the carboxylate structures to be of the same general motif. They concluded that the thermochromicity must be due to a difference in packing. They plotted the change of wavelength of maximum emission between 300 K and 70 K for the carboxylates as a function of the number of carbon atoms and observed that the curve showed minima for the carboxylates with odd numbers of carbon atoms. For carboxylates whose change in emission maximum was smaller, the melting points of their parent alkanes were also lower suggesting looser packing in the solid. Those with lower melting points or smaller change in emission maximum had odd numbers of carbon atoms. Hardt and Weber proposed that those carboxylates with an odd number of carbon atoms pack more loosely while those with an even number of carbon atoms pack closely. Tight packing leads to thermochromic emission while loose packing leads to non-thermochromic emission because loosely packed molecules are more free to oscillate and to disperse a great part of their excitation energy non-radiatively.

From a study of the emission properties of the Cu(I)iodide hexamethylenetetraamine (HMTA) complexes, Hardt and Gechnizdjani (13) suggested that thermochromicity might be related to mobility of the solid structure in the lattice. They observed that thermochromicity of the compound varies with solvent and with method of preparation. The products obtained were all fine powders therefore structural characterization was incomplete. However these authors claimed that the products were homogeneous and did not contain any residual particles of copper(I) iodide. Cu(I)iodide(HMTA) displayed yellow emission at room temperature changing to red at 77 K, when methanol or ethanol were used as the solvent. However, if the structure was 'tightened' by inclusion of additional HMTA or the presence of a second nitrogen base such as pyridine in the solid state, the compound no longer showed thermochromism. Based on this observation, they proposed a hypothesis called the " framework hypothesis" suggesting that " complexes in which each copper atom has at least 1.33 ligands available are of particularly tight structure and there is perhaps insufficient mobility in their lattices for thermochromism."

Schramm and co-workers (16, 17) suggested that thermochromicity was related to crystallographic symmetry. They found that emission of the Cu_4I_4(piperidine)$_4$ complex did not show the phenomenon of " fluorescence thermochromism." From the single crystal X-ray structure, they observed that this compound has a fourfold inversion axis (S_4) within the cubic cluster. They compared this observation with the thermochromism observed for tetrameric clusters Cu_4I_4(morpholine)$_4$ (16) and Cu_4I_4(pyridine)$_4$ (14) which have respectively a twofold axis and no symmetry element. A working hypothesis was proposed: " A tetrameric complex between copper iodide and a nitrogen base should not show a marked fluorescence thermochromism if the point symmetry of its cluster molecule is at least of fourfold order, i.e., if the Cu - N bond lengths involved are all equal by symmetry." (16). Hardt and Pierre also attempted to define the correlations between symmetry of cubic clusters and fluorescence thermochromism (17). By studying emission properties of a series of copper iodide complexes, they observed that red shifts seen on cooling the three cubic clusters are; 15 nm for Cu_4I_4(piperidine)$_4$, 35 nm for Cu_4I_4(morpholine)$_4$ and 50 nm for Cu_4I_4(pyridine)$_4$. From the crystallographic literature (14, 16, 21), they noticed that Cu...Cu distances for all three clusters are similar (overall range: 2.59 -2.72 (Å)), and that the symmetry elements within these clusters are: a fourfold inversion axis for Cu_4I_4(piperidine)$_4$, a twofold axis for Cu_4I_4(mopholine)$_4$ and a onefold axis for Cu_4I_4(pyridine)$_4$. Based upon above information, they concluded that the extent of the shift of the emission wavelength with temperature depends more on the symmetry of the cluster than on the Cu...Cu distance. They pointed out that the higher the solid state symmetry of the cluster, the less the extent of the shift.

Previous workers have suggested that emission in solid state complexes originates from five sources (15):

1) Metal to Ligand Charge Transfer (MLCT)
2) Ligand - Ligand Interaction (LLI)
3) Single Metal Excitation (SME)
4) Metal - Metal Interaction (MMI)
5) Donor-Accceptor Pairs (DAP)

Metal to ligand charge transfer (MLCT) for copper complexes involves 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 (21 - 23). This transition is observed for many copper(I) halide complexes in which copper is ligated to nitrogen electron pair donor ligands in which the donor atom is part of an unsaturated system such as pyridine or quinoline. The emission for the cubic complex, Cu_4I_4(pyridine)$_4$, was the first one assigned to MLCT (21, 24). This cubic complex shows solid state emission at 560 nm at room temperature and the emission peak shifts to 610 nm at 77 K (21). The cubic pyridine complex shows another emission band at 430 nm at low temperature which might originate from copper to copper interaction. Emission from the complexes, (CuI(quinoline)$_2$)$_2$ and Cu_4I_4(quinoline)$_4$ at 620 and 615 nm, respectively, was assigned to MLCT (15).

Ligand - ligand interaction (LLI), which involves π - π^* transition, occurs when the π systems of the ligands are packed in parallel fashion in the crystal and close to each other. The low temperature (77 K) emission spectrum of Cu_4I_4(quinoline)$_4$ (15) displays fine structure identical to that of the frozen solution of quinoline in ethanol at 77 K (25), which indicates LLI. In this complex, the ligands are lined up in a parallel fashion and the distances between ligands within each tetramer are 3.352 Å and 3.279Å at room temperature. The distances between ligands are apparently lessened on cooling, allowing a π - π^* interaction when the temperature is below 77 K.

Single metal excitation (SME) is based upon a single metal and may be described electronically as a $3d^{10}$ - $3d^94s^1$ transition. The existence of SME in copper(I) complexes may be illustrated by the CuI complexes of piperidine and morpholine. Both ligands are non - aromatic, therefore neither MLCT nor LLI can take place. The morpholine complex (Cu_4I_4(morpholine)$_4$) emits at 626 nm at room temperature (17) while the piperidine complex (Cu_4I_4(piperidine)$_4$) emits at 570 nm at room temperature (16).

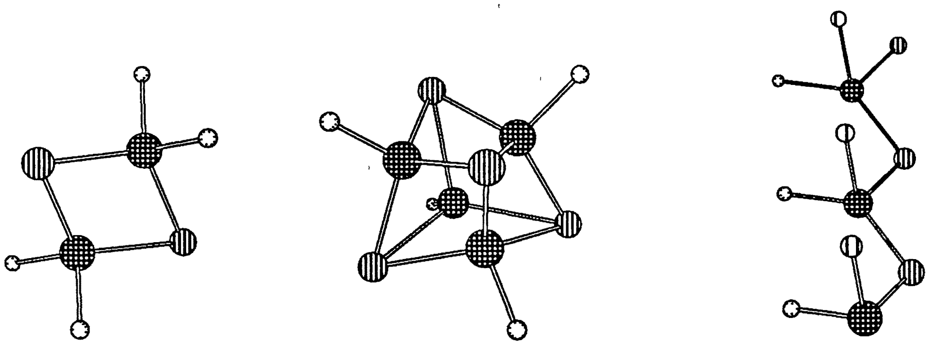
Metal to metal interaction (MMI) is observed for solid state copper(I) complexes (14, 26) in which copper atoms are less than 2.6 Å apart and may be represented as $3d^{10}3d^{10}$ - $3d^93d^{10}4s^1$ excitation. The existence of MMI in copper(I) clusters has also been supported by molecular orbital calculations (27). Mehrotra and Hoffmann reported that for Cu_2^{+2} clusters which have a Cu - Cu separation of 2.58 Å, overlap population is great enough to provide " soft attractive Cu(I) - Cu(I) interaction ". If we consider the 3d orbitals on Cu alone, the interaction between Cu atoms is repulsive which is indicated by both the binding energy becoming increasingly positive and the overlap population becoming increasingly negative as the Cu atoms are brought closer together. However, if 4s and 4p orbitals are included in the calculations, the binding energy becomes more negative and the overlap population become more positive, indicating an increase in the attraction between the Cu atoms.

Donor-accepter pairs (DAP) have been suggested to be the source of the 420 nm emission in crystalline CuI excited at 337 nm (17). The calculated values of the ionization energies for the donors and acceptors participating in the formation of DAP were Ed=0.045-0.065 eV and Ea=0.155-0.170 eV. The solid state material also displays a series of narrow band emissions at lower and higher wave lengths attributed to excitation phenomena.

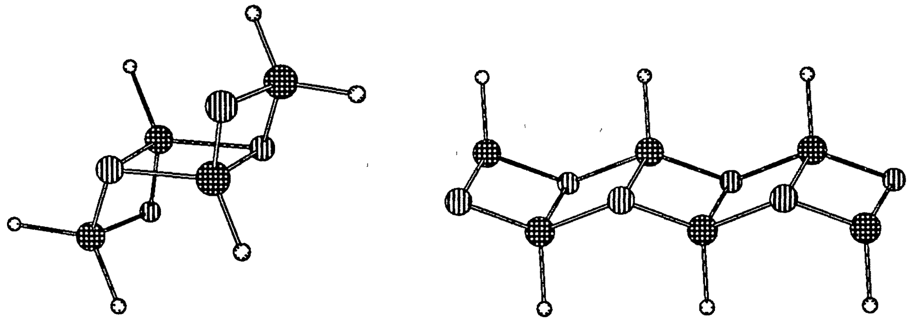
The complexes of copper(I) halides (CuX) with Lewis bases crystallize in a variety of structural motifs and stoichiometries. X may be Cl, Br or I with the iodides normally more stable with respect to air and moisture. Common stoichiometries are 1:1:1 and 1:1:2, Cu : X : L (L = ligand). Stoichiometries of 1:1:0.5, 1:1:1.5, 1:1:2.5 and 1:1:3 have also been noted. Frequently observed structural motifs of copper(I) halide complexes are rhombs, cubes, chairs, polymeric pleated sheets and polymeric chains as illustrated in Figure 1.

The goal of this research was to focus on the emission of copper(I) complexes due to nonligand based mechanisms, i.e. single metal excitation (SME) or metal to metal interaction (MMI). Attention was paid to complexes of copper(I) halides with saturated nitrogen ligands. However, as most of those compounds exhibit air and moisture sensitivity and a tendency to disproportionate, only a few of them have previously been examined by single crystal X-ray crystallographic techniques (16 - 20). The stability of the copper(I) complexes depends upon the nature of the ligated nitrogen atom. A saturated amino group stabilizes the (+ 2) oxidation state of copper atom and therefore promotes the disproportionation and oxidation of Cu(I).

In 1974, V. Schramm and co-workers reported the X-ray single crystal structure of the copper(I) iodide morpholine (1:1) complex (18) in which two rhombohedra of alternating copper and iodide atoms are combined by face sharing to give a cube with copper and iodide atoms at alternate corners. Each copper achieves tetrahedral coordination by ligation to a morpholine molecule. The compound crystallizes in space group B2/b and



romb cube polymeric chain



chair polymeric pleated sheet

Figure 1. Motifs of Copper(I) Halides Complexes

has a twofold axis within the cubic cluster. The average interatomic distances are: Cu...Cu = 2.65 (3)(Å); Cu - I = 2.75 (1)(Å); Cu - N = 2.02 (4)(Å).

The crystal structure of $Cu_4I_4(piperidine)_4$, which was reported by V. Schramm in 1978 (16), has a cubic tetrahedral Cu_4I_4 core which is similar to that of the morpholine - copper(I) iodide structure. The space group of the compound was determined as $P4_2/n$. The tetrameric molecules are centered on sites of 4 bar (S_4) symmetry. The average bond distances in this structure are: Cu...Cu = 2.65 (1)(Å); Cu - I = 2.70 (1)(Å); Cu - N = 2.05 (1)(Å). The geometry of the tetrameric molecule is shown in Figure 2.

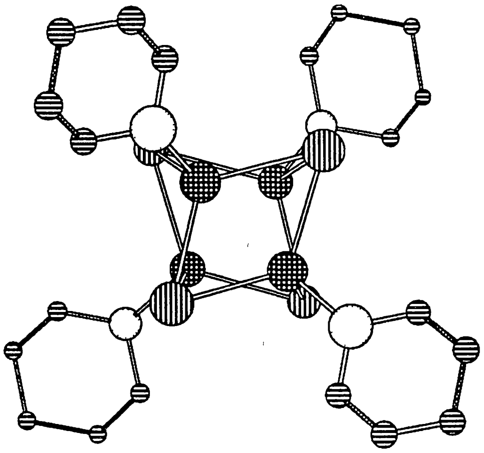


Figure 2. Tetrameric Unit of $Cu_4I_4(piperidine)_4$ with 4 bar Crystallographic Symmetry

In 1983, P. C. Healy and co-workers reported the crystal structure of the triethylamine-copper (I) iodide complex which has the novel stoichiometry: $(Cu_4I_4(NEt_3))$ (19). Polymeric strings of Cu_4I_4 units are linked to each other by one Cu - I bond (Figure 3). The polymeric direction is a threefold axis. Since one copper atom and iodide atom in the Cu_4I_4 core have a different environment from the others, there are two sets of Cu - I and Cu...Cu distances. The Cu - I distances within the Cu_4I_4 unit average

2.644(4)(Å), and the Cu - I distance between the two atoms that connect two Cu_4I_4 cores is 2.930(9)(Å). The distance between two copper atoms, each coordinated to ligands, is 2.769(8)(Å) average and the distance between copper atoms with different environments is 3.030(8)(Å). The average Cu - N distance is 2.11(3)(Å).

The copper(I) halide complexes: N, N' - diisopropylethylenediamine(DIET) copper(I) bromide and the N, N' - diisopropylethylenediamine copper(I) iodide dimer were first characterized by single-crystal X - ray diffraction by D. A. Haitko in 1984 (20). A previous attempt to characterize these complexes was unsuccessful due to their extreme air and moisture sensitivity (29). Copper atoms in the Cu(I)bromide-DIET complex adopt three - coordinate planer geometry. The space group of the compound was determined to be C2/c and the bond distances are: Cu - Br = 2.263(2)(Å) ; Cu - N = 2.062(6)(Å).

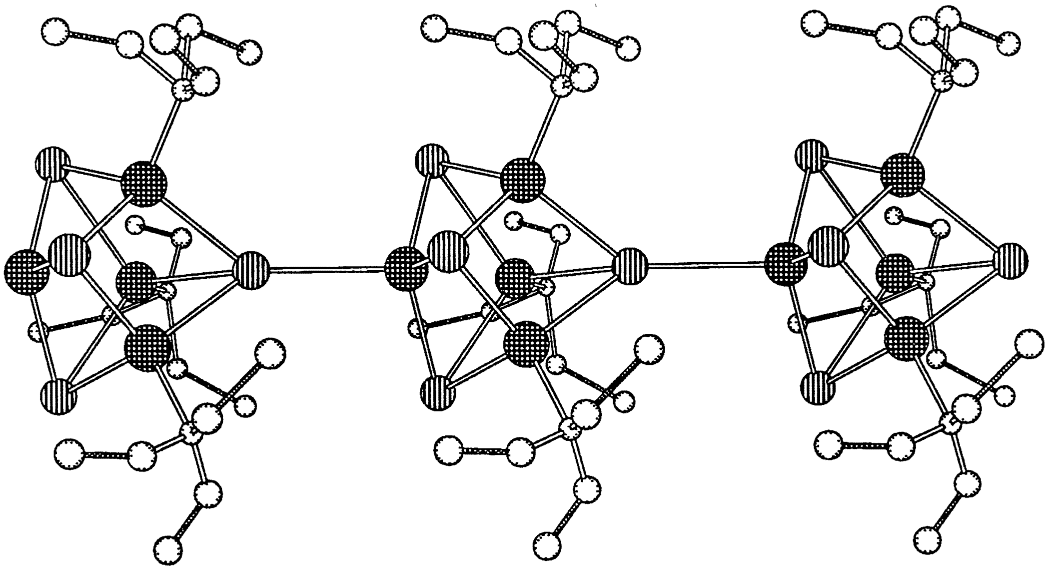


Figure 3. A Segment of Polymeric String of ($Cu_4I_4(NEt_3)_3$)

The N, N' - diisopropylethylenediamine copper(I) iodide dimer exhibits pseudo-tetrahedral geometry about each copper. Copper atoms in the $Cu_2I_2(DIET)_2$ complex adopt four-coordinate tetrahedral geometry. The space group was identified as $P2_1/c$. Average bond lengths are : Cu - I = 2.622(1)(Å); Cu...Cu'= 2.733(1)(Å); Cu - N = 2.173(3)(Å).

L. M. Engelhardt et al. reported the crystallization of N, N, N',N' - tetramethylethylenediamine (TMEDA) with the copper(I) halides to give 1:1 adducts (21). The iodide and chloride complexes were examined by single-crystal X-ray diffraction. Structural determination of the bromide complex failed because of the poor quality of the crystal. However, these authors thought the structure of the bromine complex might be similar to that of the iodide complex based on determination of a similar unit cell and space group. The 1:1 adduct of copper(I) chloride and TMEDA turned out to be an ionic complex. The asymmetric unit of the structure is comprised of a bis(ligand)copper(I) cation and a pair of dichlorocuprate(I) anions. Average Cu-N distance in the cation is 2.16(2)(Å) and the Cu-Cl distance in the anion is 2.086(1)(Å). The structure of the iodide complex shows the asymmetric unit of the structure to be a μ,μ'-diiodobridged dimer which is shown in Figure 4. The average bond distances are: Cu...Cu = 2.566(4)(Å); Cu-I = 2.601(5)(Å); Cu-N = 2.17(2)(Å).

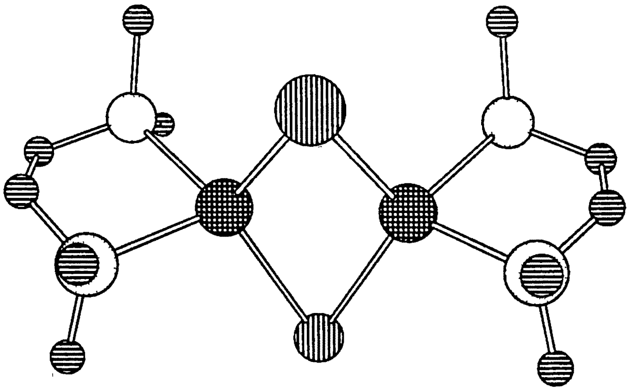


Figure 4. The Asymmetric Unit of Cu(I)-TMEDA Complex

Apart from this information, there was no published data about the emission and structural characteristics of copper(I) halides complexed with aliphatic amines. No two structures are similar; their solid state emission properties have not been reported. In most cases, the results of the investigation have been viewed in an empirical fashion. The detailed investigation of the solid state emission properties of copper(I) complexes of well characterized methods was seen as a pathway to more conclusive understanding of the excitation and emission process. Such a knowledge is important in predicting and designing luminescent materials for practical purposes.

CHAPTER II

X - RAY CRYSTALLOGRAPHY

A crystal is a solid formed by the systematic arrangement of atoms, and ions or molecules. Every crystal has a lattice as its geometric basis. A sufficient representative portion of the lattice is called the unit cell. Unit cells are lined up in an ordered fashion to form the crystal. The geometry of an 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 class to which the unit cell belongs (30).

There are seven classes of crystals:

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

The atoms or molecules in a unit cell may be related to each other by symmetry elements such as rotation axes, inversion centers, mirrors, glide planes, and screw axes. In addition, there may be a repetition of motif in the center of particular faces of the unit cell (face centering); or in the center of the volume of the unit cell (body centering). The absence of centering renders the cell primitive.

The crystals chosen for X-ray studies had the approximate dimensions 0.2, 0.2 and 0.2mm. The crystals were visually selected under a microscope on the basis of well defined edges and faces and absence of obvious cracks. If the crystal is too large, it can be cut to the appropriate size.

Beams of X - ray will be diffracted from a crystal when the Bragg equation is satisfied:

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

where λ is the wavelength of the radiation , θ is the angle of incidence and the angle of diffraction of the X - ray beam with the set of planes diffracting, and d is the the perpendicular distance between two lattice planes. Thus, the Bragg equation defines the necessary conditions for diffraction of an X - ray beam for a fixed wavelength by a set of parallel lattice planes of interplanar spacing d.

The photograph consists of a diffraction pattern which exhibits both horizontal and vertical mirror symmetry about the center of the film. A strong reflection is chosen such that $\chi > 75^o$ and $2\theta < 20^o$. This reflection is used to adjust the height of the crystal accurately. Fifteen independent reflections are then centered to determine the optimum 2θ, ω, ϕ, and χ angles for each reflection (31). From these data, unit cell dimensions are calculated accurately by the method of the least squares. If the errors (standard deviations) of the cell dimensions are unacceptably high, a fast data scan may be carried out to find fifteen intense reflections with 2θ values which are greater than 20^o. The cell determination procedure is then repeated to yield a cell with more acceptable errors. In some case a cell with greater symmetry may be found using cell vector programs NEWLAT (32) and TRACER . TRACER identifies the reduced primitive cell and may indicate the presence of higher symmetry. A set of data is collected such that the diffraction symmetry of the cell generates a complete sphere of data (33). Thus the minimum diffraction symmetry of the crystal must be considered in selecting parameters for data collection.

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

The diffraction data is reduced by a computer program called DATRDN which applies four correction factors (34): for background, polarization, Lorentz effect, and crystal decomposition.

Correction for left and right background is calculated as follows:

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

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

where :

I_{int} = Integrated Intensity

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

I_{meas} = Measured Intensity

Lbg = Left Background

Rbg = Right Background

The reflection is considered observed if:

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

The polarization term arises because of the nature of the X - ray beam and the manner in which the efficiency of diffraction varies with the reflection angle. The unpolarized vector of the X - ray beam has a parallel component (I_{para}) and a perpendicular component (I_{perp}). 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 an 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. The factor ($1 + \cos^2 2\theta$) is thus a simple function of 2θ and is independent of the method of collection; it is known as the polarization factor (p).

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

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

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

$$LP = (1 + \cos^2 2\theta) / 2\sin 2\theta \qquad (9)$$

The final correction is applied in those cases in which the crystal decomposes during data collection. This correction assumes that decomposition is linear with respect to time and is indicated by:

$$I_{orig} / I_{ave} \qquad (10)$$

where:

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

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

These four corrections are combined to form the following expression:

$$I_{cor} = I_{int} \times (LP)^{-1} \times (I_{orig} / I_{ave}) \qquad (11)$$

The structure factor, F_{hkl}, expresses the combined scattering of all atoms in the cell compared to that of a single electron, its amplitude is determined as the square root of the corrected integrated intensity, I_{cor}:

$$| F_{hkl} | = (I_{cor})^{1/2} \qquad (12)$$

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:

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

$$(N_t - N_{lbg} - N_{Rbg})^{1/2} \qquad (13)$$

where:

N_t = no.of counts

N_{lbg} = no. of left background counts

N_{rbg} = no. of right background counts

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

The algebraic representation for two waves is represented:

$$x_1 = a_1 \cos (\phi + \alpha_1) \qquad (14)$$

$$x_2 = a_2 \cos (\phi + \alpha_2) \qquad (15)$$

where:

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

a = amplitude of the wave

ϕ = an angular variable proportional to time and frequency

α = the phase

When these two waves are superposed the result is:

$$x_r = x_1 + x_2 = a_1 \cos (\phi + \alpha_1) + a_2 \cos (\phi + \alpha_2) \qquad (16)$$

or

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

$$= a_r \cos (\phi + \alpha_r)$$

The amplitudes are related to the phases such that

$$a_r \cos\alpha_r = a_1 \cos\alpha_1 + a_2 \cos\alpha_2 = \Sigma\, a_j \cos\alpha_j \qquad (17)$$

$$a_r \sin\alpha_r = a_1 \sin\alpha_1 + a_2 \sin\alpha_2 = \Sigma\, a_j \sin\alpha_j \qquad (18)$$

Equation (16) and (17) can be abbreviated as A and B respectively

Thus:

$$A = \Sigma\, a_j \cos\alpha_j \qquad (19)$$

$$B = \Sigma\, a_j \sin\alpha_j \qquad (20)$$

and

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

Equation (20) can be represented in complex form as:

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

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

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

$$F_{hkl} = A_{hkl} + iB_{hkl} = | F_{hkl} | e^{i\alpha(h\,k\,l)} \tag{23}$$

where:

$$A_{hkl} = \Sigma f_j \cos\alpha_j \tag{24}$$

$$B_{hkl} = \Sigma f_j \sin\alpha_j \tag{25}$$

$$| F_{hkl} | = ((A_{hkl})^2 + (B_{hkl})^2)^{1/2} \tag{26}$$

where f_j represent individual atomic scattering factors. The phase α_j are expressed by:

$$\alpha_j = 2\pi (hx_j + ky_j + lz_j) \tag{27}$$

thus to obtain a three dimensional electron density map one needs to know amplitudes of the structure factors and their phase

$$\rho (xyz) = (| F (000) | / V_c) + (2 / V_c) \Sigma\Sigma\Sigma \; F \cos (\phi - \alpha) \tag{28}$$

where:

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

V_c = unit cell volume

Determination of a structure must accommodate both amplitude and phase, but the phase α_{hkl} is not directly measurable (33). The phase is determined as the difference in period, expressed as an angle, between that resulting from a specific set of planes and a wave resulting from scattering at the origin. To find the atomic positions in a model, information about the phase of at least some reflections is required so that a Fourier transform of the summation of ΣF leads to an interpretable electron density map showing the atomic positional parameters.

The phase problem can be solved by direct methods or by the Patterson method. The Patterson method may be used only for structures which contain heavy atoms. In this method a function P (u,v,w) is defined such that

$$P(u,v,w) = 1/v_c\Sigma\Sigma\Sigma \mid F_{hkl} \mid^2 \cos 2\pi (hu + kv + lw) \qquad (29)$$

This function, which eliminates phase, is always centrosymmetric and defines a map which gives interatomic distances plotted from the origin. A peak in the Patterson map at u, v, w implies that there are two atoms in crystal structure at $x_1\ y_1\ z_1$ and $x_2\ y_2\ z_2$ such that $x_2 - x_1 = u$, $y_2 - y_1 = v$, $z_2 - z_1 = w$. Use of the knowledge of the space group general equivalent positions allows calculation of heavy atom positional parameters.

Direct methods of solving the phase problem are now an important technique, particularly for their ability to yield phase information for structures containing no heavy atoms. The physical basis of these methods is based on two statements: in a crystal

1) the electron density is everywhere positive,

2) the electron density consists of discrete spherically symmetric atoms.

The first step in the direct methods solution procedure requires the conversion of the observed intensities into normalized structure factors

$$\mid E_{hkl} \mid^2 = \mid F_{hkl} \mid^2 / \Sigma f^2_i \qquad (30)$$

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

The principle of symbolic addition or positivity of electron density allows the determination of the phases of many hkl planes from knowledge of the phases of a few. For example, if the 1 0 0 reflection is large, it may have a maximum at x = 0 and a minimum at x = 0.5, i.e. the sign of the structure factor is positive (the phase angle is zero). Conversely, if the maximum is at x = 0.5, then the sign is negative (the phase angle is zero). If the 2 0 0 reflection is strong, then it is related to the 1 0 0 reflection by the Harker - Kaspar inequality (34).

$$U_h^2 \leq 1/2 (1 + U_{2h}) \qquad (31)$$

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

$$2U_h^2 \leq U_{2h} + 1 \qquad (32)$$

or

$$U_{2h} \geq 2U_h^2 - 1 \qquad (33)$$

To illustrate its use, consider the 1 0 0 peak and the 2 0 0 peak whose unitary structure factors $|U_h|$ and $|U_{2h}|$ are 0.6 and 0.5, respectively. Using the inequality, the right side becomes -0.28. Only if the sign of U_{2h} is positive, is this inequality satisfied. If the 1 0 0 reflection has a peak (positive) or a valley (negative) at x = 0.5, it follows that the 2 0 0 will have a peak at x = 0.5, if the 2 0 0 reflection had a negative phase, then the maximum would disagree with that of 1 0 0. Therefore, if both the 2 0 0 and 1 0 0 reflections are intense, the phase of the 2 0 0 must be positive to agree with either choice of phase for the 1 0 0 reflection. Symbolic addition then can be used to expand the number of phases using the triplet relationship:

$$s(h_1, k_1, l_1) \cdot s(h_2, k_2, l_2) \approx s(h_1 + h_2, k_1 + k_2, l_1 + l_2) \qquad (34)$$

where s is " sign of ". After a significant number of phases is known, a trial structure can be determined and the phased structure factors (F_{calc}) can be calculated and compared with those that have been measured (F_{obs}). The difference Fourier synthesis ($||F_{obs}| - |F_{calc}||$) allows location of missing atoms.

Once a model of a structure has been found by one of the previous methods, it is necessary to improve the preliminary coordinates by a process of refinement. The correctness of the model is indicated by the " Residual Factor " (R_f) which is defined as:

$$R_f = (\Sigma ||F_{obs}| - |F_{calc}||) / (\Sigma |F_{obs}|) \qquad (35)$$

after this initial R factor is determined, the least - squares method is used to refine the positions of atoms in the crystal structure. The least squares program fits the observed structure amplitudes to the calculated amplitudes. Then the parameters of the calculated structure factors are altered so that the least squares fit improves. When the structure is complete, only peaks of low intensity will remain on this map. As the model approaches completion, the difference between F_{obs} and F_{calc} is reflected in a lower value of R_f.

The 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 reflects the decrease in the atomic scattering factors as 2θ increases. It is given by the expression:

$$F\exp\left[-B_{iso}\left(\sin^2\theta\right)/\lambda^2\right] \qquad (36)$$

where B_{iso} is the isotropic thermal parameter. The atomic scattering ability may be more accurately represented by the anisotropic thermal parameter which is expressed as:

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

where b is the individual anisotropic thermal parameter.

When the R factor reaches a minimum and all atoms have been located, the refinement is considered complete. Tables of positional parameters, anisotropic thermal parameters, bond distances and angles, and a table showing the F_{obs} and F_{calc} structure factors are drawn up. A projection view of the molecule is prepared showing atoms as ellipsoids of 90% probability. From these data, structure can be interpreted including bond type, atomic hybridization, and electron location.

CHAPTER III

LUMINESCENCE

Luminescence is the process whereby electromagnetic radiation is produced by molecules or atoms that have been excited by the absorption of a specific quantum of energy. The electromagnetic radiation is characteristic of the particular luminescent material. The kinds of luminescence depend upon how the emitter is excited (29):

photoluminescence ------ due to excitation by electromagnetic radiation,
cathodeluminescence ------ excitation is caused by electron bombardment,
electroluminescence ------ caused by electric field,
chemiluminescence ------ excitation is caused by chemical reaction,
bioluminescence ------ due to excitation by biological process,
sonoluminescence ------ caused by excitation by ultrasonic waves.

In this work, the term luminescence is limited to photoluminescence. Luminescence is subdivided into fluorescence and phosphorescence, depending on the mechanism by which the electron falls from excited state back to the ground state. Emission which remains in a metastable state for a time after the excitation is turned off is called phosphorescence which typically has a lifetime of 10^{-6} to 100 seconds. Emission which does not persist after excitation is called fluorescence. The lifetime of fluorescence is 10^{-8} seconds or less (30). In the process of phosphorescence, excitation to a singlet excited state is followed by nonradiative decay to an intermediate triplet state, and then from that triplet state, radiactive decay to the ground state. In fluorescence, radiactive decay takes place directly from the first singlet excited state.

In the singlet state, electrons in each orbital are spin coupled, the spin orientation of the two electrons is opposite to each other. The the triplet excited state arises when the spin of one electron is re-oriented such that the orientation of the two electrons become parallel to each other. The singlet state has both electrons in the same energy state, while the triplet state has three energy levels due to two possibilities for parallel spin and two possibilities for spin couped orientation which are equal in energy.

The fundamental excitation and emission process is illustrated in Figure 6. The ground state of a phosphor has energy E_0 and E_1 . At low temperatures and in the absence of any excitation, only electronic level 0 is occupied. After excitation of the phosphor, electronic level 5 is occupied. Since the energy gaps among adjacent levels are small, the excitated electron drops from level 5 to 2 by a non-radiactive cascade process which releases the energy as heat to the surroundings. The energy gap between levels 2 and 1 is greater than a critical value thus transition from level 2 to level 1 or 0 occurs radiactively, i.e. is accompanied by emission of a photon of electromagnetic radiation. For these two possible luminescence transitions, frequencies ν_1 and ν_2 can be calculated by equation (38) and (39):

$$h\nu 1 = E_2 - E_1 \qquad (38)$$

$$h\nu 2 = E_1 - E_0 \qquad (39)$$

The fluorescence of a phosphor is studied by using fluorometer which measures the light emitted at right angles to the path of the incident beam. The essential components of a fluorometer are indicated in Figure 7.

The radiation source is commonly a mercury or xenon arc lamp which are the brightest and most powerful sources of ultra - violet radiation. The mercury lamp has the advantage of giving very high intensities at its emission lines, however, it has a less continuous spectrum than a xenon arc lamp. The xenon arc lamp gives radiation with lower intensity and produces a small number of lines in the 4000 Å and 6600 - 8000 Å region.

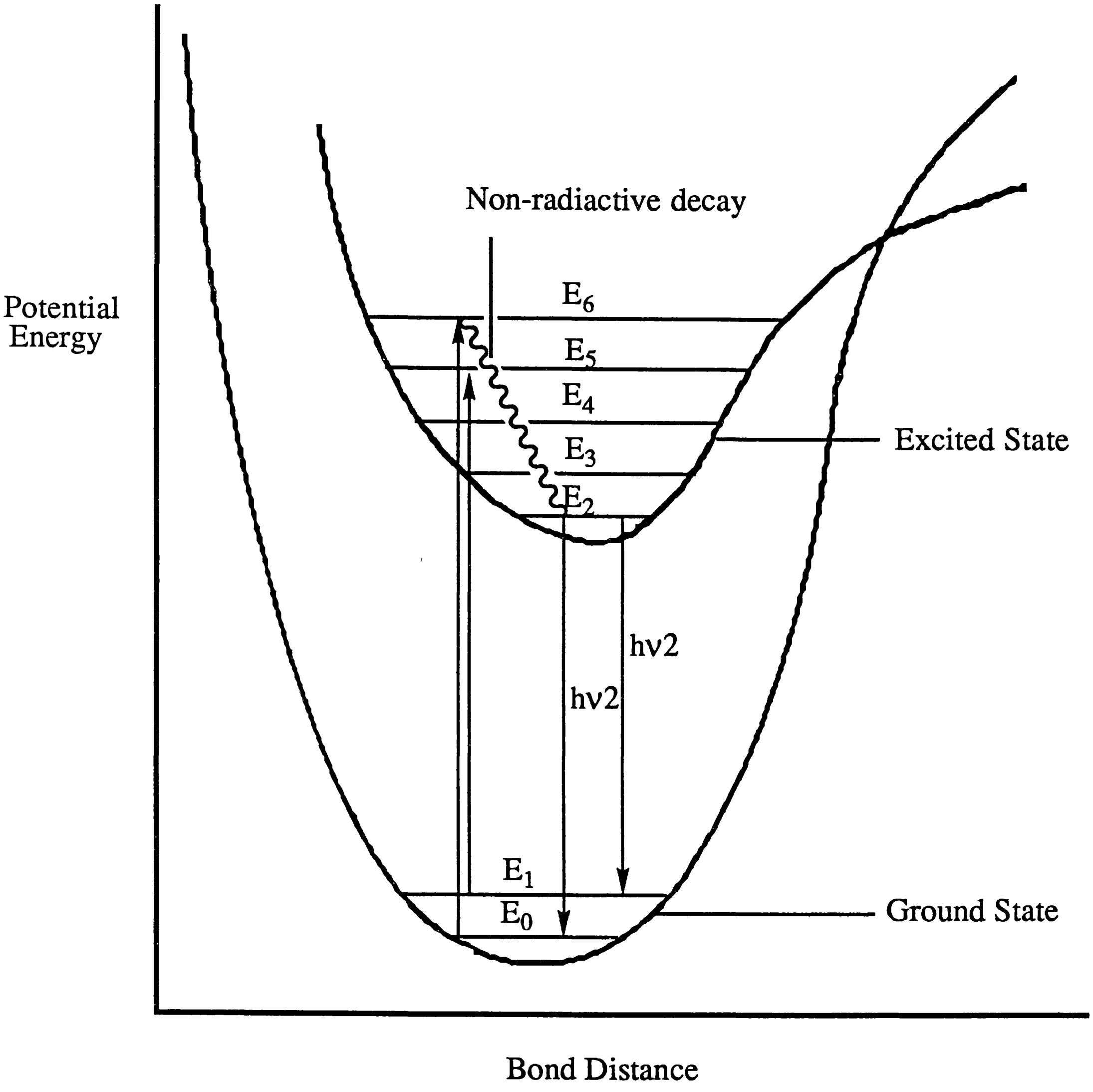


Figure 6. The Process of Excitation and Luminescence of a Phosphor

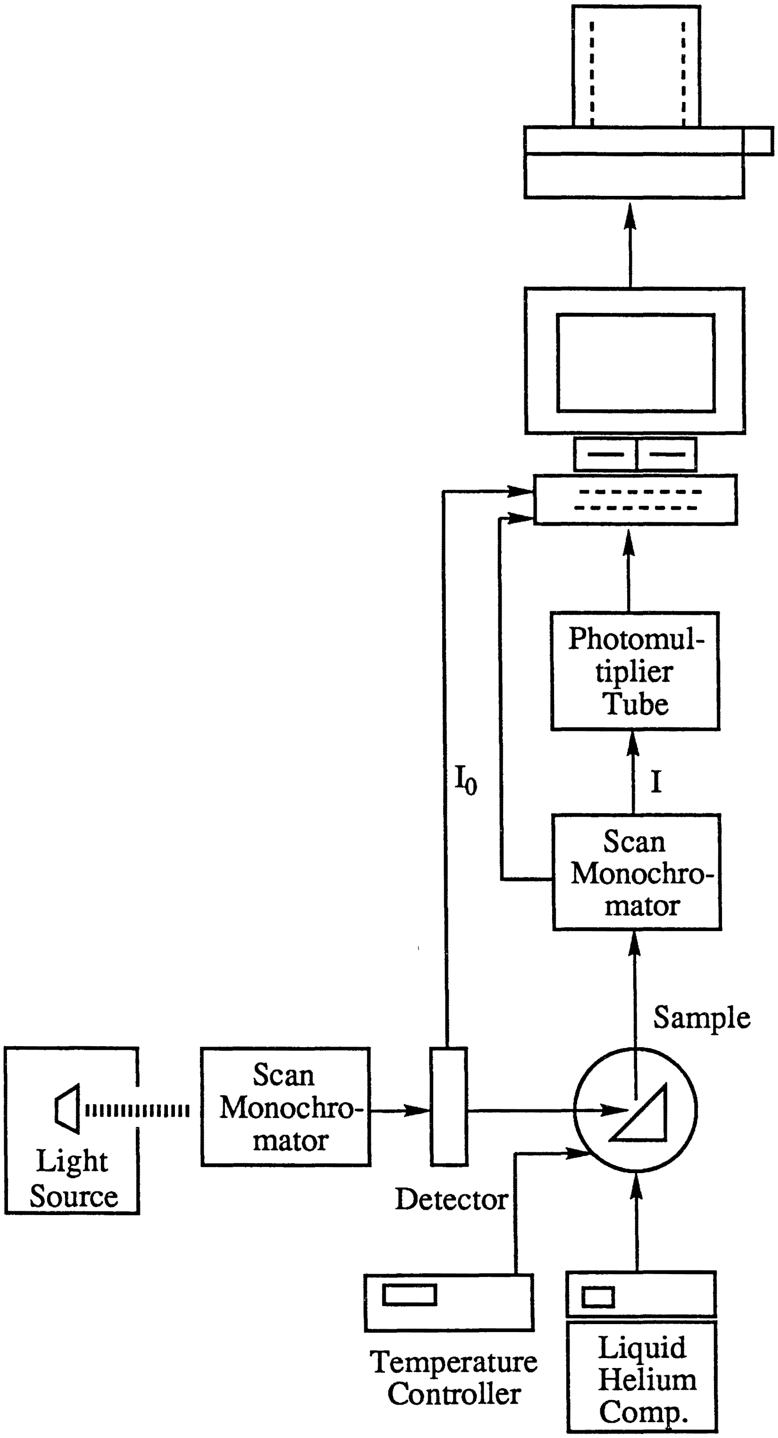


Figure 7. Diagram of a Typical Fluorometer

These can cause errors in high resolution work but have little effect in low resolution studies. Radiation sources are cooled by water or forced air to protect from overheating.

Monochromators are placed before and after the sample chamber. These monochromators are used to select the excitation and the emission wavelengths. The beam of light is separated into a band of narrow wavelength by the monochromater using gratings or prisms. Grating monochrometors have a lower loss of intensity than prism ones due to absorbance. However, these suffer from the disadvantage that in the visible or red regions the grating will transmit light of shorter wavelength. Materials used for fluorometer prisms must be selected to minimize absorbance in the area of interest. Quartz can be used when measurement are made in the ultraviolet region of the spectrum. Wavelength calibration of monochromators in a fluorescence spectrometer can be achieved by 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 decreased because of the decrease in intensity which is caused by the narrowed band of light allowed to pass through the monochromator.

The sample cell is placed in a sample chamber with the incident beam inlet window oriented 90^o from the window toward the emission measurement pathway. The material of 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 the usual material chosen for sample chamber windows.

High gain photomultiplier tubes with high voltage power supplies are the most commonly used detection systems although some semiconductor photodiodes also offer good performance. The wavelength response of a photomultiplier varies depending upon 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 wavelength sensitive response to improve the accuracy of the emission spectrum.

The output is normally recorded on magnetic media, floppy disk or tape although it can also be displayed by meter or strip recorder. The data recorded on disk need a correction for background effect from the sample chamber and can be plotted using various scales.

CHAPTER IV

EXPERIMENTAL

Syntheses

General.

Starting materials. Owing to the air sensitivity of the complexes, all operations were carried out under nitrogen using standard Schlenk techniques (38). Solvents were dried and redistilled following standard procedures. Reagent - grade nitrogen bases and copper(I) halides were purchased from Aldrich Chemical Company and used without further purification.

Crystallographic. In the data collection process of the structure determination, crystals were sealed in 0.2 mm quartz capillary tubes which were then affixed to a brass nib. Crystals insensitve to air and moisture were attached to a glass fiber using an epoxy glue and the fiber then fixed to a brass nib. The brass nib was attached on a goniometer head which was then positioned on a four circle Syntex P3 automated diffractometer. The mounted crystal was visually centered at the crosshairs of a microscope and a rotation photograph was taken to provide a starting point for the unit cell determination and alignment sequence of the diffractometer. Unit cell dimensions were determined by least squares refinement of the best angular positions for fifteen in dependent reflections ($2\theta >$ 15°). Data were collected at room temperature. A variable scan mode, a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 45.0° was used.

Fluorometric. All spectra were determined using an Oriel modular spectrofluorometer with an evacuated liquid helium cooled sample chamber. Sample crystals were ground into fine powder and evenly spreaded on double-sided tape which was attached to a piece of 0.5 x 1.5 inch glass and then placed in the sample chamber at 45° angle from the excitation beam. Spectra were measured from 350 nm - 700 nm in 0.2 nm intervals with a scan speed of a nm per second at temperatures; 10, 25, 50, 75, 125, 175, 225 and 275K. The scattering of the tape was subtracted before the spectrum was plotted.

Cu_2I_2(1-methylpiperazine)$_4$. Copper (I) iodide (0.47g, 2.5mmol) was suspended in a solution of 1-methylpiperazine (0.55mL, 5mmol) in acetonitrile (20mL) under anhydrous oxygen free conditions. The solution was stirred at room temperature for 6 hours. After filtration under nitrogen, clear crystals suitable for X-ray analysis were obtained upon slow evaporation of the solvent by passing nitrogen through the flask for about 6 minutes and standing overnight at room temperature. The needlelike crystals do not emit at room temperature. At low temperature, the crystals emit at 495 - 500 nm with a decreasing intensity as the temperature is raised.

Cu_2I_2(4-methylpiperidine)$_4$. Copper(I) iodide (0.47g, 2.5mmol) was suspended in a solution of 4-methylpiperidine (0.57 mL, 5mmol) in a 1:1 mixture of acetonitrile and ethyleneglycoldimethyl ether (20 mL) under the same conditions as above. The solution was stirred at room temperature for 4 hours. When the solution was started to turn pale blue, indicating that some Cu(I) was oxidized to Cu(II), 0.01g of L-ascorbic acid was added to reduce the Cu(II) back to Cu(I). After filtration under nitrogen, the solvent was reduced by slowly passing nitrogen through the flask for about 6 minutes. Crystals suitable for X-ray analysis were obtained after standing at room temperature for 2 days. The needlelike clear crystals emit at 490 - 500 nm with decreasing intensity as the temperature is raised.

Cu_2I_2(3,3-dimethylpiperidine)$_4$. Copper(I) iodide (0.47g, 2.5mmol) was suspended in a solution of 3,3-dimethylpiperidine (0.68mL, 5mmol) in a 1:1 mixture of acetonitrile and ethyleneglycoldimethyl ether (20mL) under the same condition as above. Crystals suitable for X-ray analysis were obtained by the same procedure as those used for the 4 - methylpiperidine complex. The yellowish needlelike crystals do not emit at room temperature. At 10k, the crystals emit at 650 nm.

Cu_2I_2(3-azaspiro(5.5)undecane)$_4$. Copper(I) iodide (0.47g, 2.5mmol) was suspended in a solution of 3-azaspiro(5.5)undecane (0.81mL, 5mmol) in acetonitrile (20mL). Crystals suitable for X-ray analysis were obtained by the same procedure as those used for the 1-methylpiperazine complex. The clear needlelike crystals have the same emission properties as Cu_2I_2(3,3-dimethylpiperidine)$_4$ complex described above.

Cu_4I_4(1,2,3,6,tetrahydropyridine)$_4$. Copper(I)iodide (0.47g, 2.5mmol) and 1,2,3,6-tetrahydropypidine (0.2mL, 2.5mmol) were heated in a refluxing mixture of acetonitrile and ethyleneglycoldimethyl ether (1:1, 20mL) for 4 hours in an atmosphere of nitrogen. L-ascorbic acid (0.02g) was added to reduce the Cu(II) formed by oxidation of Cu(I). The hot orange solution was filtered and cooled to room temperature. Needlelike colorless crystals suitable for X-ray analysis formed overnight. The crystals emit at 620 nm independent of temperature (10 K to 298K). The intensity of the emission decreases as the temperature increases.

Cu_4I_4(3-pyrroline)$_4$. Copper(I) iodide (0.47g, 2.5mmol) was suspended in a solution of 3-pyrroline (0.2mL, 2.5mmol) in acetonitrile (20mL) under anhydrous oxygen free condition. After filtration of the orange solution under nitrogen, the solvent was reduced by passing nitrogen slowly for about 10 minutes. Short yellowish needles suitable for X-ray analysis were obtained after 4 days. The crystals emit at 620 - 660 nm. The intensity of the emission decreases as the temperature increases.

Cu_4I_4(hexamethyleneimine)$_4$. Copper(I) iodide (0.47g, 2.5mmol) and hexamethyleneimine (2.8mL, 2.5mmol) were heated in a refluxing mixture of acetonitrile and ethyleneglycoldimethyl ether (1:1, 20mL) for 5 hours in an atmosphere of nitrogen. Since the solution was turning pale blue, 0.02g of L-ascorbic acid was added to reduce the

Cu(II) back to Cu(I). The hot orange solution was filtered and cooled to room temperature. Colorless flat crystals suitable for X-ray analysis were formed after two days. These crystals emit at 500 nm non-thermochromically from 10K to 298K. The intensity of the emission decreases as the temperature increases.

Cu_4I_4(morpholine)$_2$(acetonitrile)$_2$. Copper(I) iodide (0.47g, 2.5mmol) was suspended in a solution of morpholine (0.2mL, 2.4mmol) in acetonitrile (20mL) under anhydrous and oxygen free conditions. The solution was stirred at room temperature for 5 hours. After filtration under nitrogen, pale yellow crystals suitable for X-ray analysis were obtained upon slow evaporation of the solvent by passing nitrogen through the flask for about 6 minutes and then standing for two days at room temperature. The crystals emit non-thermochromically at 585 nm from 10K to 298K.

Cu_4I_4(3,5-dimethylpiperidine)$_4$. Copper(I) iodide (0.47g, 2.5mmol) was suspended in a solution of 3,5-dimethylpiperidine (0.33mL, 2.5mmol) in a 1:1 mixture of acetonitrile and ethyleneglycoldimethyl ether (20mL) under the same condition as above. The solution was stirred at room temperature for 6 hours. After filtration under nitrogen, the solvent was reduced by slowly passing nitrogen through the flask. Large flat crystals formed at room temperature after 4 days. The crystals emit at 620 - 650 nm. The intensity of the emission decreases as the temperature increases.

Cu_nI_n(morpholine)$_{2n}$ Copper(I)iodide (0.47g, 2.5mmol) was suspended in a solution of morpholine (0.44mL, 5.0mmol) in acetonitrile (20mL) under anhydrous and oxygen free conditions. The solution was stirred at room temperature for 8 hours. After filtration under nitrogen, long needlelike colorless crystals suitable for X-ray analysis were obtained upon slow evaporation of the solvent by passing nitrogen through the flask for about 6 minutes and standing for four days at room temperature.

$(CuC_{12}N_4H_{24})^+I^-$ Copper(I)iodide (0.47g, 2.5mmol) was suspended in a solution of pyrrolidine (0.42mL, 5.0mmol) in acetonitrile (20mL) under anhydrous and oxygen free conditions. The solution was stirred at room temperature for 5 hours. After filtration under nitrogen, the solvent was reduced by slowly passing nitrogen through the flask for about 5 minutes. Small needlelike crystals which emit orange under UV light were formed overnight. However, these crystals disappeared before growing big enough for X-ray analysis and large cubic crystals, which do not emit under UV light, were formed after two days.

Cu_nI_n(4-(2-aminoethyl)morphline)$_{2n}$ Copper(I)iodide (0.47g, 2.5mmol) was suspended in a solution of 4-(2-aminoethyl)morpholine (0.66mL, 5.0mmol) in a 1:1 mixture of acetonitrile and ethyleneglycoldimethyl ether (20mL) under anhydrous and oxygen free conditions. The solution was stirred at room temperature for 6 hours. After filtration under nitrogen, Needlelike colorless crystals suitable for X-ray analysis were obtained upon slow evaporation of the solvent by passing nitrogen through the flask for about 6 minutes and standing overnight at room temperature.

CuI(2-(2-aminoethyl)pyridine) Copper(I)iodide (0.47g, 2.5mmol) was suspended in a solution of 2-(2-aminoethyl)pyridine (0.30mL, 2.5mmol) in ethyleneglycoldimethyl ether (20mL) under anhydrous and oxygen free conditions. The solution was stirred at room temperature for 4 hours. After the dark brown solution was filtered under nitrogen, brownish needles suitable for X-ray analysis were obtained upon slow evaporation of the solvent by passing nitrogen through the flask for about 5 minutes and standing overnight at room temperature.

CuI(2-(2-piperidinoethyl)pyridine) Copper(I)iodide (0.47g, 2.5mmol) was suspended in a solution of 2-(2-aminoethyl)pyridine (0.48mL, 2.5mmol) in ethyleneglycoldimethyl ether (20mL) under anhydrous and oxygen free conditions. Brownish needlelike crystals for X-ray analysis were obtained by the same procedure as that used for CuI(2-(2-aminoethyl)pyridine) complex described above.

CHAPTER V

RESULT AND DISCUSSION

The goal of this research has been to explore and understand the correlation between structural factors and the emission properties of copper iodide Lewis base complexes. Efforts have been focused on copper(I)iodide complexed with aliphatic amines, in which the emission can only originate from a metal - metal interaction or single metal excitation of copper atoms. These complexes may crystallize with different copper iodide motifs; polymeric pleated sheets, rhombohedra, cubes, monomers or chains. Most of those prepared in this research are rhombohedra, $Cu_2I_2L_4$ and distorted cubes, $(CuIL)_4$. Four new rhombohedral complexes and five new cubic complexes have been prepared and structurally characterized by single crystal X - ray diffraction techniques. Emission spectra of these complexes were measured by exciting the compounds with radiation of wavelength 300 nm, at temperatures ranging from 10 K to 298 K. In addition, five new solid state Cu(I) compounds of other structural motifs have been synthesized and characterized by X-ray diffraction. Structural details; Cu...Cu separation, Cu - I and Cu - N bond distances, and Cu - I - Cu bond angles of these compounds are summarized in Table 1. The complete crystallographic data for the fourteen complexes can be found in Tables 7 to 71.

Crystals of Cu_2I_2(1-methylpirazine)$_4$, Cu_2I_2(4-methylpiperidine)$_4$, Cu_2I_2(3,3-dimethylpiperidine)$_4$, Cu_2I_2(3-azaspiro[5.5]undecane)$_4$, crystallize in a rhombohedral format, $Cu_2I_2L_4$, in which coordination at the copper atoms is tetrahedral with each copper bound to two iodide atoms (bridging) and two ligand molecules. Projection views and emission spectra of the four compounds are shown in Figures 7 - 10 respectively. From entries 1 to 4 in Table 1, it can be seen that all four compounds exhibit similar Cu - I

TABLE 1

SPACE GROUPS, BOND DISTANCES AND BOND ANGLES OF THE 16 COMPOUNDS

motif	Comp.	Space group	Cu...Cu ave.(Å)	Cu - I ave.(Å)	Cu - N ave.(Å)	Cu-I-Cu ave.(Å)	I-Cu-I ave.(Å)
rhomb	1	$Pn2_1a$	2.80(1)	2.66(1)	2.14(3)	63.3(2)	116.5(2)
	2	Pbn21	2.79(1)	2.68(1)	2.15(4)	63.2(2)	113.7(2)
	3	P1bar	2.67(1)	2.65(1)	2.10(3)	63.0(4)	116.8(2)
	4	P1bar	2.67(1)	2.86(1)	2.12(3)	61.4(3)	118.6(2)
cube	5	P1bar	2.64(1)	2.72(1)	2.00(6)	57.9(3)	113.8(4)
	6	P1bar	2.71(1)	2.70(1)	2.01(5)	59.9(2)	112.7(3)
	7	P1bar	2.64(1)	2.70(1)	2.06(3)	58.5(2)	113.6(3)
	8	$P4_2/nmc$	2.71(1)	2.68(1)	1.92(9)	60.2(2)	112.8(2)
	9	$P2_1/n$	2.71(1)	2.69(4)	2.01(2)	60.5(1)	112.4(1)
	10	$P4_2/n$	2.65(1)	2.75(1)	2.02(4)	——	——
	11	B2/b	2.65(3)	2.75(1)	2.02(4)	——	——
chain	12	$Pna2_1$	——	2.73(1)	2.08(5)	——	——
	13	$P2_1/n$	——	2.64(1)	1.94(1)	——	——
mono	14	P1bar	——	——	1.85(1)	——	——
	15	$P2_1/c$	——	2.60(1)	2.06(1)	——	——
	16	$P2_1/n$	——	2.64(1)	2.11(1)	——	——

1. Cu_2I_2(1-methylpiperazine)$_4$
2. Cu_2I_2(4-methylpiperidine)$_4$
3. Cu_2I_2(3,3-dimethylpiperidine)$_4$
4. Cu_2I_2(3-azaspiro(5.5)undecane)$_4$
5. Cu_4I_4(3-pyrroline)$_4$
6. Cu_4I_4(hexamethyleneimine)$_4$
7. Cu_4I_4(1,2,3,6-tetrahydropyridine)$_4$
8. Cu_4I_4(3,5-dimethylpiperidine)$_4$
9. Cu_4I_4(morpholine)$_2$(acetonitrile)$_2$
10. Cu_4I_4(piperidine)$_4$
11. Cu_4I_4(morpholine)$_4$
12. Cu_nI_n(morpholine)$_{2n}$
13. Cu_nI_n(4(-2-aminoethyl)morpholine)$_{2n}$
14. $(CuC_{12}N_4H_{24})^+I^-$
15. CuI(2-(2-aminoethyl)pyridine)
16. CuI(2-(2-piperidinoethyl)pyridine)

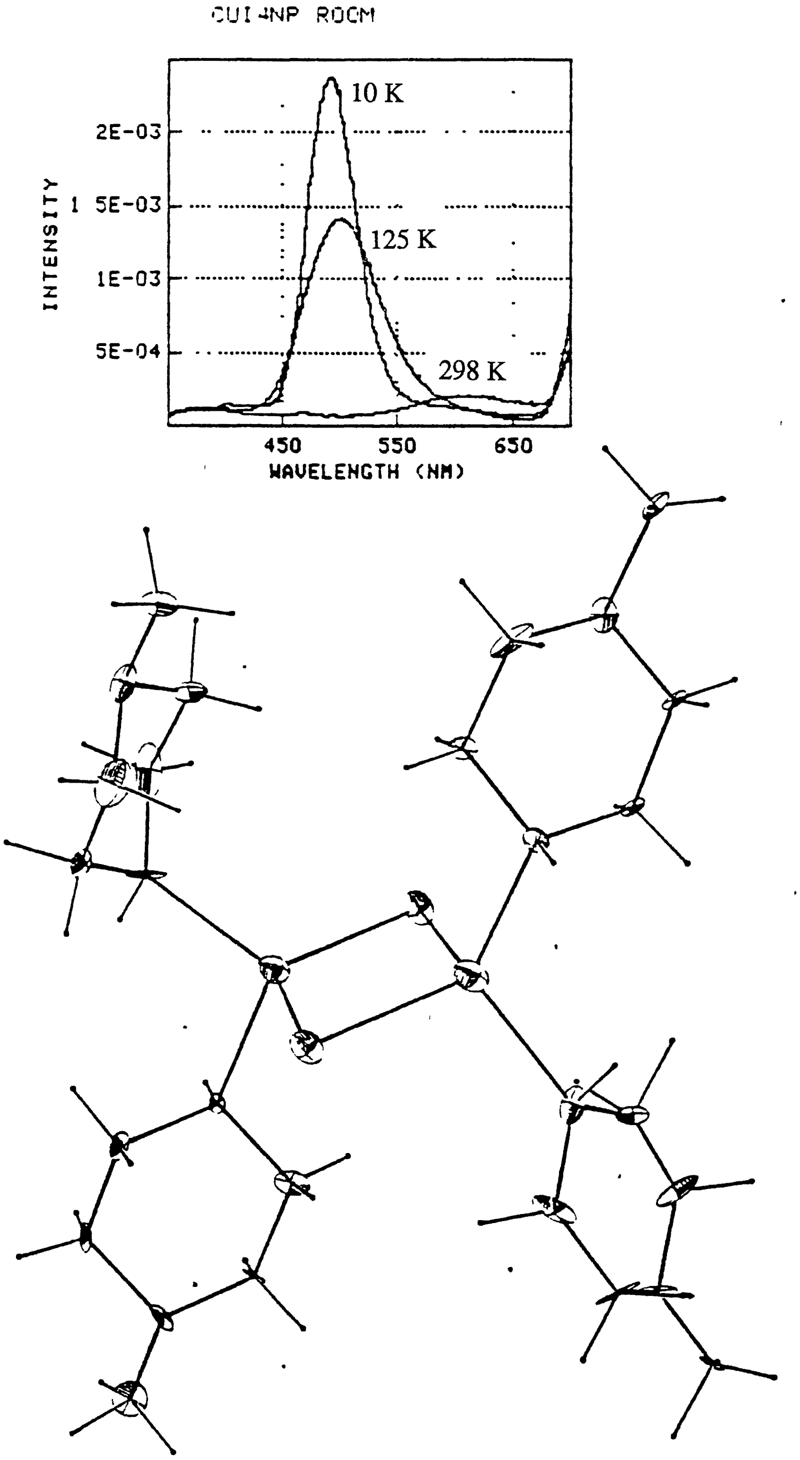


Figure 7. Projection View and Emission Spectrum of Cu_2I_2(1-methylpiperazine)$_4$

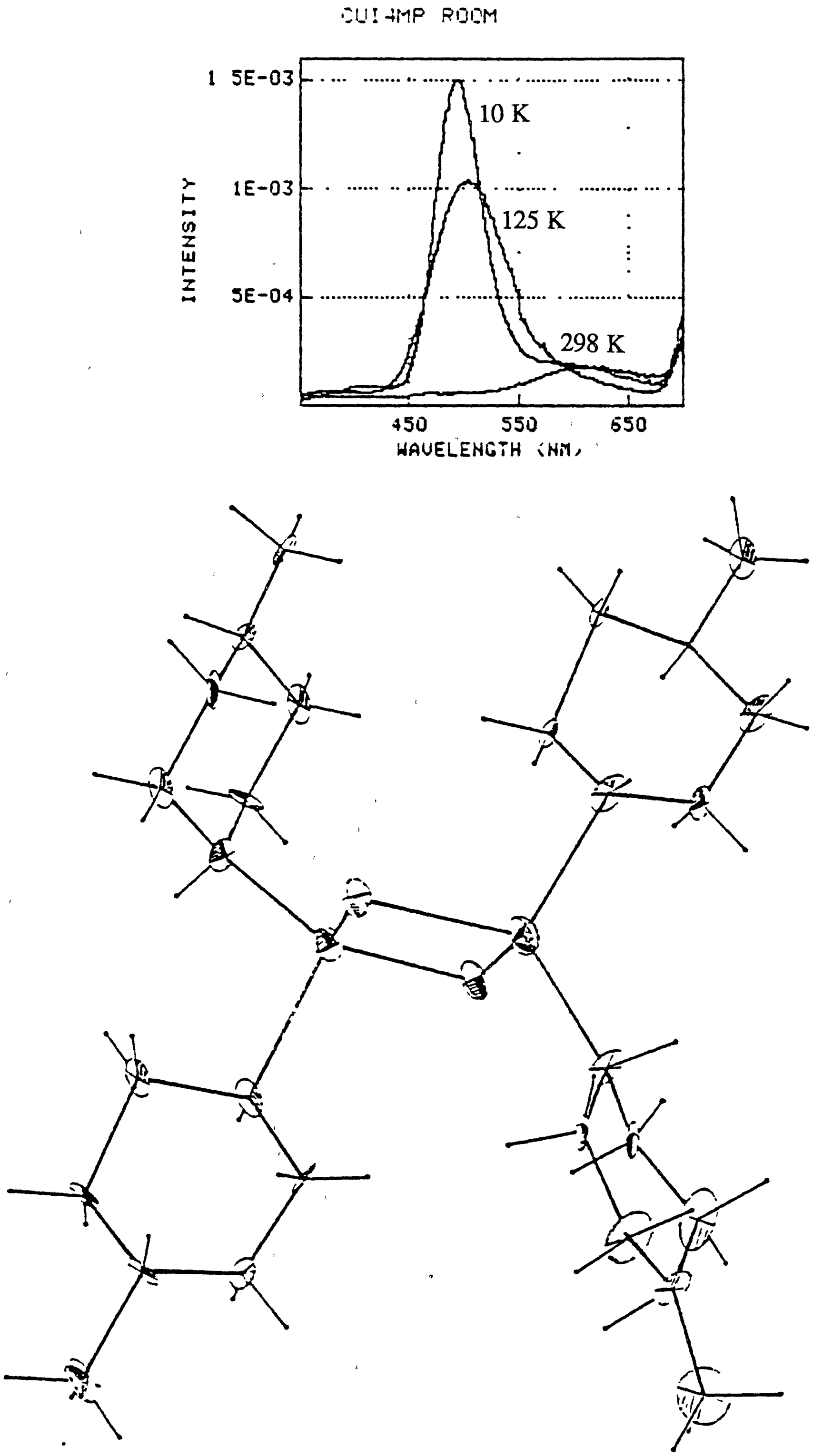


Figure 8. Projection View and Emission Spectrum of $Cu_2I_2(4\text{-methylpiperidine})_4$

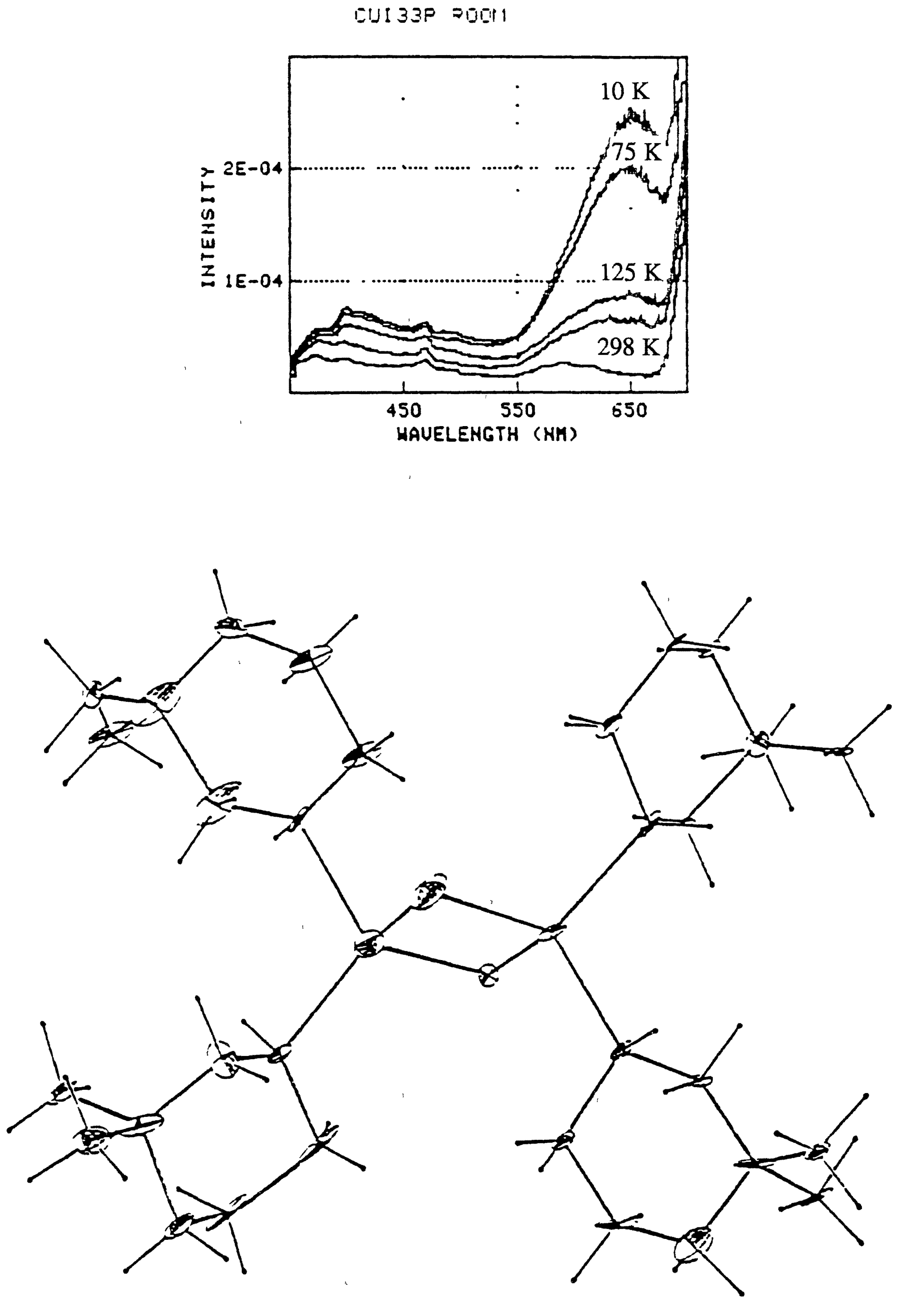


Figure 9. Projection View and Emission Spectrum of Cu_2I_2(3,3-dimethylpiperidine)$_4$

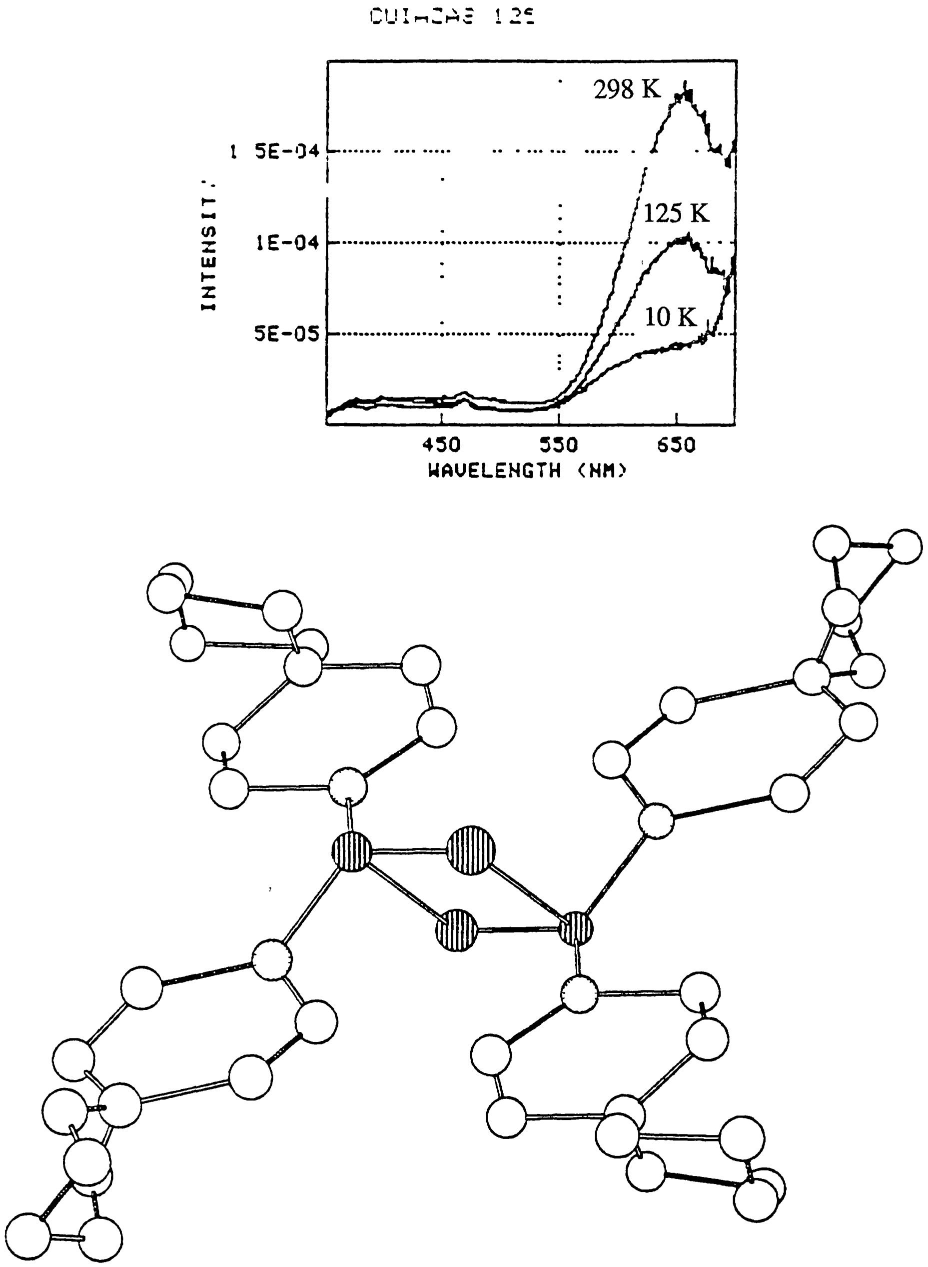


Figure 10. Projection View and Emission Spectum of Cu_2I_2(3-azaspiro(5.5)undicane)$_4$

distances and noninteractive Cu...Cu distances (>2.66Å). However those crystallizing in space group P1bar show solid state emission at 650 - 655 nm when excited at 300 nm, whereas those in the solid state space group $Pn2_1a$ (version $Pbn2_1$) emit at higher energy (495 - 500 nm). These four systems lack π electron density and none has significant Cu...Cu interaction. Therefore the metal to ligand π system and ligand to ligand interactions seen in previous work in this laboratory are absent. The differences in copper based emission may be analyzed in terms of differences in crystallographic symmetry within the $Cu_2I_2L_4$ rhombohedron. Those compounds crystallizing in space group $Pn2_1a$ and $Pbn2_1$ (version) have no symmetry element relating the atoms in the copper iodide rhombohedron, however, those crystallizing in space group P1 bar have a center of symmetry (Ci group) within the rhombohedron.

For those molecules without an intramolecular symmetry element (C1 group), a qualitative molecular orbital energy level diagram can be drawn by direct combination of 4s and 4p orbitals of two copper atoms and the sp^3 orbitals of two iodide and two nitrogen atoms (Figure 13). For instance, combination of two p_y orbitals of copper atoms and a sp^3 orbital of iodide atoms forms a bonding and an antibonding molecular orbital as shown below:

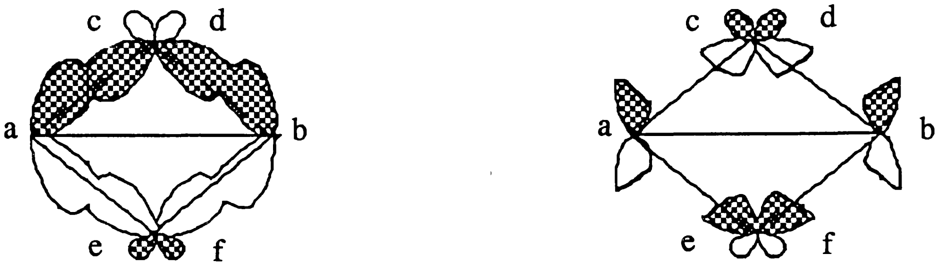


Figure 11. Bonding and Antibonding Molecular Orbitals Formed from Combinaton of Two p_y Orbitals of Copper atoms and two sp^3 Obitals of Iodide Atoms

However, for molecules which have a center of symmetry within the rhombohedron, symmetry adapted combinations of atomic orbitals and the symmetry forbidden rule must be considered when constructing the molecular orbital energy diagram (32). The character table of the Ci group, given in Table 2, was used in the qualitative discussion of the electronic structures of the centrosymmetric rhombohedral molecules.

TABLE 2

CHARACTER TABLE OF C_i GROUP

Ci	E	i
Ag	1	1
Au	1	-1

First the transformation properties of 4s, 4p, and 3d orbitals of the two copper atoms and the four sp^3 orbitals of iodide and nitrogen atoms were investigated under the irreducible representations of the Ci group (Table 2) and then linear combinations of these orbitals were formed. The p_y orbitals of two copper atoms serve as an example. Under a center of symmetry, p_y(a) coverts to p_y(b), opposite in phase (Figure 12). Before these two symmetrically related atomic orbitals, p_y(a) and p_y(b), can be considered under the

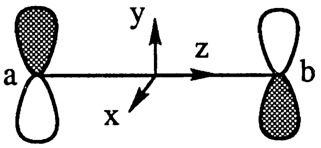


Figure 12. p_y Orbitals of Two Copper Atoms.

irreducible representation in Table 2, the numbers of each irreducible representation appearing in the linear combination need to be determined. To do this, the corresponding characters of the Ag and Au irreducible representations are added up as shown below:

	E	i	
Ag	1	1	
Au	1	-1	
Ag + Au	2	0	(reducible representation)

On multiplying the characters of reducible and irreducible representations in the same column, adding the products together and then dividing the sum by the order of the group:

$$2/2 = 1$$

we conclude that the reducible representation contains an Ag and an Au component. To generate the linear combinations of copper $4p_y$ orbitals for each irreducible representations, a projection operator method (33) was used:

					E	i
Under the a b		[illegible]	-b		a	-b
	Ag:	1	1	Au :	1	-1
	Multiply	a	-b		a	b
		Sum = a - b			Sum = a + b	

After normalizing the two functions, we obtain the two linear combinations of copper $4p_y$ orbitals:

$$Ag(p_y) = 1/\sqrt{2}\ (p_y(a)-p_y(b))$$

$$Au(p_y) = 1/\sqrt{2}\ (p_y(a)+p_y(b))$$

Molecular orbitals can only form between linear combinations of different elements with the same symmetry. Therefore, formation of molecular orbitals in compounds with symmetry elements within the molecules is more restricted than that of compounds without symmetry elements within the molecule. Linear combinations of all copper 4s, 4p,and 3d orbitals and the sp^3 orbitals of iodide and nitrogen atoms are given in Figures 15 - 19. Finally, the symmetry allowed interactions between linear combinations of the orbitals of elements within the rhombohedra are considered and a qualitative molecular orbital energy diagram obtained (Figure 14). The relative energy sequence of the orbitals in the diagram was decided by using the 'nodal plane criterion' which states that " the orbital with the fewest nodal planes is expected to be the most stable" (32). Effectiveness of overlap between orbitals was also considered.

From the schematic bonding orbital energy diagram of the noncentric rhombohedral compound, it is reasonable to consider that the solid state emission arises from : a) excitation of a d^{10} electron (HOMO) from the ground state to one of the quantized vibrational excited states, b) relaxation nonradiatively to the lowest vibrational state (LUMO), and c) return to the ground state giving off a quantum of energy in the form of visible radiation.

For the centrosymmetric rhombohedral compound, the selection rule of the electon transition requires that the triple product of the ground state, excited state and the operater must be nonzero. In Figure 14, ground state (HOMO) is occupied by two electrons with Ag symmetry, therefore it has a symmetry of Ag (Ag x Ag = Ag). If an electron is excited from HOMO to LUMO, the symmetry of excited state will be Au (Ag x Au = Au). The symmetry of the operater is Au. The direct product between ground state and excited state has the same symmetry as the operater, therefore, transition between HOMO and LUMO is alowed. The difference in the emission wavelength observed for the centrosymmetric motif as compared to that of the noncentric one arises because the symmetry adapted combinations of the 3d orbitals of copper atoms for the centric motif raise the orbital energy

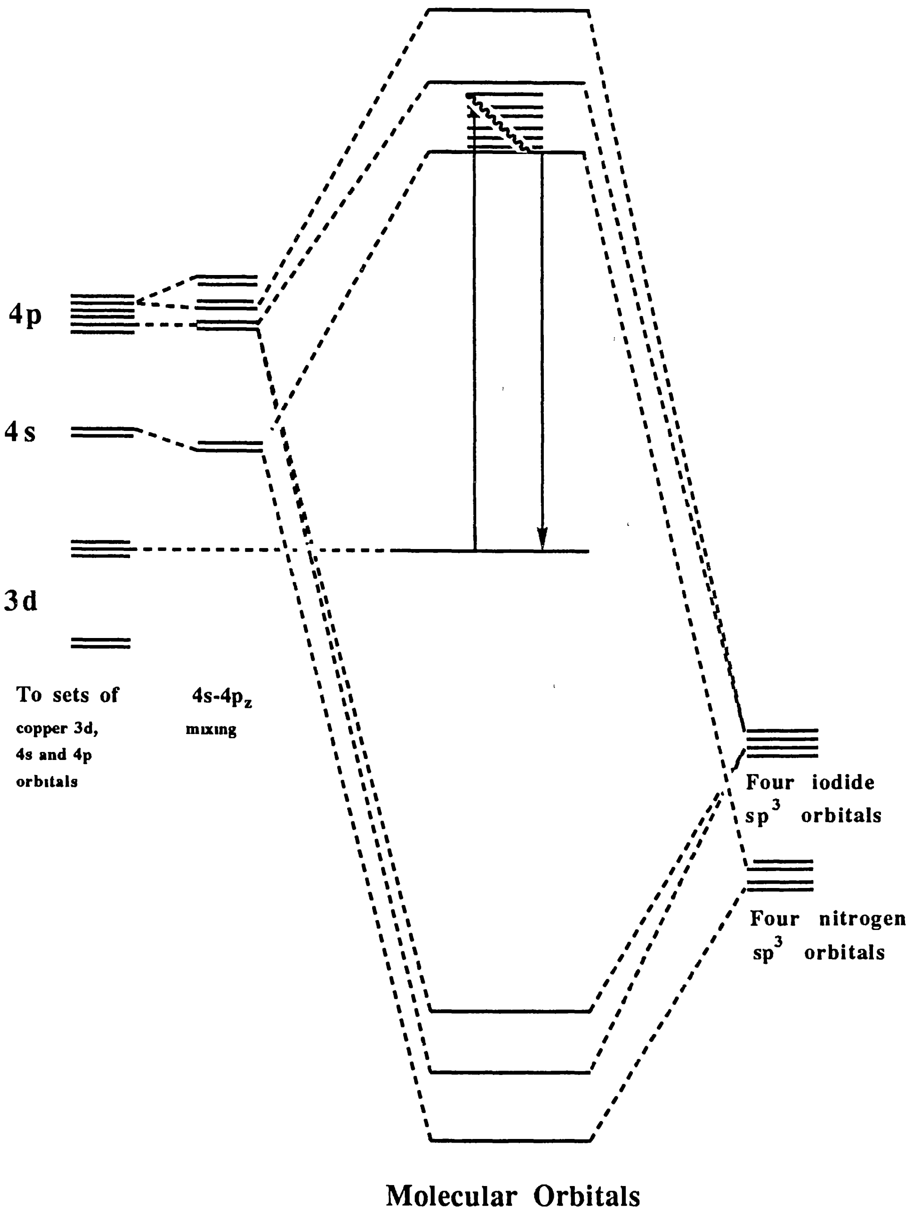


Figure 13. Schematic molecular Orbital Energy Level Diagram of Rhombohedral Complexes without an Intramolecular Symmetry Element

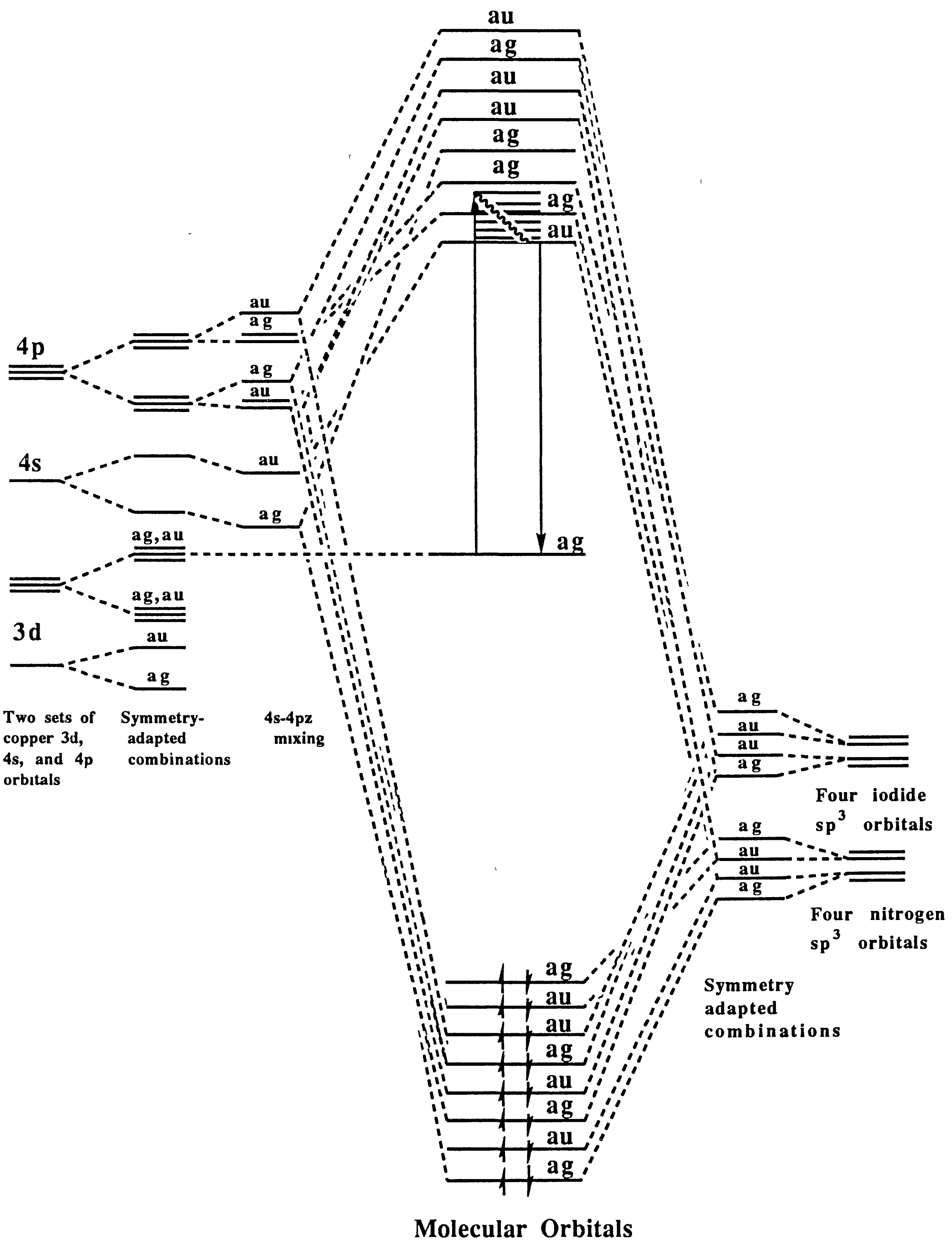
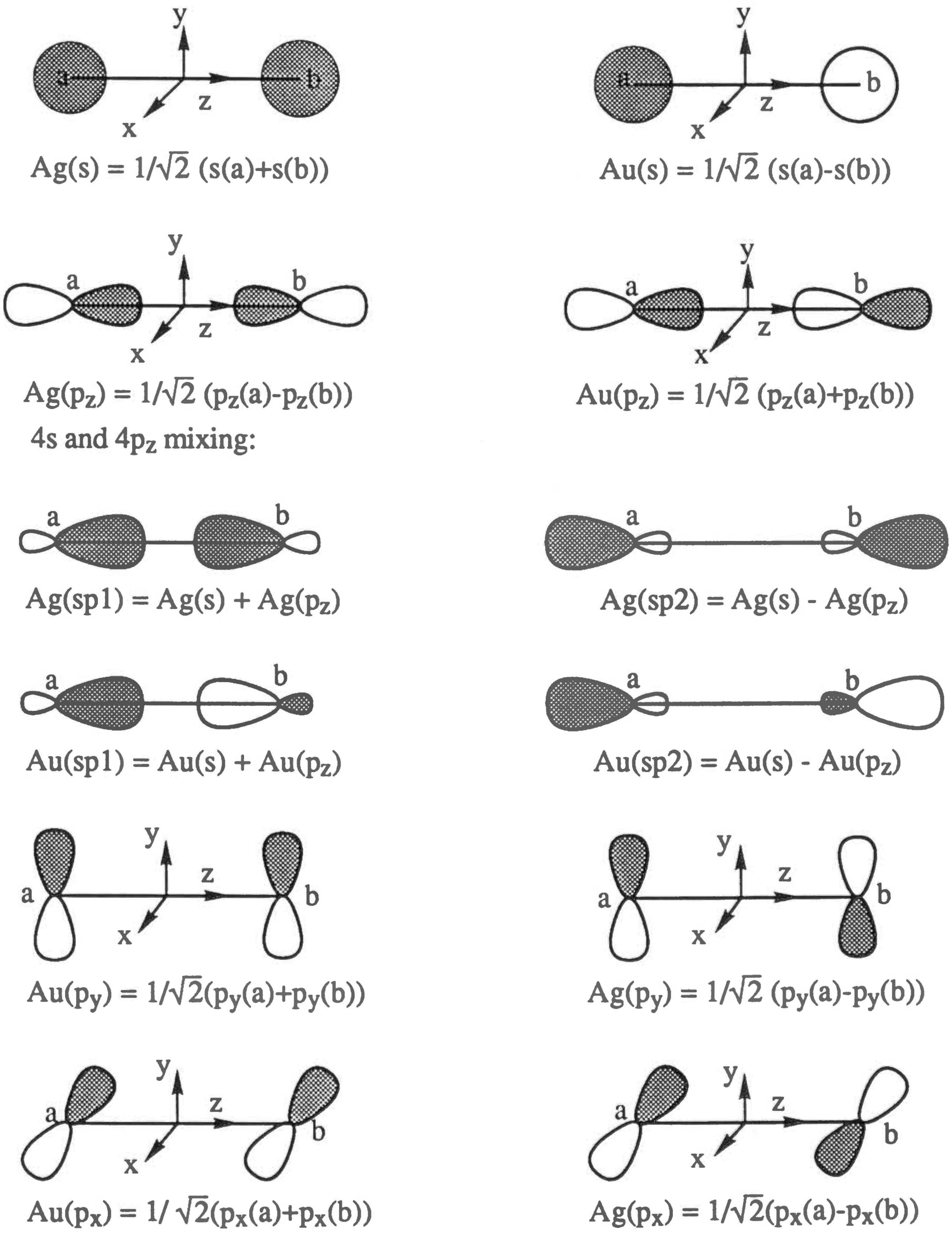


Figure 14. Schematic Molecular Orbital Energy Level Diagram of Rhombohedral Complexes with a Center of symmetry in the Molecule



$Ag(s) = 1/\sqrt{2}\,(s(a)+s(b))$

$Au(s) = 1/\sqrt{2}\,(s(a)-s(b))$

$Ag(p_z) = 1/\sqrt{2}\,(p_z(a)-p_z(b))$

$Au(p_z) = 1/\sqrt{2}\,(p_z(a)+p_z(b))$

4s and $4p_z$ mixing:

$Ag(sp1) = Ag(s) + Ag(p_z)$

$Ag(sp2) = Ag(s) - Ag(p_z)$

$Au(sp1) = Au(s) + Au(p_z)$

$Au(sp2) = Au(s) - Au(p_z)$

$Au(p_y) = 1/\sqrt{2}(p_y(a)+p_y(b))$

$Ag(p_y) = 1/\sqrt{2}\,(p_y(a)-p_y(b))$

$Au(p_x) = 1/\sqrt{2}(p_x(a)+p_x(b))$

$Ag(p_x) = 1/\sqrt{2}(p_x(a)-p_x(b))$

Figure 15. Linear Combinations of 4s and 4p Orbitals of Copper Atoms

$Ag(d_z) = 1/\sqrt{2}\ (d_z(a)+d_z(b))$

$Au(d_z) = 1/\sqrt{2}(d_z(a)-d_z(b))$

$Ag(d_{x2-y2}) = 1/\sqrt{2}\ (d_{x2-y2}(a)+ d_{x2-y2}(b))$

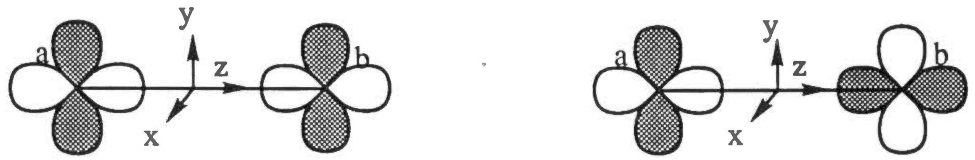
$Au(d_{x2-y2}) = 1/\sqrt{2}\ (d_{x2-y2}(a)- d_{x2-y2}(b))$

$Ag(d_{xy}) = 1/\sqrt{2}\ (d_{xy}(a)+d_{xy}(b))$

$Au(d_{xy}) = 1/\sqrt{2}\ (d_{xy}(a)-d_{xy}(b))$

$Ag(d_{xz}) = 1/\sqrt{2}\ (d_{xz}(a)+d_{xz}(b))$

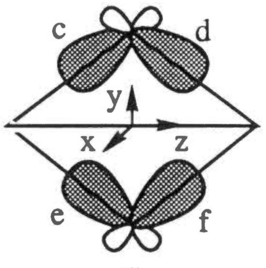
$Au(d_{xz}) = 1/\sqrt{2}\ (d_{xz}(a)-d_{xz}(b))$



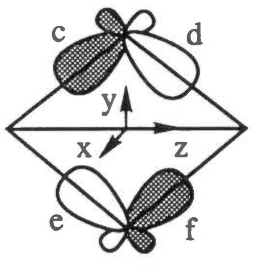
$Ag(d_{yz}) = 1/\sqrt{2}\ (d_{yz}(a)+d_{yz}(b))$

$Au(d_{yz}) = 1/\sqrt{2}\ (d_{yz}(a)-d_{yz}(b))$

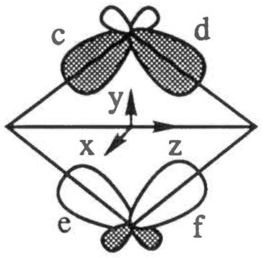
Figure 16. Linear Combinations of 3d Orbitals of Copper Atoms



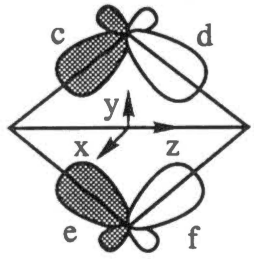
$Ag(I1) = 1/\sqrt{2}\,(I(c)+I(d)+I(e)+I(f))$



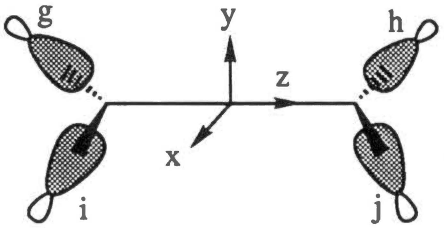
$Ag(I2) = 1/\sqrt{2}\,(I(c)-I(d)-I(e)+I(f))$



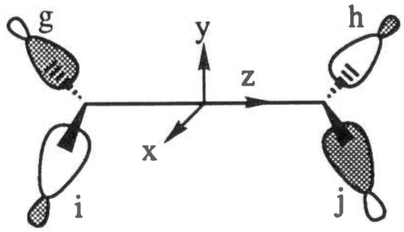
$Au(I1) = 1/\sqrt{2}\,(I(c)+I(d)-I(e)-I(f))$



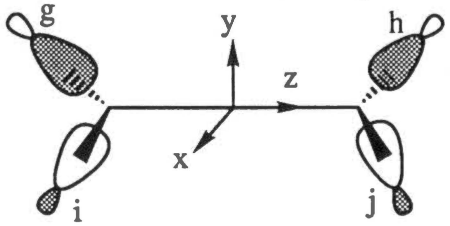
$Au(I2) = 1/\sqrt{2}\,(I(c)-I(d)+I(e)-I(f))$



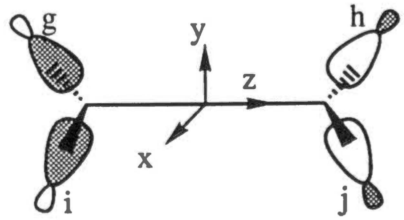
$Ag(N1) = 1/\sqrt{2}\,(N(g)+N(h)+N(i)+N(j))$



$Ag(N2) = 1/\sqrt{2}\,(N(g)-N(h)-N(i)+N(j))$

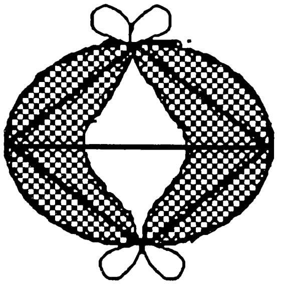


$Au(N1) = 1/\sqrt{2}\,(N(g)+N(h)-N(i)-N(j))$

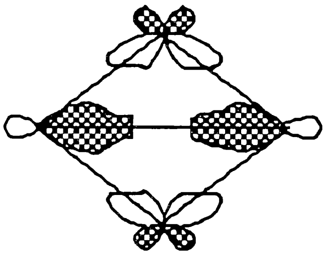


$Au(N2) = 1/\sqrt{2}\,(N(g)-N(h)+N(i)-N(j))$

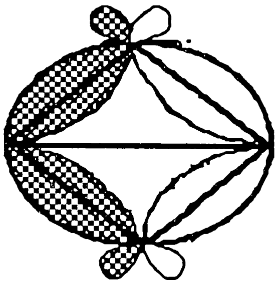
Figure 17. Linear Combinations of sp^3 Orbitals of the Iodide and Nitrogen Atoms



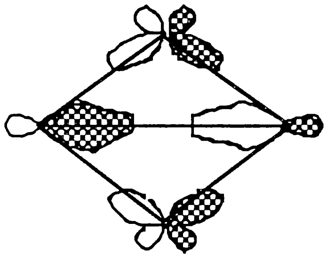
Ag(B1) = Ag(sp1) + Ag(I1)



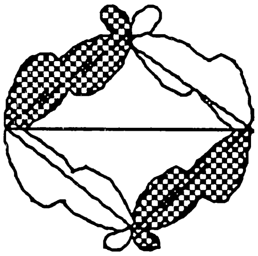
Ag(AB1) = Ag(sp1) - Ag(I1)



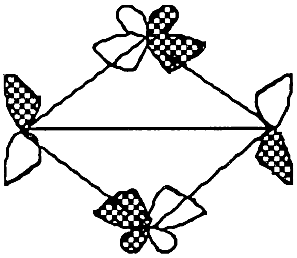
Au(B1) = Au(sp1) + Au(I2)



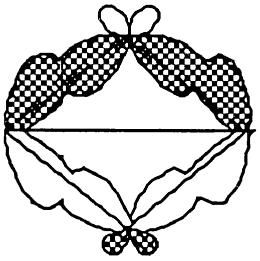
Au(AB1) = Au(sp1) - Au(I2)



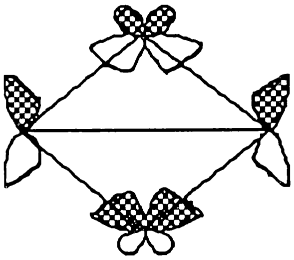
Ag(B2) = Ag(p_y) + Ag(I2)



Ag(AB2) = Ag(p_y) - Ag(I2)

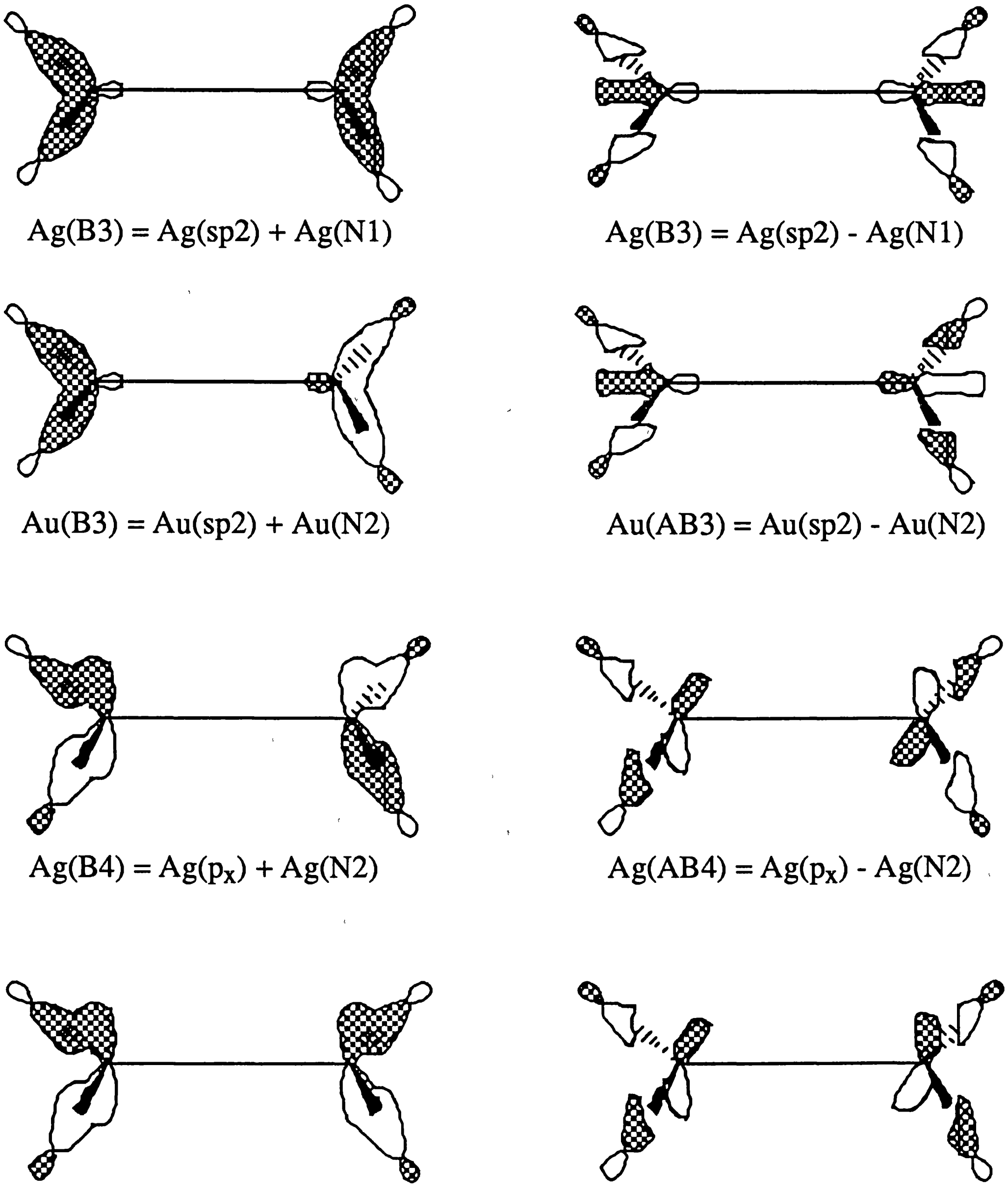


Au(B2) = Au(p_y) + Au(I1)



Au(AB2) = Au(p_y) - Au(I1)

Figure 18. Molecular Orbitals Contributed by Copper Atoms And Bridging Iodide Atoms



Ag(B3) = Ag(sp2) + Ag(N1)

Ag(B3) = Ag(sp2) - Ag(N1)

Au(B3) = Au(sp2) + Au(N2)

Au(AB3) = Au(sp2) - Au(N2)

Ag(B4) = Ag(p_x) + Ag(N2)

Ag(AB4) = Ag(p_x) - Ag(N2)

Au(B4) = Au(p_x) + Au(N1)

Au(AB4) = Au(p_x) - Au(N1)

Figure 19. Molecular Orbitals Contributed by Copper and Nitrogen Atoms

of the HOMO. Therefore, the energy difference between HOMO and LUMO is smaller in the centered motif than that of noncentric system. As a result, emission appears at a longer wavelength.

Crystals of cubic clusters: Cu_4I_4(3-pyrroline)$_4$, Cu_4I_4(hexamethyleneimine)$_4$, Cu_4I_4(1,2,3,6-tetrahydropyridine)$_4$, Cu_4I_4(3,5-dimethylmorpholine)$_4$, Cu_4I_4(acetonitrile)$_2$(morpholine)$_2$, Cu_4I_4(morpholine)$_4$, and Cu_4I_4(piperidine)$_4$, crystallize in distorted cubic format in which coordination at the copper atoms is tetrahedral with each copper atom bonded to three iodide atoms and a ligand molecule. The repetition of the most common motif observed for CuI compound, the Cu_2I_2, can be seen in all these (CuIL)$_4$ clusters: two of the rhombohedra are placed one above the other to form the cube. Projection views and emission spectra of the five new cubic clusters (compounds 5 - 9) are given in Figures 20 - 24 respectively. The crystalographic data for compounds, Cu_4I_4(morpholine)$_4$ and Cu_4I_4(piperidine)$_4$, were obtained from references (7,8) and the emission spectra of these two compounds are shown in Figure 25. From Table 1, it can seen that the bond distances and angles of the seven cubic compounds are comparable and that none of them has significant Cu...Cu interactions (Cu...Cu > 2.60 Å).

The cubic clusters; Cu_4I_4(3-pyrroline)$_4$, Cu_4I_4(hexamethyleneimine)$_4$, Cu_4I_4(1,2,3,6-tetrahydropyridine)$_4$, and Cu_4I_4(morpholine)$_2$(acetonitrile)$_2$ do not have a symmetry element within the cube and these all show solid state emission at 580 - 630 nm at room temperature. A qualitative molecular orbital energy level diagram (Figure 26) can be drawn by direct combination of the 4s and 4p orbitals of four copper and iodide atoms and the four sp3 orbitals of four nitrogen atoms in a procedure similar to that described for Figure 13.

Cu_4I_4(morpholine)$_4$ (compound 11) has a twofold rotation axis within the cubic cluster (7) and shows solid state emission at 640 - 680 nm. On the basis of symmetry, this compound belongs to the C_2 point group (Table 3) which imposes the same constraints on transformations of the orbitals within a rhombohedral unit as does the Ci

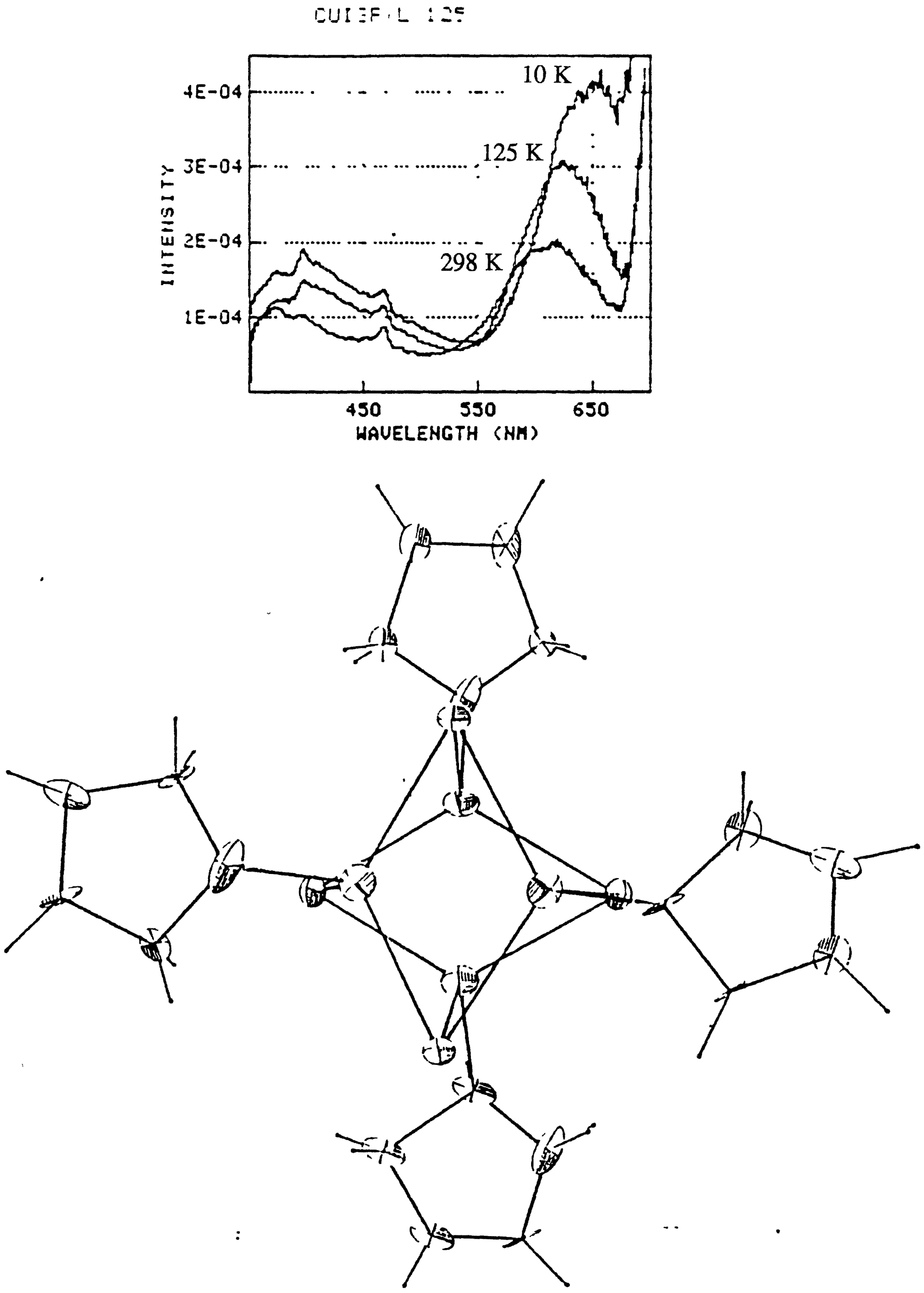


Figure 20. Projection View and Emission Spectrum of Cu$_4$I$_4$(3-pyrroline)$_4$

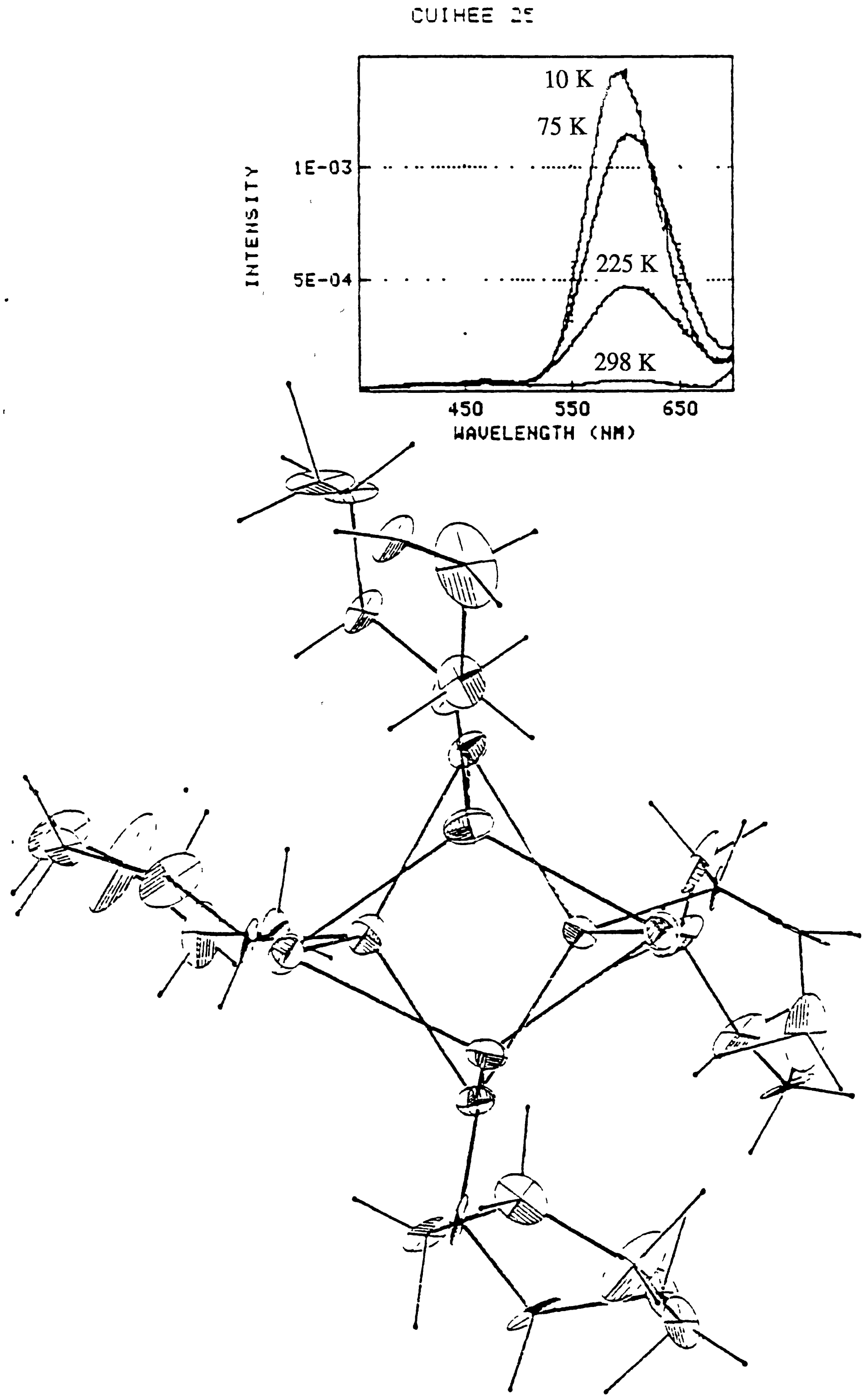


Figure 21. Projection View and Emission Spectrum of Cu_4I_4(hexamethyleneimine)$_4$

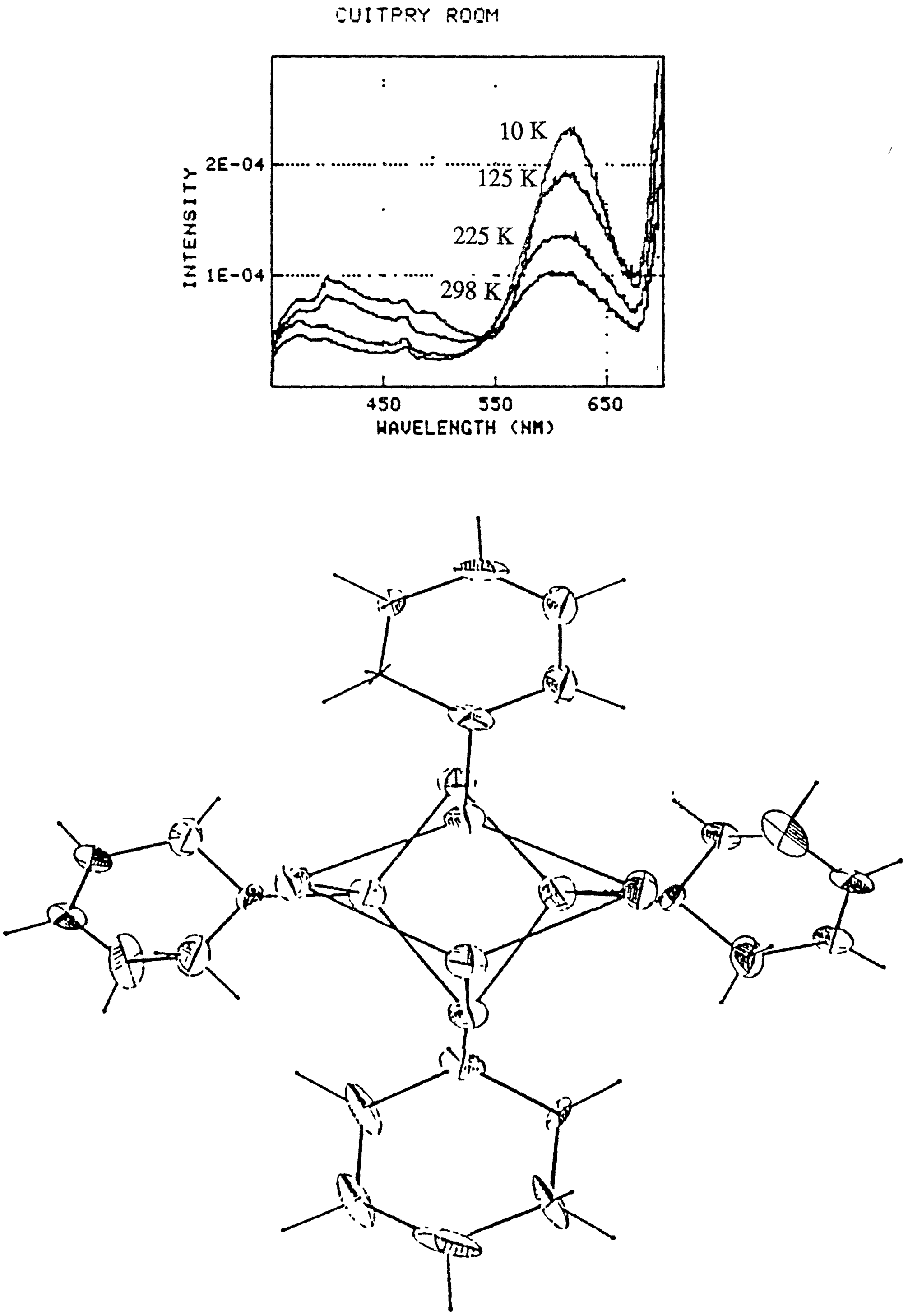


Figure 22. Projection View and Emission Spectrum of Cu_4I_4(1,3,4,6-tetrahydropyridine)$_4$

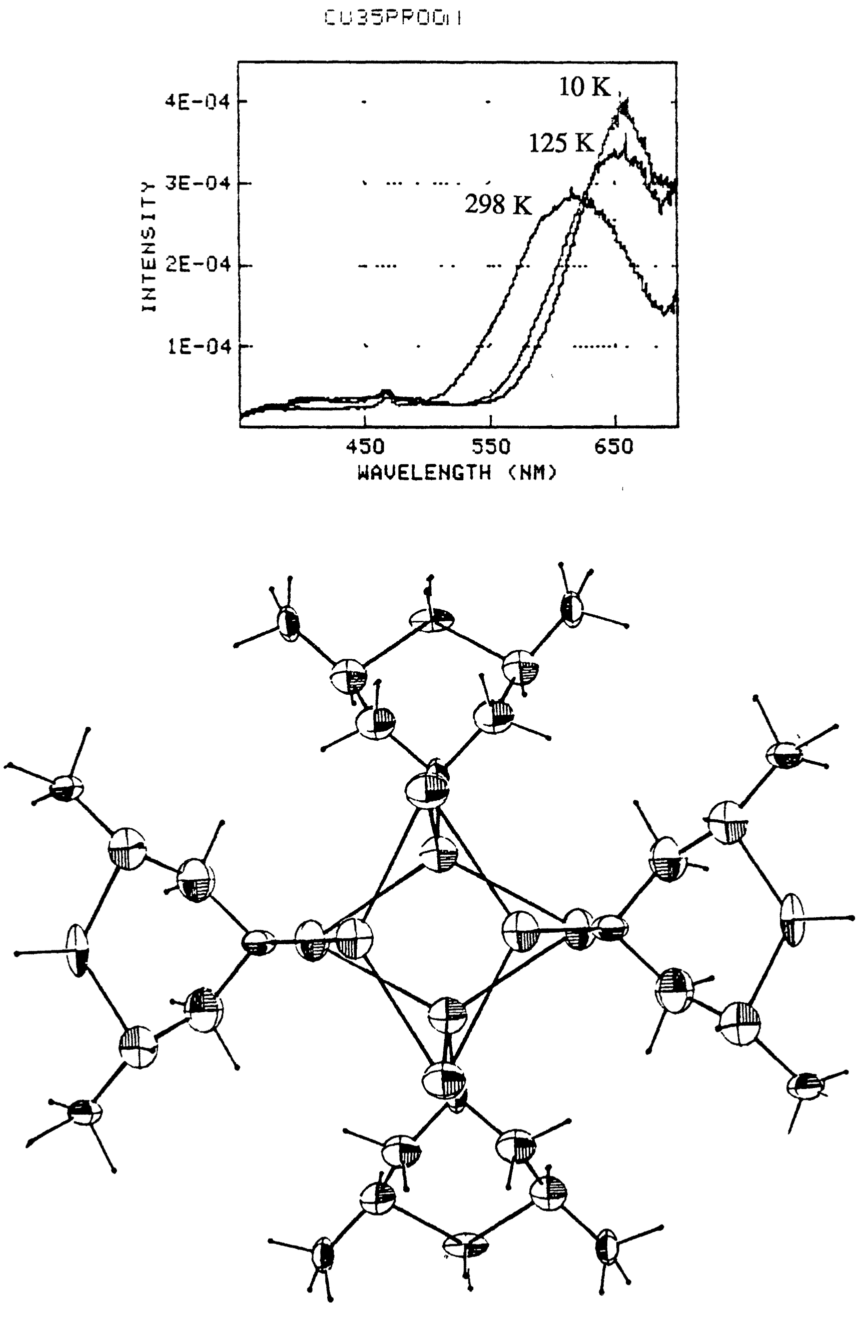


Figure 23. Projection View and Emission Spectrum of
Cu_4I_4(3,5-dimethylmorpholine)$_4$

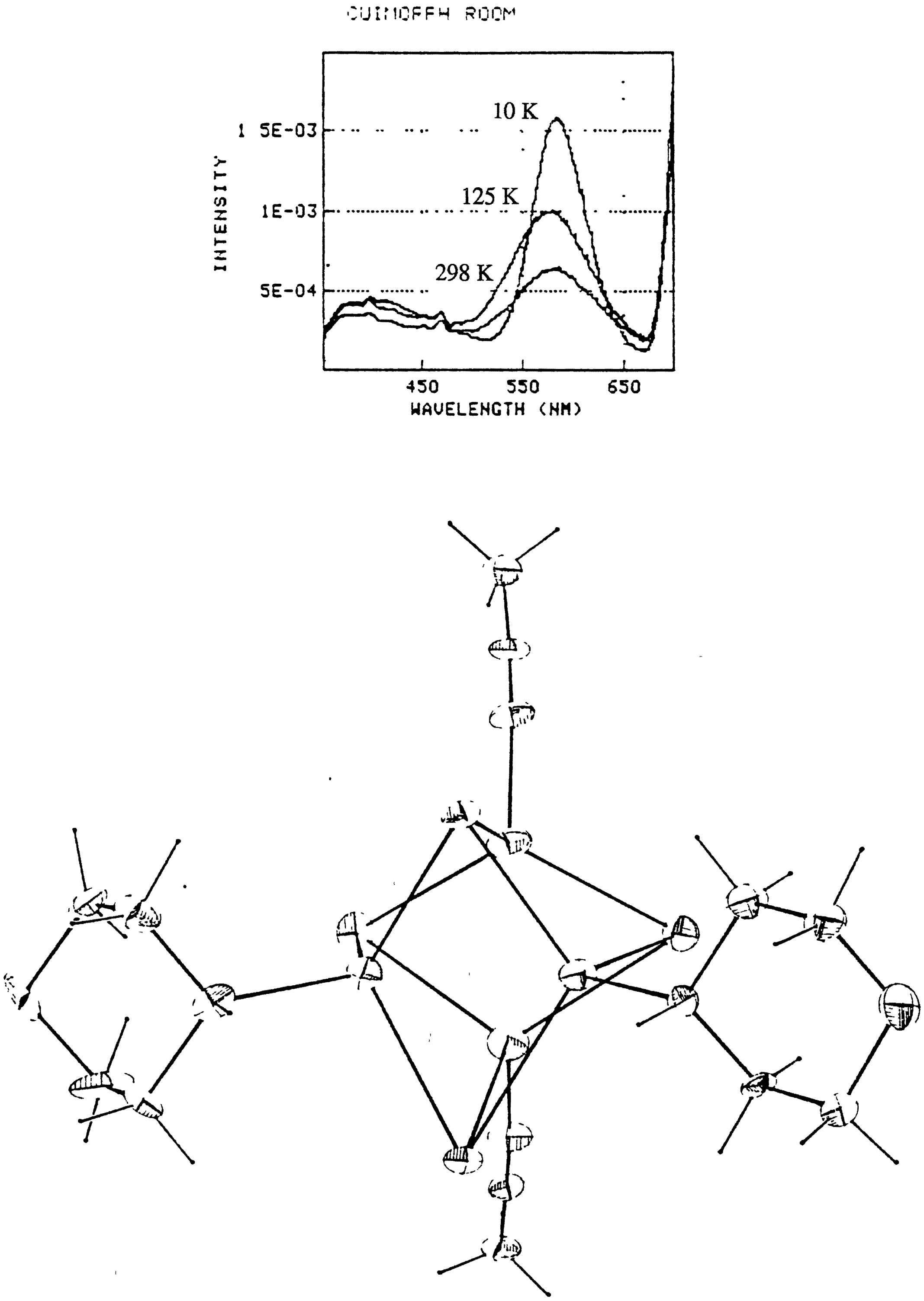
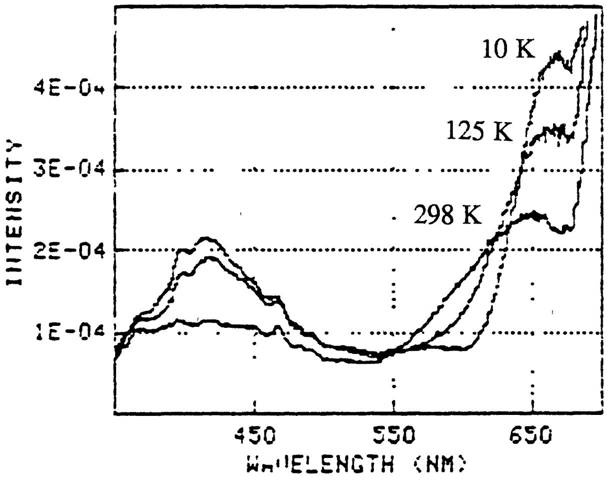
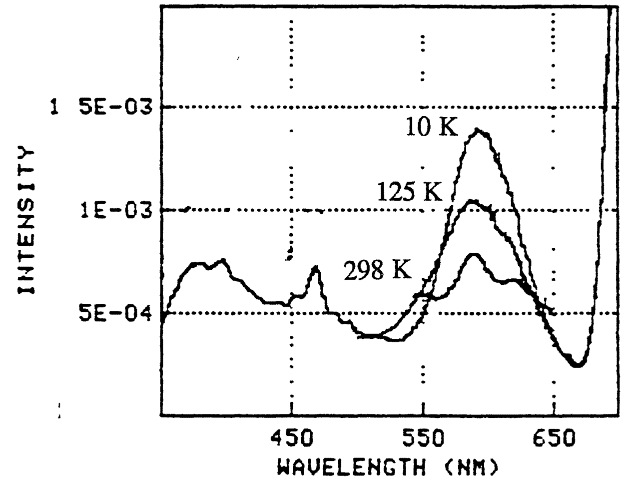


Figure 24. Projection View and Emission Spectrum of $Cu_4I_4(\text{acetonitrile})_2(\text{morpholine})_2$



Cu_4I_4(morpholine)$_4$



Cu_4I_4(piperidine)$_4$

Figure 25. Emission Spectra of Cu_4I_4(morpholine)$_4$ and Cu_4I_4(piperidine)$_4$

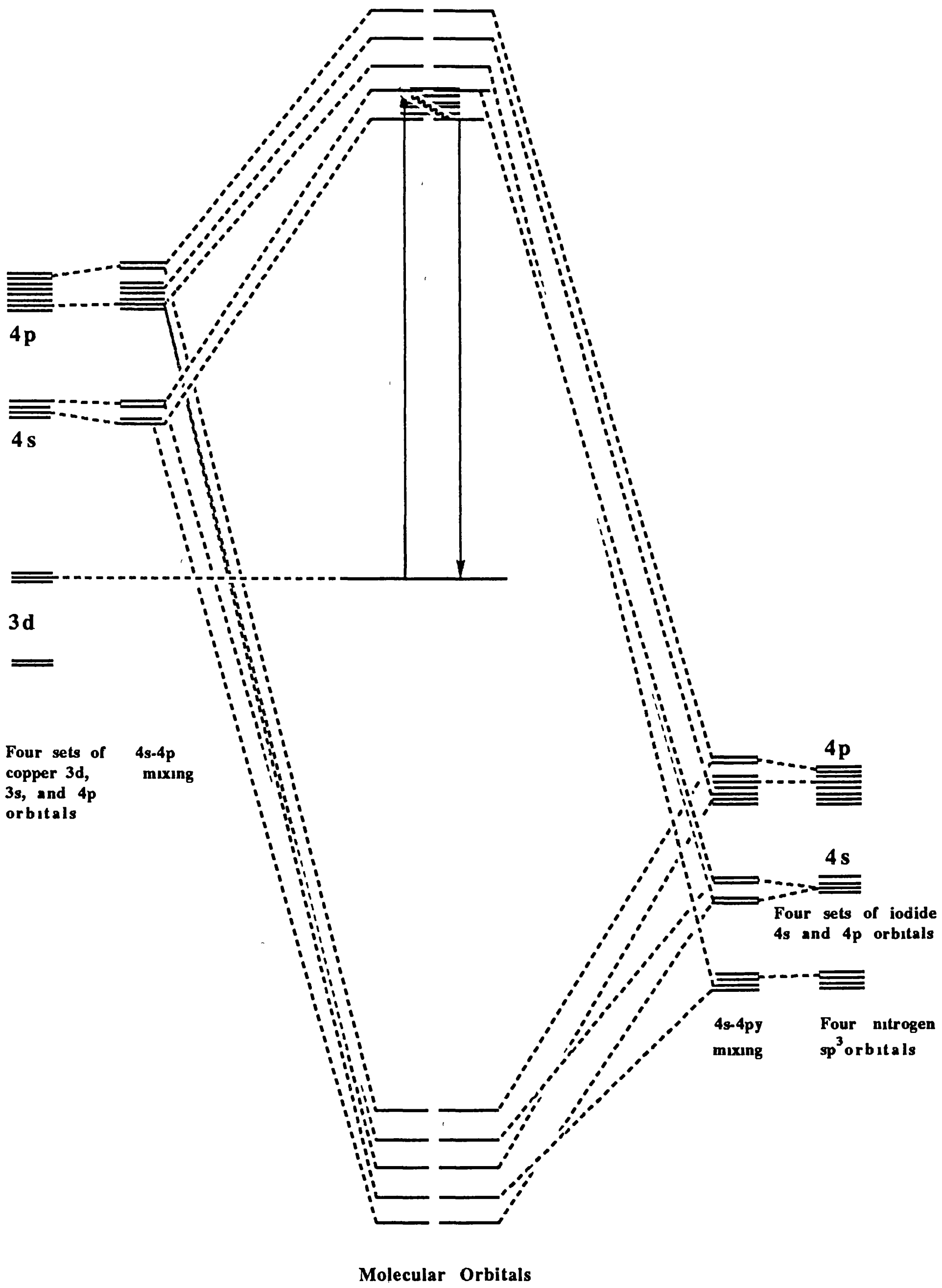


Figure 26. Schematic Molecular Orbital Energy Level Diagram of Cubic Complexes without Symmetry Elements in Molecules

point group. From Figure 27, it can be seen that in the cubic cluster, overlap can only take place between orbitals of atoms a and b or between c and d, i.e. within a rhombohedron but not between rhombohedra. Two pairs of normalized linear combinations were obtained under A and B symmetry,

$$A(Cu1)=1/\sqrt{2}(Pz(a)+Pz(b))$$

$$B(Cu1)=1\sqrt{2}(Pz(a)-Pz(b))$$

$$A(Cu2)=1/\sqrt{2}(Pz(c)+Pz(d))$$

$$B(Cu2)=q/\sqrt{2}(Pz(c)-Pz(d)$$

TABLE 3

CHARACTER TABLE OF C_2 GROUP

C2	E	C2
A	1	1
B	1	-1

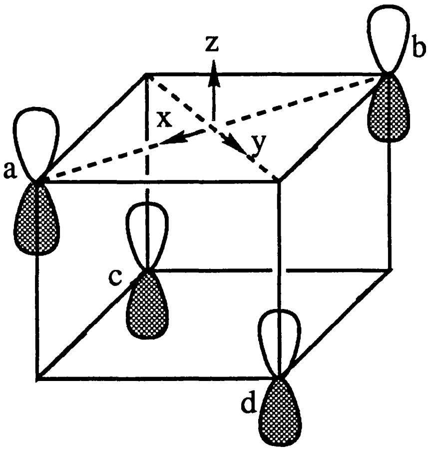


Figure 27. Four p_z Orbitals of Copper Atoms in the C_4I_4(morpholine)$_4$ Molecule

then, the orbitals were further combined according to their symmetry for the convenience of later treatment ,

$$A(Cu3)=A(Cu1)+A(Cu2)=1/2(Pz(a)+Pz(b)+Pz(c)+Pz(d))$$

A(Cu4)=A(Cu1)-A(Cu2)=1/2(Pz(a)+Pz(b)-Pz(c)-Pz(d))

B(Cu3)=B(Cu1)+B(Cu2)=1/2(Pz(a)+Pz(b)+Pz(c)+Pz(d))

B(Cu4)=B(Cu1)-B(Cu2)=1/2(Pz(a)+Pz(b)-Pz(c)-Pz(d))

Transformations and drawings of orbitals of copper, iodide, and nitrogen atoms according to the group, C_2, as well as the bonding and the antibonding molecular orbitals are shown in Figures 29 to 41. The relative sequence of the orbital energies was judged by the nodal plane criterion. Figure 28 shows the qualitative molecular orbital energy diagram which was obtained by applying procedures similar to those used for the rhombohedral complexes with a center of symmetry within the molecule. In this case, electron transition between HOMO and LUMO is also alowed because the triple product of groud state, excited state and the operater is non-zero. The energy differences between HOMO and LUMO were reduced when symmetry adapted combinations of the 3d orbitals are required compared to the cases without symmetry (Figure 13. and Figure 26.). Therefore, the solid state emission of the system apears at lower wavelength.

Compound 8 (Cu_4I_4(3,5-dimethylpiperidine)$_4$) has two mirror planes perpendicular to each other and a twofold rotation axis which lies on both of the mirror planes, thus it belongs to C_{2v} point group (Table 4.). The solid state emission spectrum

TABLE 4.

CHARACTER TABLE OF C2V GROUP

C_{2v}	E	C_2	σ_v	$\sigma_{v'}$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

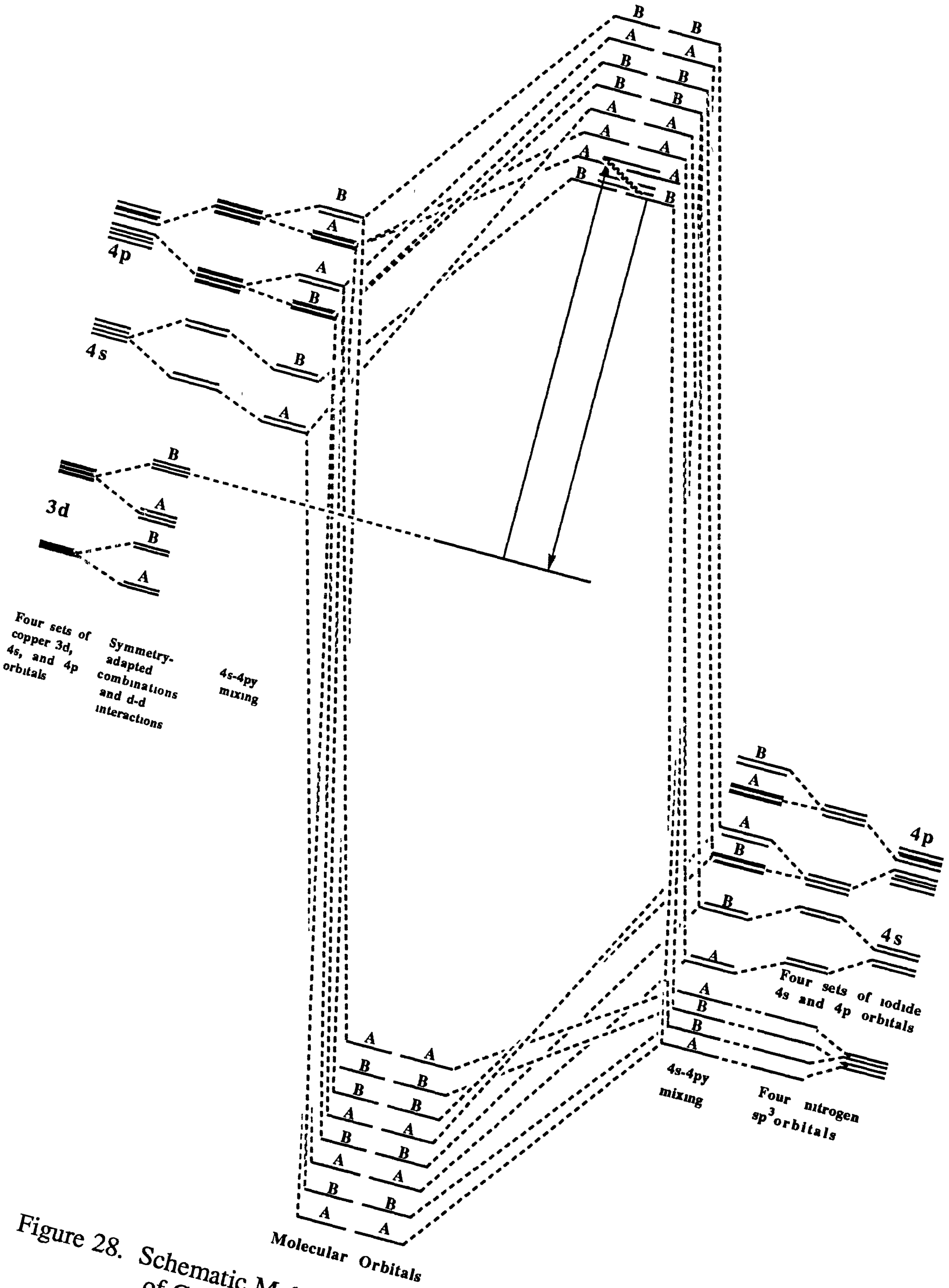
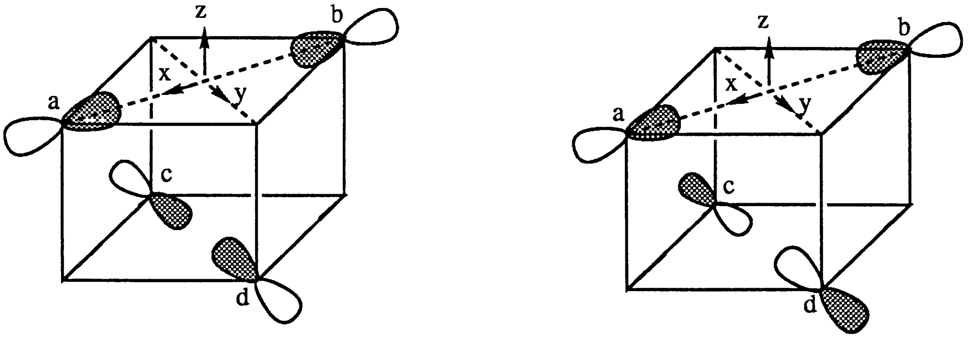
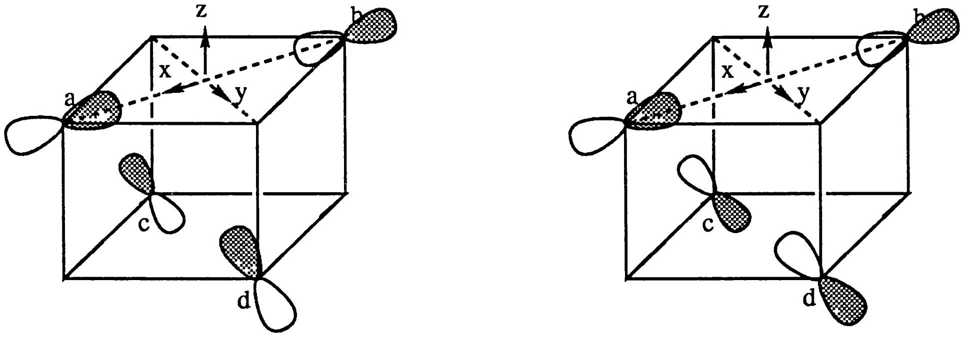


Figure 28. Schematic Molecular Orbital Energy Level Diagram of Compound $Cu_4I_4(morpholine)_4$



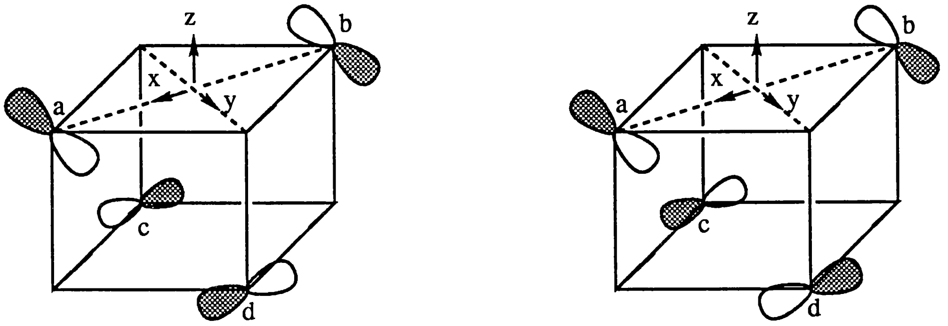
A(Cu1)=1/2(Px(a)-Px(b)-Py(c)+Py(d))

A(Cu2)=1/2(Px(a)-Px(b)+Py(c)-Py(d))



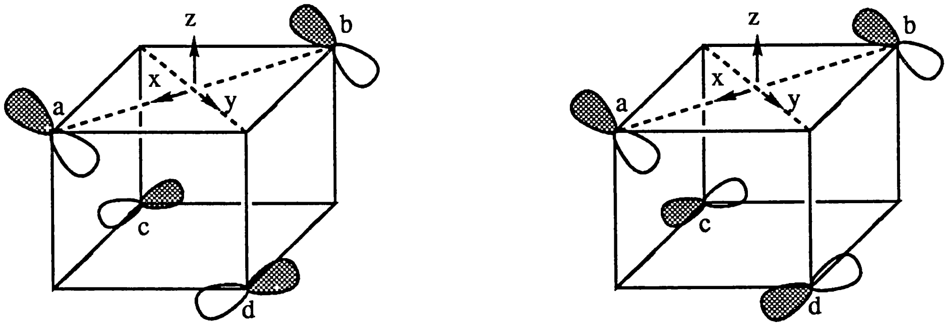
B(Cu1)=1/2(Px(a)+Px(b)+Py(c)+1Py(d))

B(Cu2)=1/2(Px(a)+Px(b)-Py(c)-Py(d))



A(Cu3)=1/2(Py(a)-Py(b)+Px(c)-Px(d))

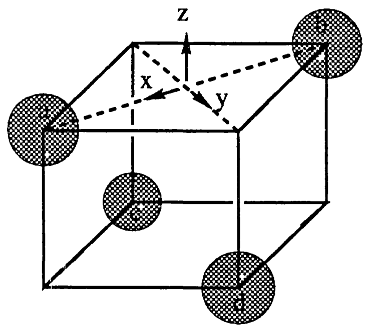
A(Cu4)=1/2(Py(a)-Px(b)-Py(c)+Px(d))



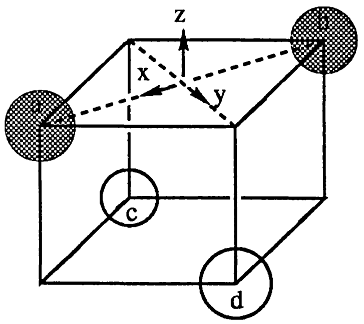
B(Cu3)=1/2(Py(a)+Py(b)+Px(c)+Px(d))

B(Cu4)=1/2(Py(a)+Py(b)-Px(c)-Px(d))

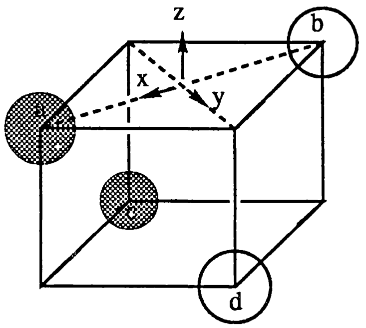
Figure 29. Linear Combinations of Copper $4p_x$ and $4p_y$ Orbitals



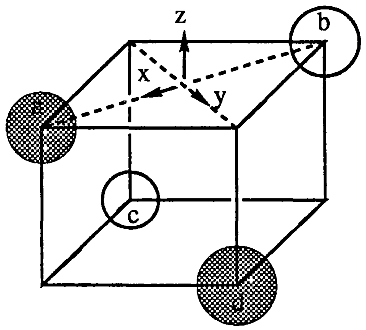
$A(Cu5)=1/2(S(a)+S(b)+S(c)+S(d))$



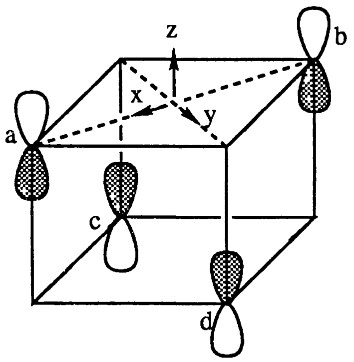
$A(Cu6)=1/2(S(a)+S(b)-S(c)-S(d))$



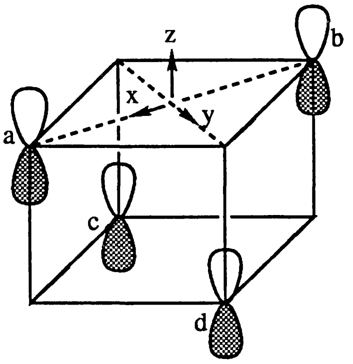
$B(Cu5)=1/2(S(a)-S(b)+S(c)-S(d))$



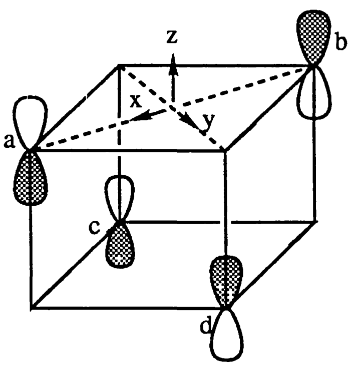
$B(Cu6)=1/2(S(a)-S(b)-S(c)+S(d))$



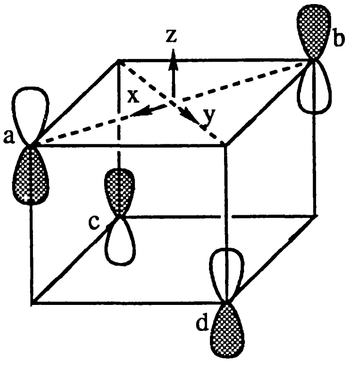
$A(Cu7)=1/2(Pz(a)+Pz(b)-Pz(c)-Pz(d))$



$A(Cu8)=1/2(Pz(a)+Pz(b)+Pz(c)+Pz(d))$

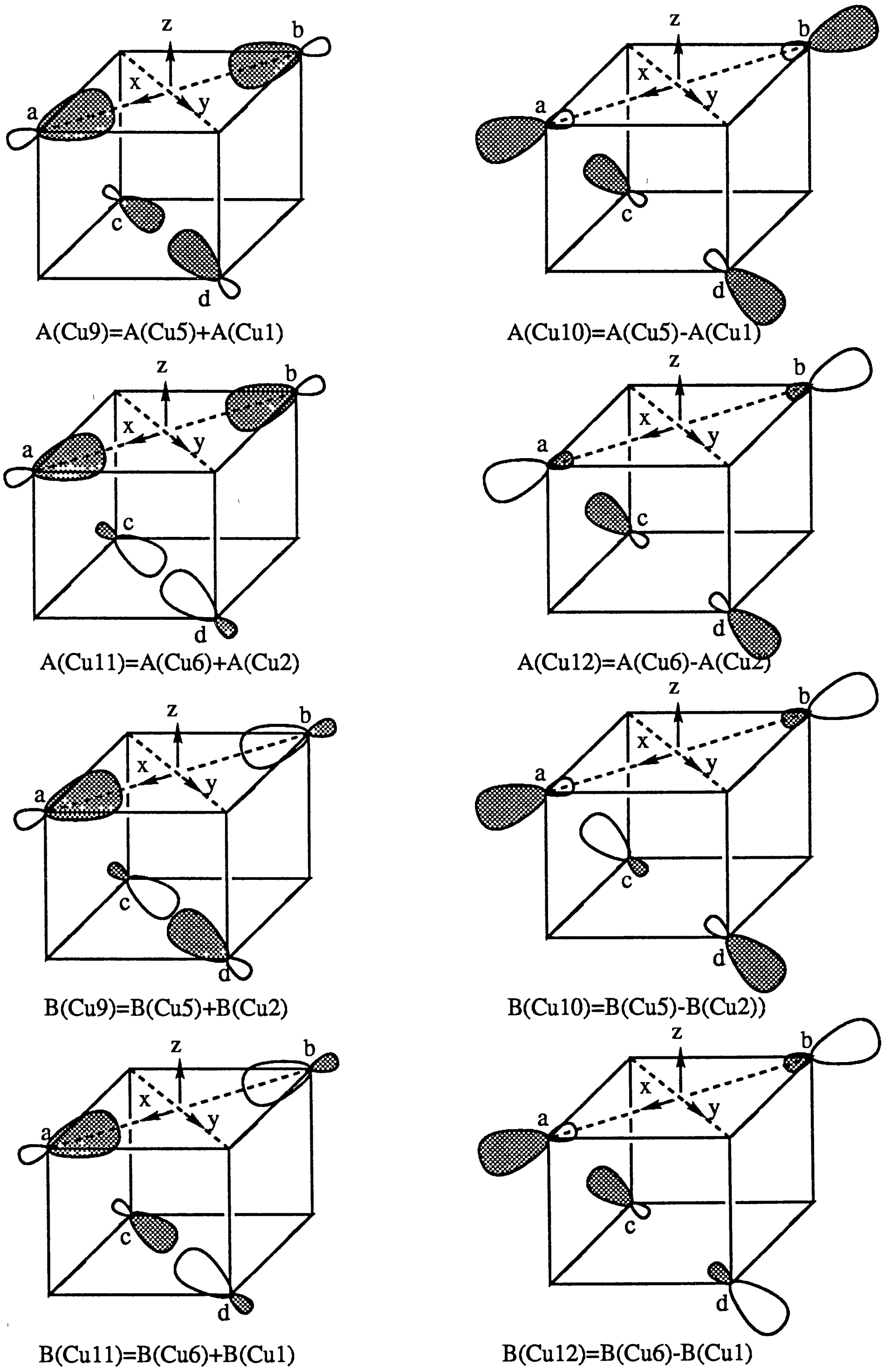


$B(Cu7)=1/2(Pz(a)-Pz(b)+Pz(c)-Pz(d))$



$B(Cu8)=1/2(Pz(a)-Pz(b)-Pz(c)+Pz(d))$

Figure 30. Linear Combinations of Copper 4s and $4p_z$ Orbitals



A(Cu9)=A(Cu5)+A(Cu1)

A(Cu10)=A(Cu5)-A(Cu1)

A(Cu11)=A(Cu6)+A(Cu2)

A(Cu12)=A(Cu6)-A(Cu2)

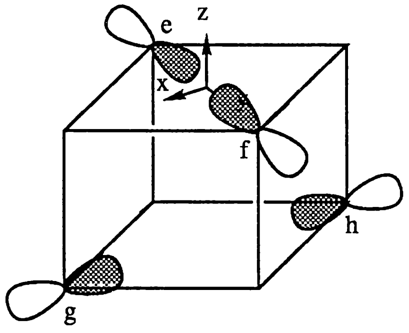
B(Cu9)=B(Cu5)+B(Cu2)

B(Cu10)=B(Cu5)-B(Cu2))

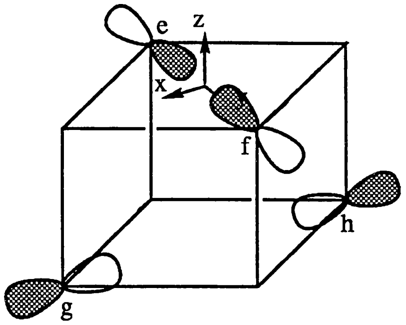
B(Cu11)=B(Cu6)+B(Cu1)

B(Cu12)=B(Cu6)-B(Cu1)

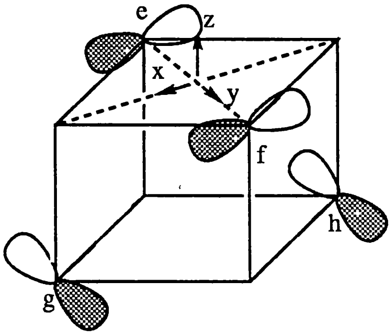
Figure 31. 4s and 4p Mixing of Copper Orbitals



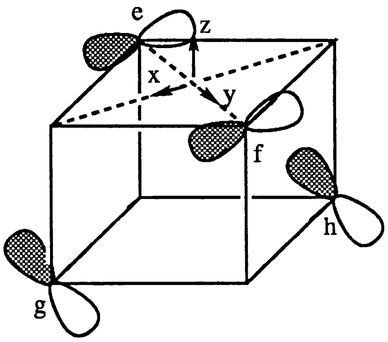
A(I1)=1/2(Px(e)-Px(f)+Py(g)-Py(h))



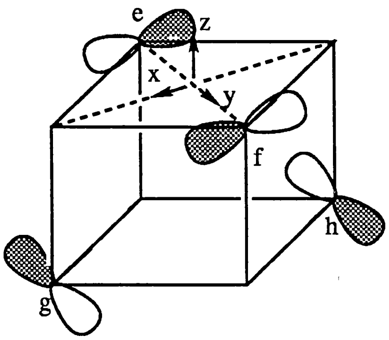
A(I2)=1/2(Px(e)-Px(f)-Py(g)+Py(h))



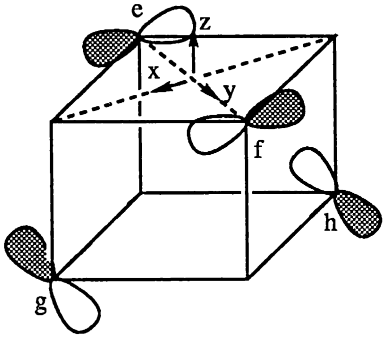
B(I1)=1/2(Px(e)+Px(f)-Py(g)-Py(h))



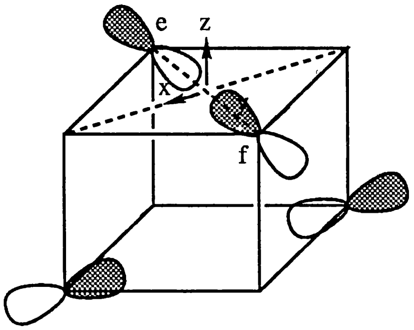
B(I2)=1/2(Px(e)+Px(f)+Py(g)+Py(h))



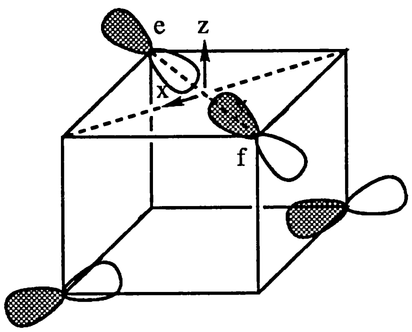
A(I3)=1/2(Py(e)-Py(f)-Px(g)+Px(h))



A(I4)=1/2(Py(e)-Py(f)+Px(g)-Px(h))

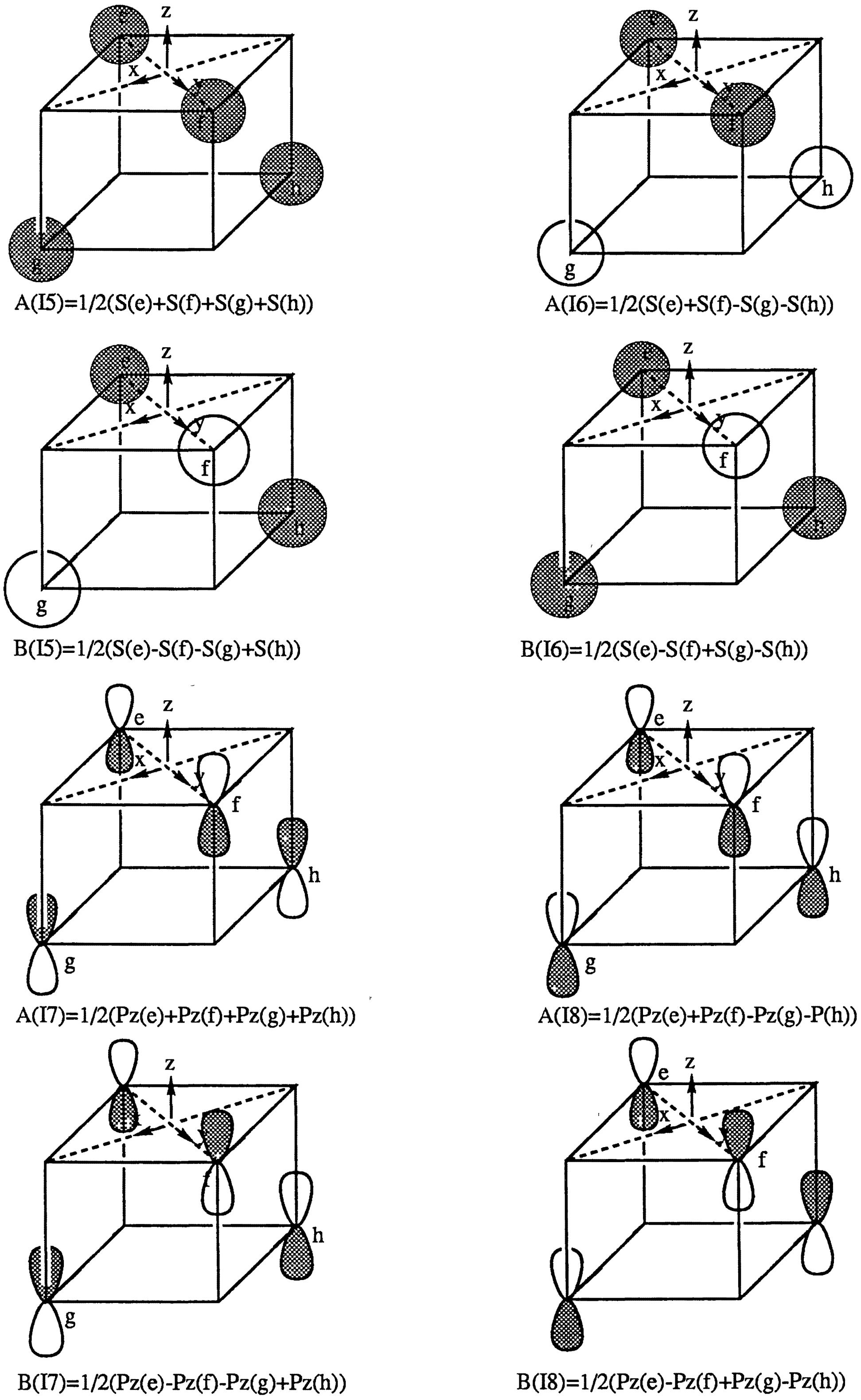


B(I3)=1/2(Py(e)+Py(f)+Px(g)+Px(h))



B(I4)=1/2(Py(e)+Py(f)-Px(g)-P(h))

Figure 32. Linear Combinations of Iodide $4p_x$ and $4p_y$ Orbitals



A(I5)=1/2(S(e)+S(f)+S(g)+S(h))

A(I6)=1/2(S(e)+S(f)-S(g)-S(h))

B(I5)=1/2(S(e)-S(f)-S(g)+S(h))

B(I6)=1/2(S(e)-S(f)+S(g)-S(h))

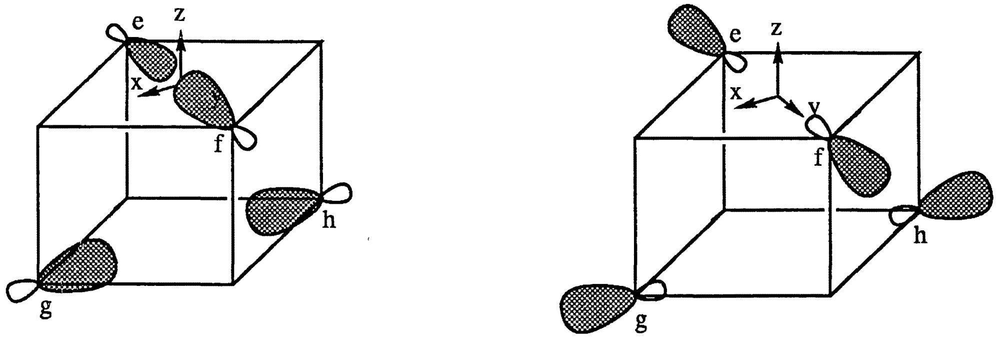
A(I7)=1/2(Pz(e)+Pz(f)+Pz(g)+Pz(h))

A(I8)=1/2(Pz(e)+Pz(f)-Pz(g)-P(h))

B(I7)=1/2(Pz(e)-Pz(f)-Pz(g)+Pz(h))

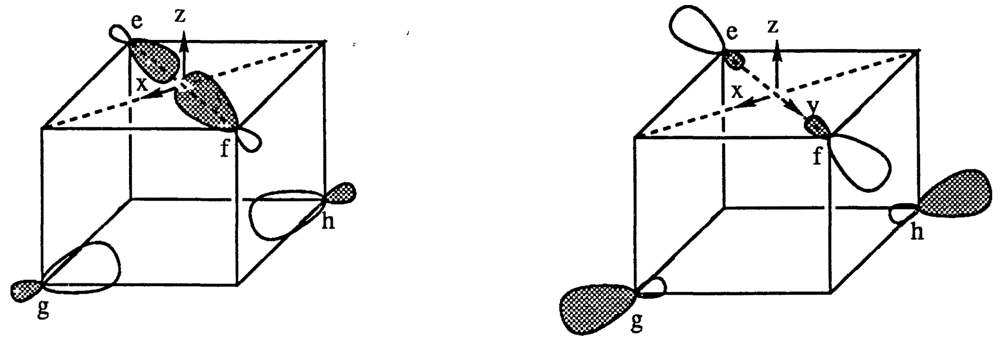
B(I8)=1/2(Pz(e)-Pz(f)+Pz(g)-Pz(h))

Figure 33. Linear Combinations of Iodide 4s and $4p_z$ Orbitals



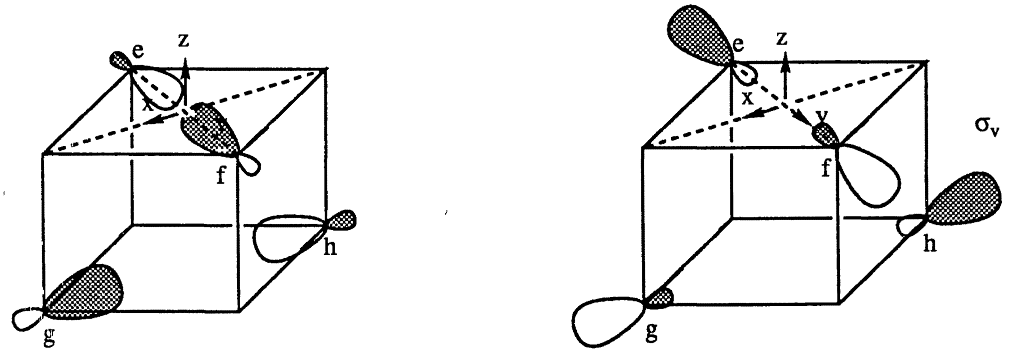
A(I9)=A(I5)+A(I1)

A(I10)=A(I5)-A(I1)



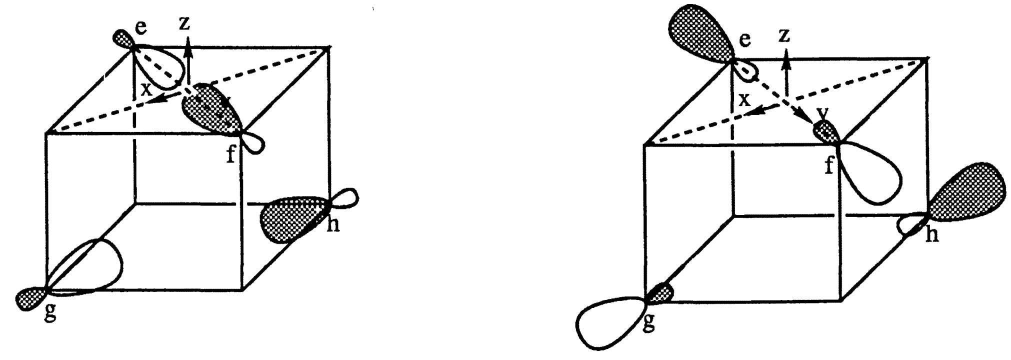
A(I11)=A(I2)+A(I6)

A(I6)=A(I2)-A(I6)



B(I9)=B(I3)-E(I5)

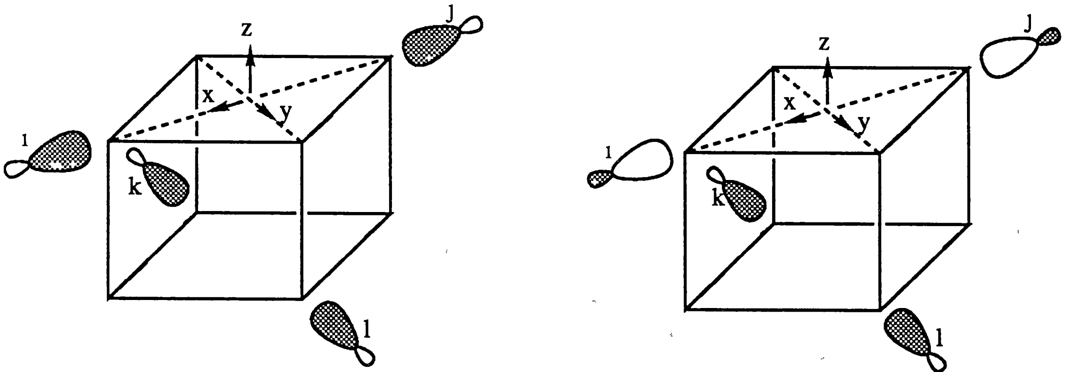
B(I10)=B(I3)+B(I5)



B(I11)=B(I4)-B(I6)

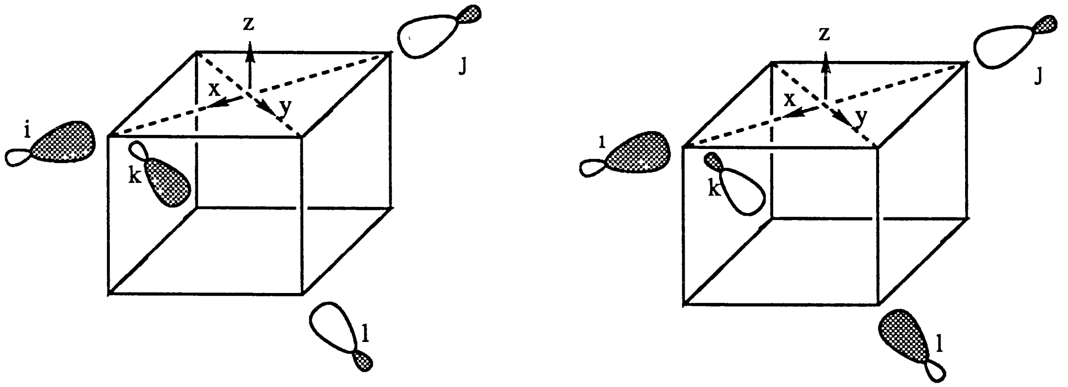
B(I12)=B(I4)+B(I6)

Figure 34. 4s and 4p Mixing of Iodide Orbitals



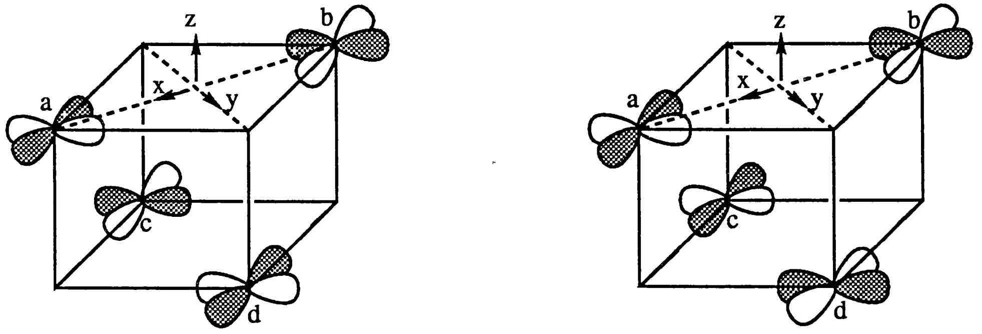
A(N1)=1/2(N(i)+N(j)+N(k)+N(l))

A(N2)=1/2(N(k)+N(l)-N(i)+N(j))



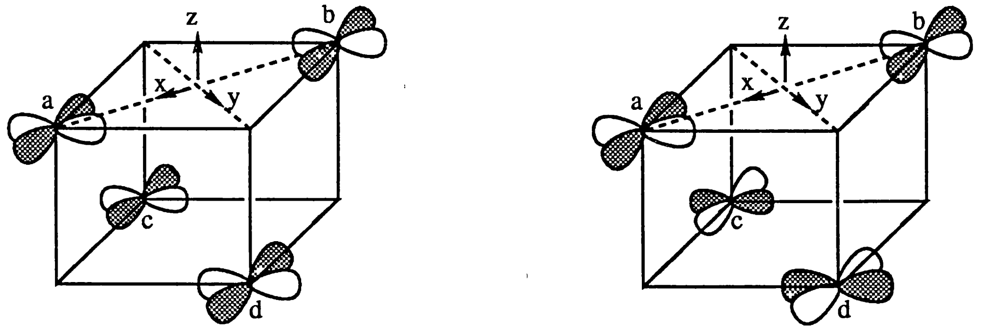
B(N1)=1/2(N(i)-N(j)+N(k)-N(l))

B(N2)=1/2(N(i)-N(j)-N(k)+N(l))



$A(D1)=1/2(d_{xy}(a)-d_{xy}(b)-d_{xy}(c)+d_{xy}(d))$

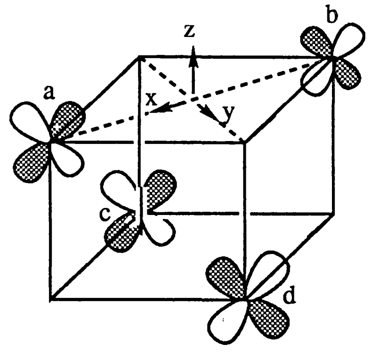
$A(D2)=1/2(d_{xy}(a)-d_{xy}(b)+d_{xy}(c)-d_{xy}(d))$



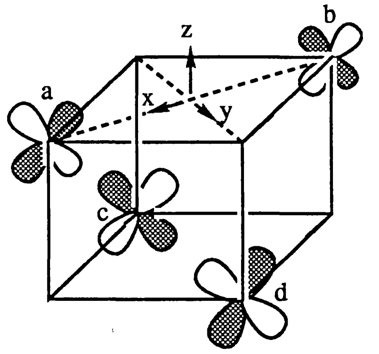
$B(D1)=1/2(d_{xy}(a)+d_{xy}(b)-d_{xy}(c)-d_{xy}(d))$

$B(D2)=1/2(d_{xy}(a)+d_{xy}(b)+d_{xy}(c)+d_{xy}(d))$

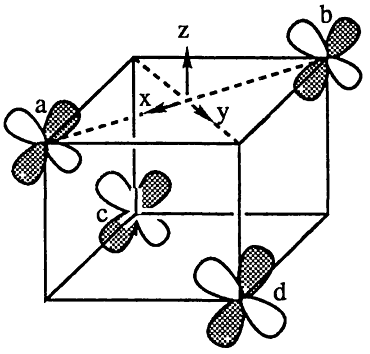
Figure 35. Linear Combinations of Nitrogen sp^3 Orbitals and Copper d_{xy} Orbitals



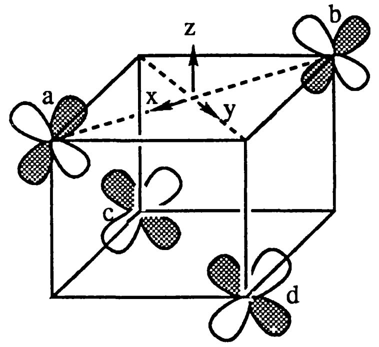
$A(D3)=1/2(d_{xz}(a)-d_{xz}(b)+d_{xz}(c)-d_{xz}(d))$



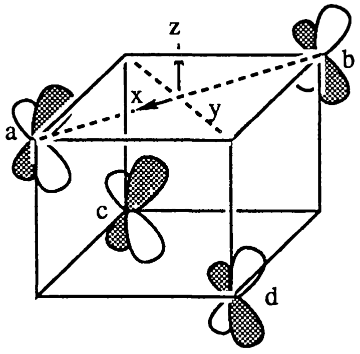
$A(D4)=(d_{xz}(a)-d_{xz}(b)-d_{xz}(c)+d_{xz}(d))$



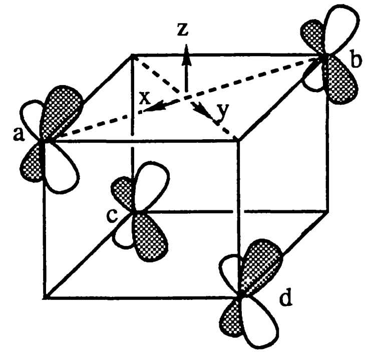
$B(D3)=1/2(d_{xz}(a)+d_{xz}(b)-d_{xz}(c)-d_{xz}(d))$



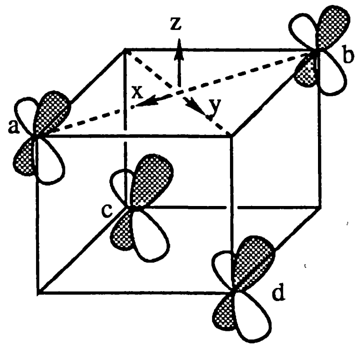
$B(D4)=(d_{xz}(a)+d_{xz}(b)+d_{xz}(c)+d_{xz}(d))$



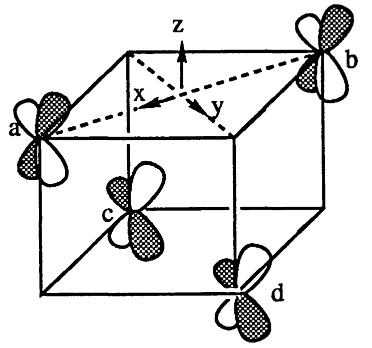
$A(D5)=1/2(d_{yz}(a)-d_{yz}(b)+d_{yz}(c)-d_{yz}(d))$



$A(D6)=(d_{yz}(a)-d_{yz}(b)-d_{yz}(c)+d_{yz}(d))$

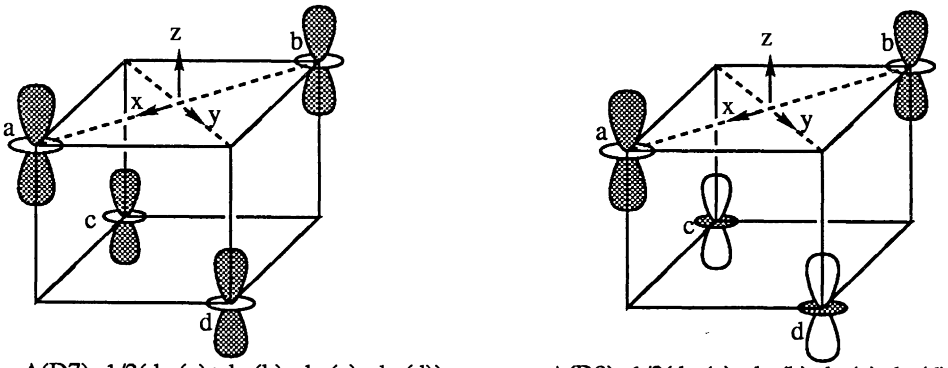


$B(D5)=1/2(d_{yz}(a)+d_{yz}(b)+d_{yz}(c)+d_{yz}(d))$

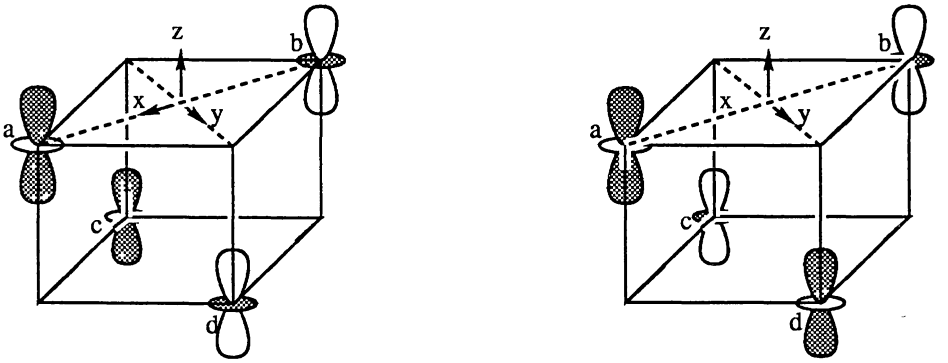


$B(D6)=(d_{yz}(a)+d_{yz}(b)-d_{yz}(c)-d_{yz}(d))$

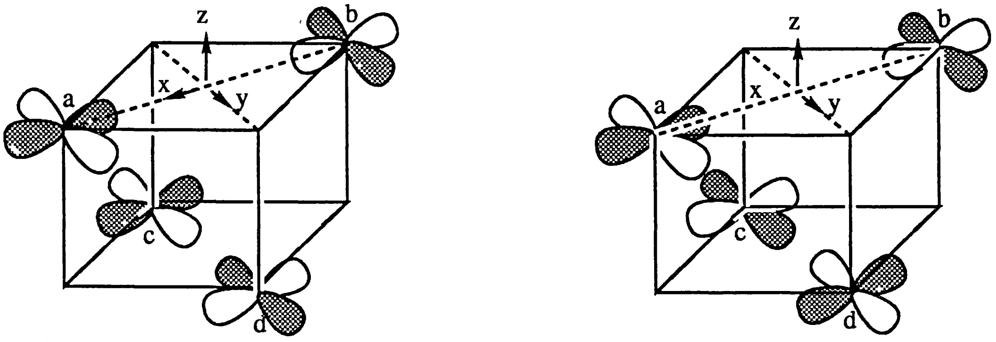
Figure 36. Linear Combinations of Copper d_{xz} and d_{yz} Orbitals



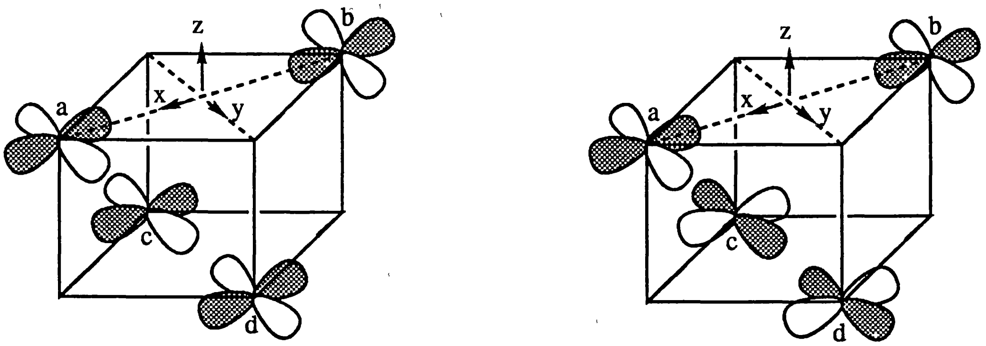
$A(D7)=1/2(d_{z2}(a)+d_{z2}(b)+d_{z2}(c)+d_{z2}(d))$ $A(D8)=1/2(d_{z2}(a)+d_{z2}(b)-d_{z2}(c)-d_{z2}(d))$



$B(D7)=1/2(d_{z2}(a)-d_{z2}(b)+d_{z2}(c)-d_{z2}(d))$ $B(D8)=1/2(d_{z2}(a)-d_{z2}(b)-d_{z2}(c)+d_{z2}(d))$

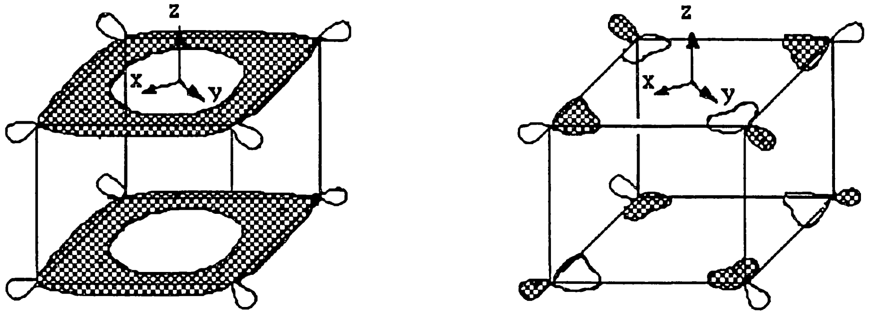


$A(D9)=1/2(d_{x2-y2}(a)-d_{x2-y2}(b)-d_{x2-y2}(c)+d_{X2-y2}(d))$ $A(D10)=1/2(d_{x2-y2}(a)-d_{x2-y2}(b)+d_{x2-y2}(c)-d_{x2-y2}(d))$



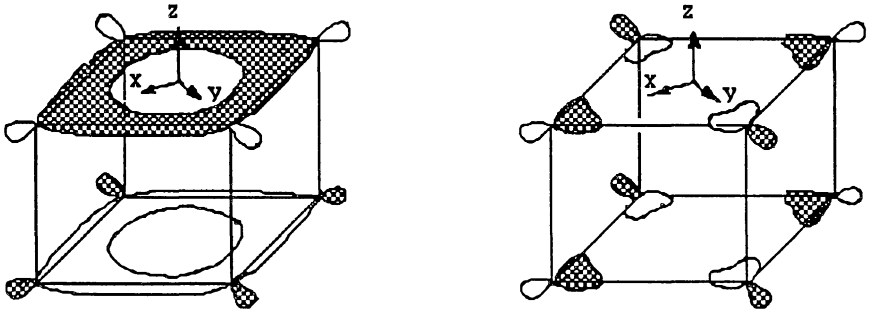
$B(D9)=1/2(d_{x2-y2}(a)+d_{x2-y2}(b)+d_{x2-y2}(c)+d_{X2-y2}(d))$ $B(D10)=1/2(d_{x2-y2}(a)+d_{x2-y2}(b)-d_{x2-y2}(c)-d_{x2-y2}(d))$

Figure37. Linear Combinations of Copper d_{z2} and d_{x2-y2} Orbitals



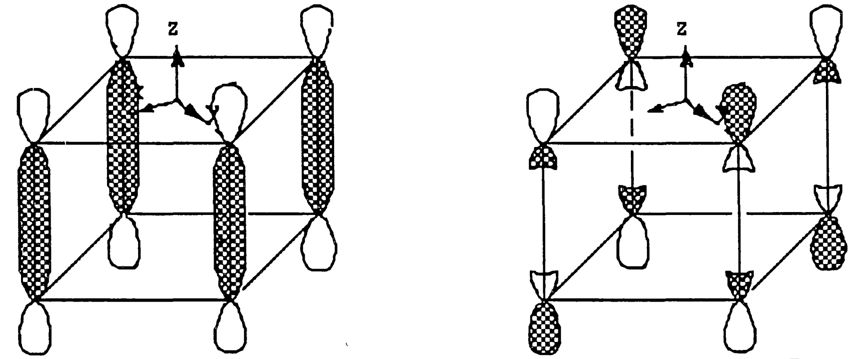
A(B1)=A(Cu9)+A(I9)

A(A1)=A(Cu9)-A(I9)



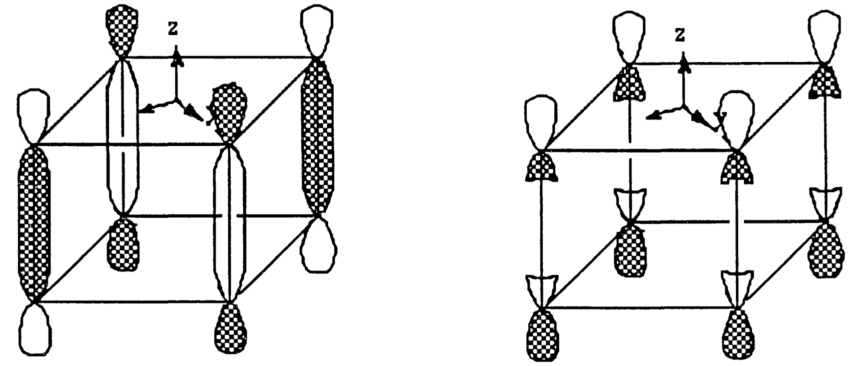
A(B2)=A(Cu11)+A(I11)

A(A2)=A(cu11)-A(I11)



A(B3)=A(Cu7)+A(I7)

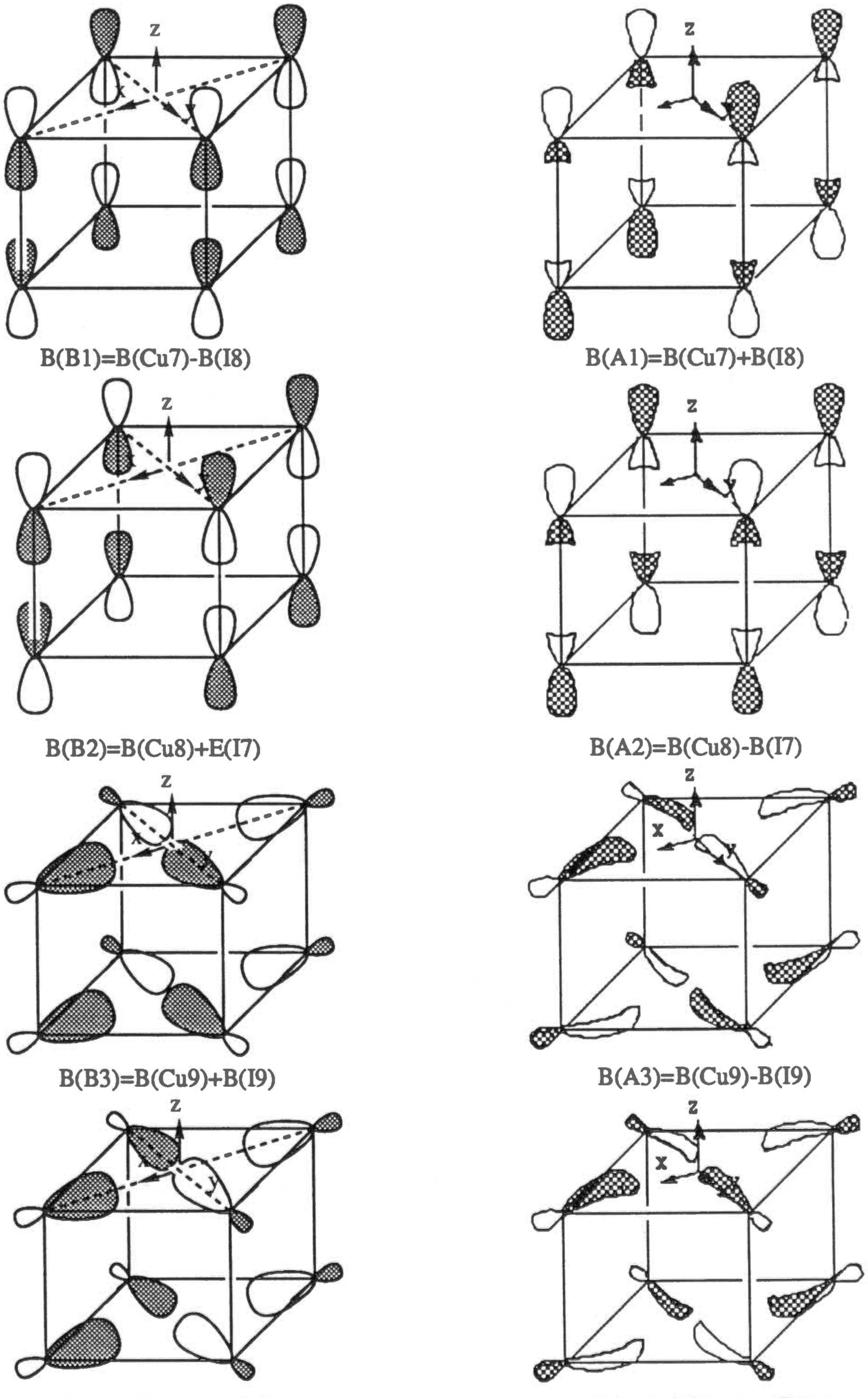
A(A3)=A(Cu7)-A(I7)



A(B4)=A(Cu8)-A(I8)

A(A4)=A(Cu8)+A(I8)

Figure 38. Bonding and Antibonding Molecular Orbitals



B(B1)=B(Cu7)-B(I8)

B(A1)=B(Cu7)+B(I8)

B(B2)=B(Cu8)+E(I7)

B(A2)=B(Cu8)-B(I7)

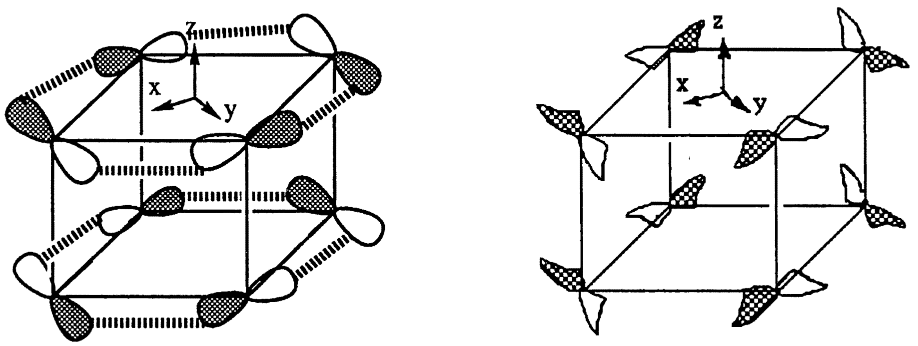
B(B3)=B(Cu9)+B(I9)

B(A3)=B(Cu9)-B(I9)

B(B4)=B(Cu11)-B(I11)

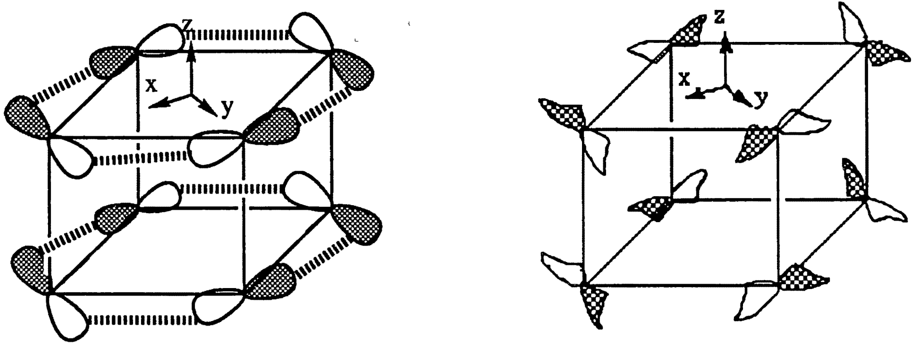
B(A4)=B(Cu11)+(BI11)

Figure 39. Bonding and Antibonding Molecular Orbitals



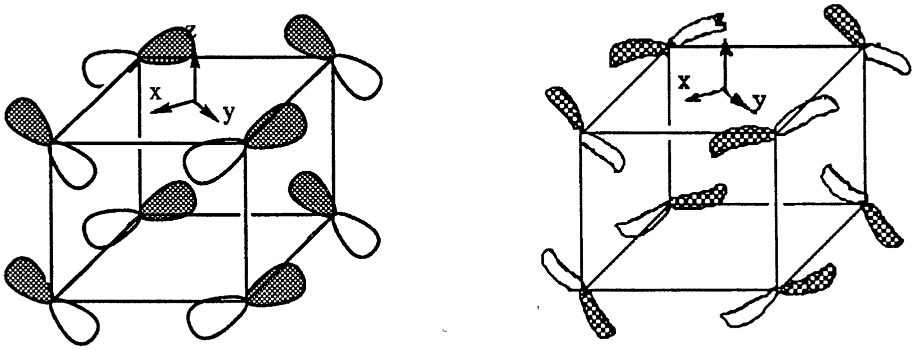
A(B5)=A(Cu3)-A(I3)

A(A5)=A(Cu3)+A(I3)



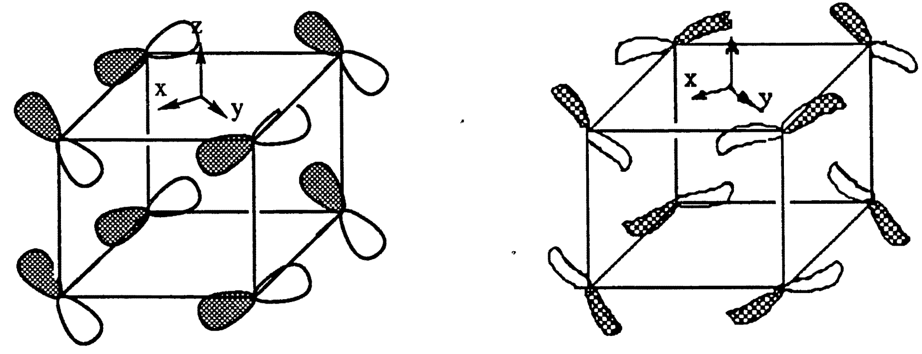
A(B6)=B(Cu4)+B(I4)

A(A6)=B(Cu4)-B(I4)



B(B5)=B(Cu3)-B(I1)

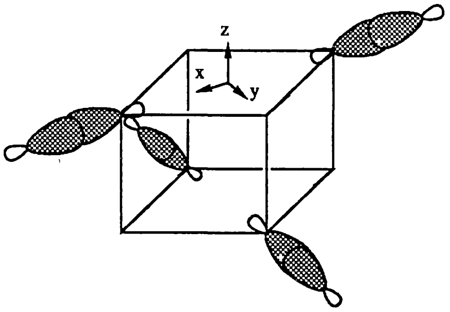
B(A5)=B(Cu3)+B(I1)



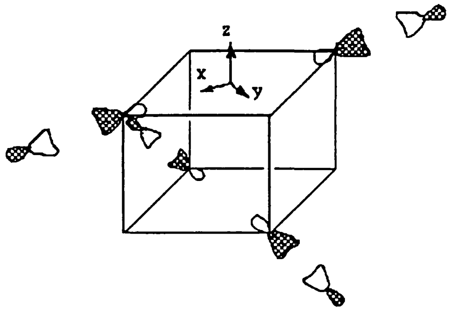
B(B6)=B(Cu4)+B(I2)

B(A6)=B(Cu4)-E(I2)

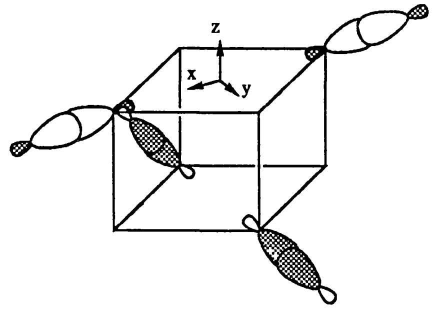
Figure 40. Bonding and Antibonding Molecular Orbitals.



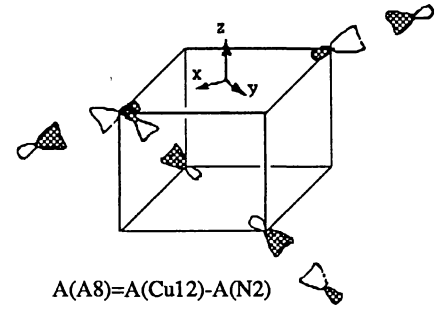
A(B7)=A(Cu10)+A(N1)



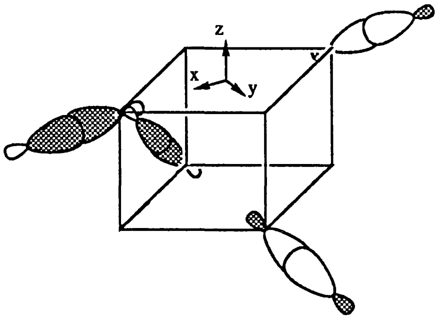
A(A7)=A(Cu10)-A(N1)



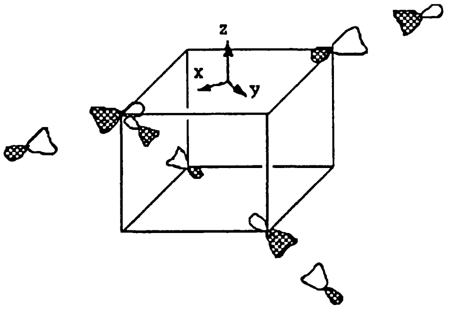
A(B8)=A(Cu12)+A(N2)



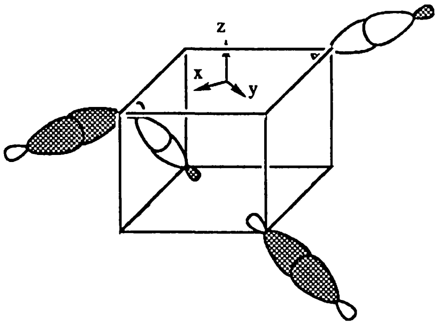
A(A8)=A(Cu12)-A(N2)



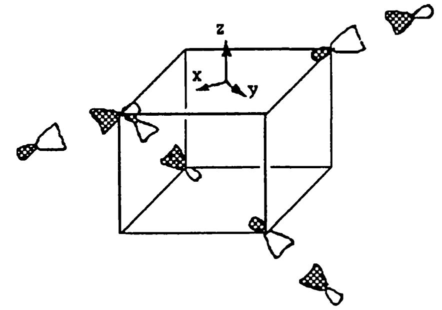
B(B7)=B(Cu12)+B(N1)



B(A7)=B(Cu12)-B(N1)



B(B8)=B(Cu10)+B(N2)



B(A8)=B(Cu10)-B(N2)

Figure 41. Bonding and Antibonding Molecular Orbitals

of the compound shows two different emission maxima depending upon temperature: 10K (580 - 630 nm), 298K(640 - 670). This observation might be explained by a phase change occuring in the crystal as the temperature is lowered. The change in maximum emission wavelength suggests that the molecules in the crystal lose the two mirrors at low temperature and change to symmetry, C_2. The solid state emission of the the compound at low temperature (10 K) is similar to that of compound C_4I_4(morpholine)$_4$ (Figure 26.) (symmetry, C_2).

The solid state emission of Cu_4I_4(3,5-dimethylpiperidine)$_4$ at room temperature can be discussed based upon the symmetry of the molecule (C_{2v}) by the same procedures applied to other systems with symmetry elements within the molecule. The character table of the C_{2v} group is given in Table 4. Transformations and drawings of the orbitals of copper, iodide and nitrogen atoms under the C_{2v} group and bonding and antibonding combinations of the orbitals are shown in Figures 43 to 55. The relative sequence of the orbital energies was assigned based on the nodal plane criterion. In Figure 42, transition between the HOMO (B1 or B2) and LUMO (A1) is not allowed because the triple product of ground state excited state and operater is zero. The emission of the compound must originate from transition between lowest antibonding orbital with B1 or B2 symmetry to HOMO from which excitation took place. Therefore the compound emits in higher energy than the cubic morpholine complex (Figure 26).

Compound 10, (Cu_4I_4(piperidine)$_4$), has a fourfold inversion axis (S_4) within the molecule and thus belongs to point group S_4 (Table 5). Transformations of orbitals can

TABLE 5

CHARACTER TABLE OF S_4 GROUP

S_4	E	S_4	C_2	S_4^3
A	1	1	1	1
B	1	-1	1	-1
E	1	1	-1	-1
	1	-1	-1	1

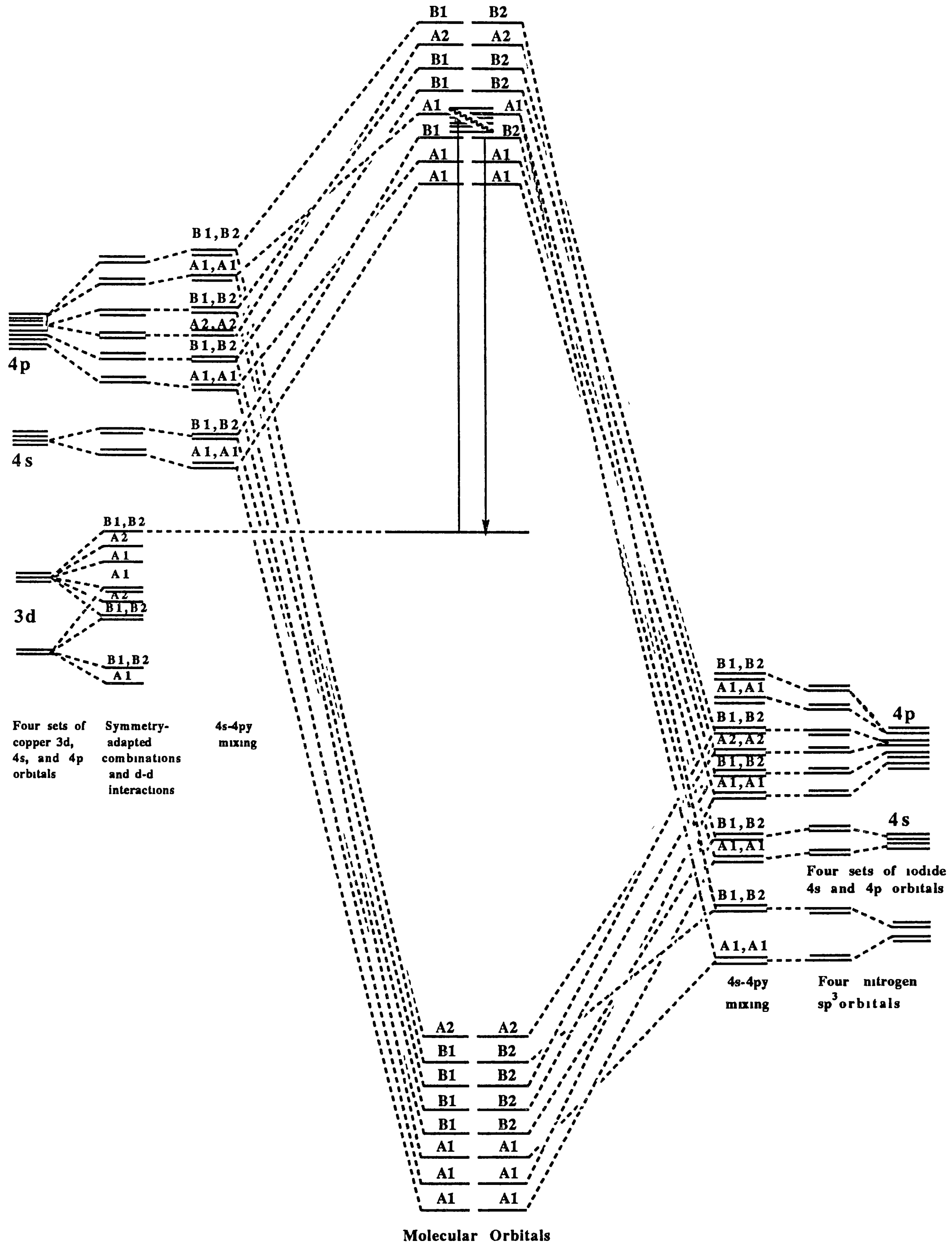
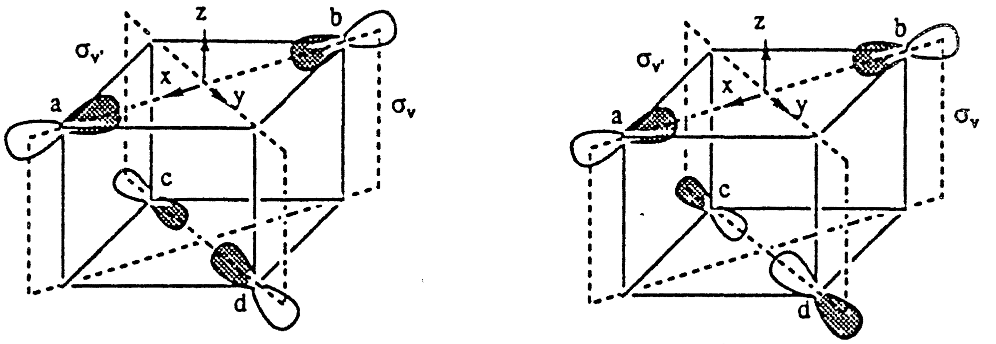
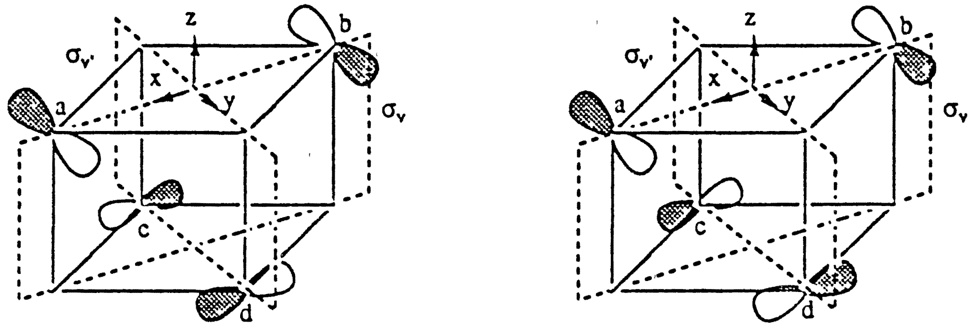


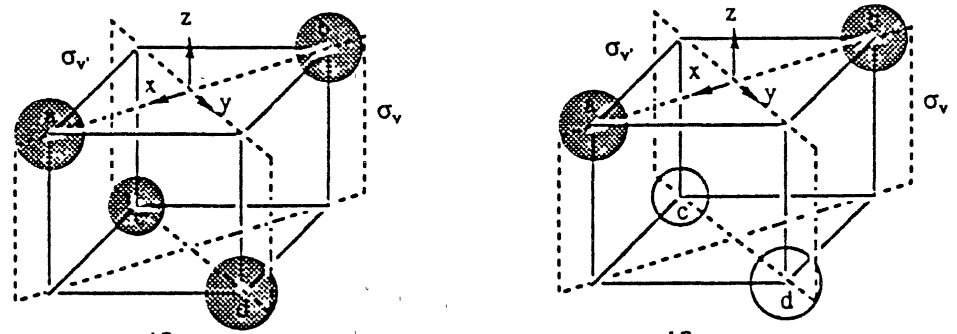
Figure 42. Schematic Molecular Orbital Energy Level Diagram of Compound Cu_4I_4(3,5-dimethylpiperidine)$_4$



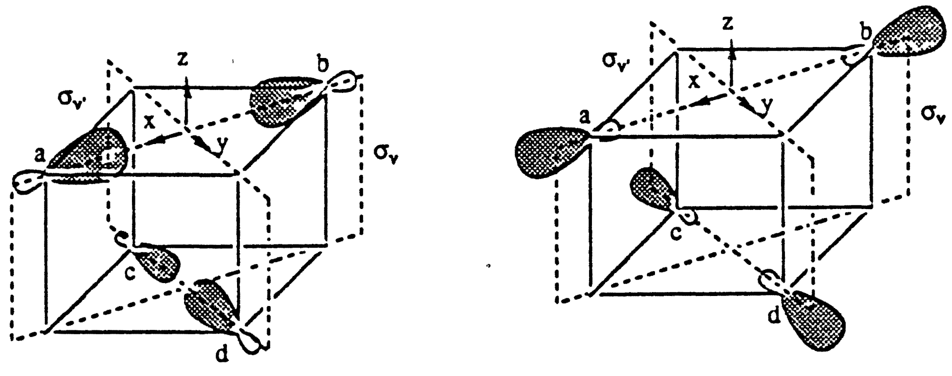
$A1(Cu1)=1/(2)^{1/2}(Px(a)-Px(b)+Py(c)-Py(d))$ $A1(Cu2)=1/(2)^{1/2}(Px(a)-Px(b)-Py(c)+Py(d))$



$A2(Cu1)=1/(2)^{1/2}(Py(a)-Py(b)+Px(c)-Px(b))$ $A2(Cu2)=1/(2)^{1/2}(Py(a)-Py(b)-Px(c)+Px(d))$

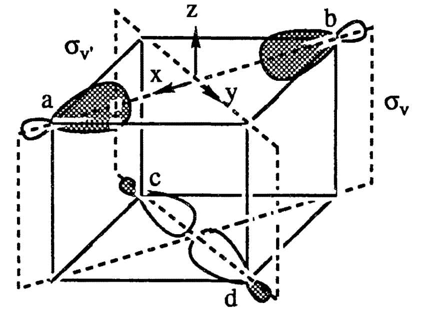


$A1(Cu3)=1/(2)^{1/2}(S(a)+S(b)+S(c)+S(d))$ $A1(Cu4)=1/(2)^{1/2}(S(a)+S(b)-S(c)-S(d))$

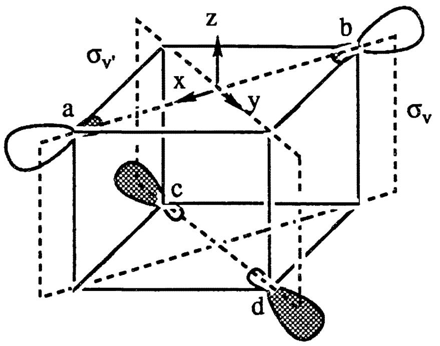


A1(Cu5)=A1(Cu1)+A1(Cu3) A1(Cu6)=A1(Cu3)-A1(Cu1)

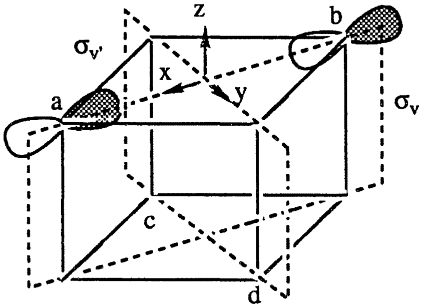
Figure 43. Linear Combinations of Copper $4p_x$,$4p_y$ obitals and 4s and 4p mixing



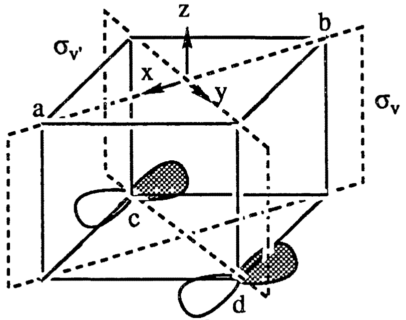
A1(Cu7)=A1(Cu2)+A1(Cu4)



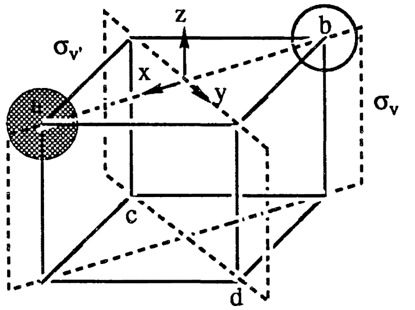
A1(Cu8)=A1(Cu2)-A1(Cu4)



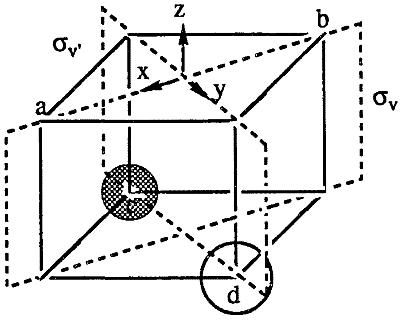
B1(Cu1)=1/(2$^{)1/2}$(Px(a)+Px(b))



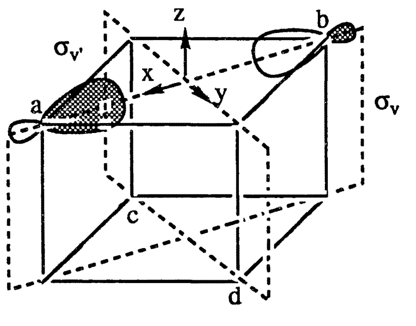
B1(Cu2)=1/(2)$^{1/2}$(Px(c)+Px(d))



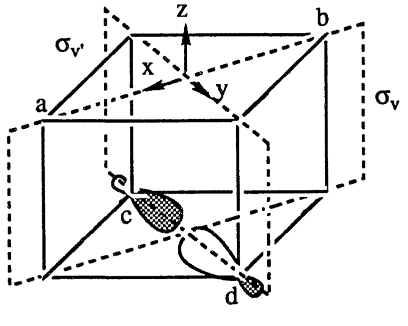
B1(Cu3)=1/(2)$^{1/2}$(S(a)-S(b))



B2(Cu3)=1/(2)$^{1/2}$(S(c)-S(d))

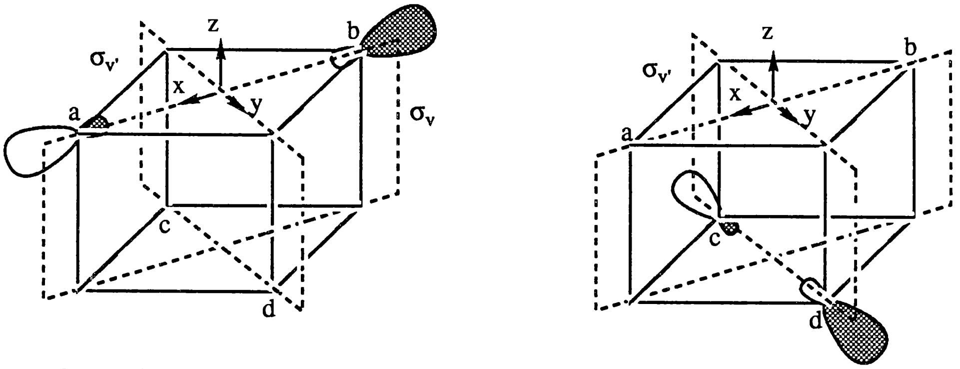


Cu4)=B1(Cu1)+B1(Cu3)



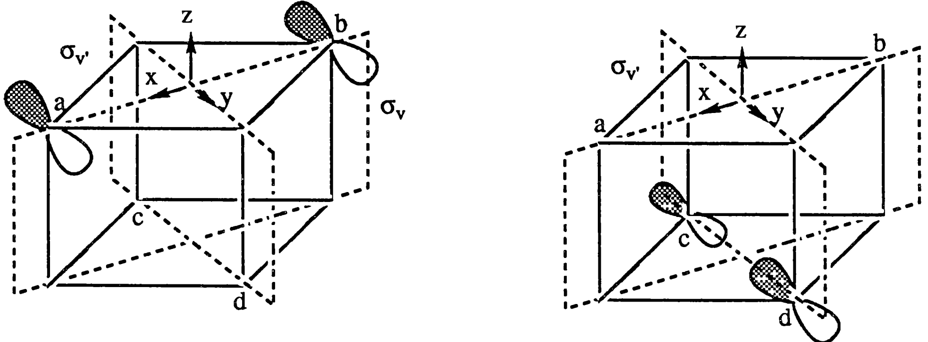
B2(Cu4)=B2(Cu3)-B2(Cu2)

Figure 44. Linear Combinations of Copper 4s, 4p$_x$ orbitals and 4s, 4p mixing



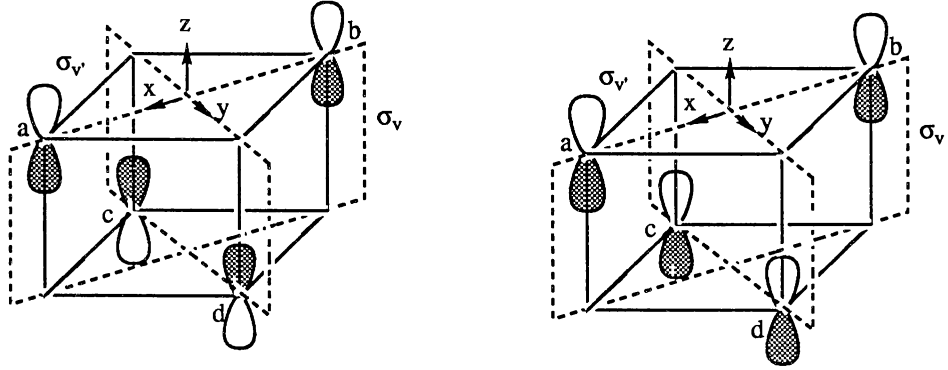
B1(Cu5)=B1(Cu1)-B1(Cu3)

B2(Cu5)=B2(Cu2)+B2(Cu3)



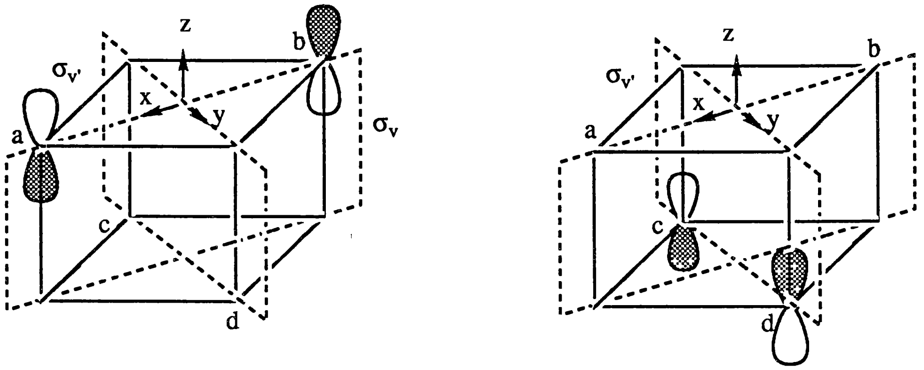
B2(Cu1)=1/(2)$^{1/2}$(Py(a)+Py(b))

B2(Cu2)=1/(2)$^{1/2}$(Py(c)+Py(d))



A1(Cu9)=1/(2)$^{1/2}$(Pz(a)+Pz(b)-Pz(c)-Pz(d))

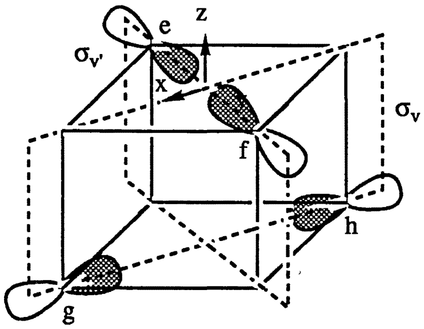
A1(Cu10)=1/(2)$^{1/2}$(Pz(a)+pz(b)+Pz(c)+Pz(d))



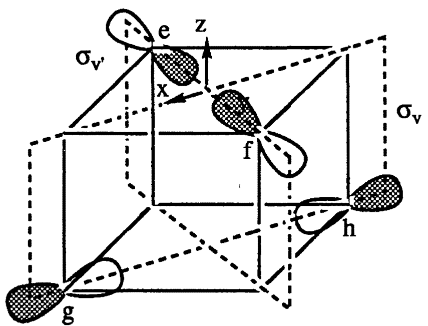
B1(Cu6)=1/(2)$^{1/2}$(Pz(a)-Pz(b))

B2(Cu6)=1/(2)$^{1/2}$(Pz(c)-Pc(d))

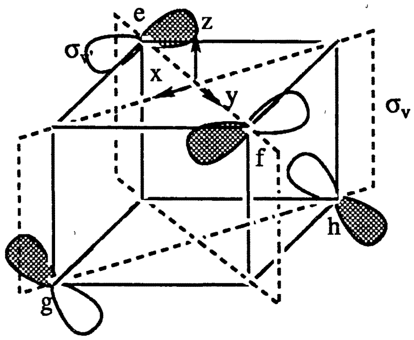
Figure 45. Linear Combinations of Copper 4p_z Orbitals and 4s, 4p Mixing



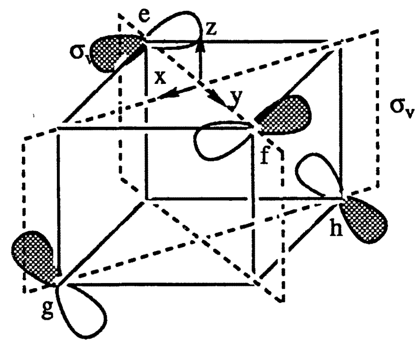
A1(I1)=1/(2)$^{1/2}$(Py(f)-Py(e)+Px(g)-Px(h))



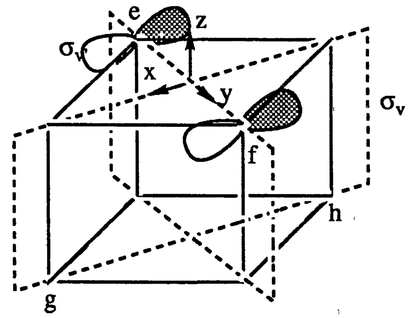
A1(I2)=1/(2)$^{1/2}$(Py(f)-Py(e)-Px(g)+Px(h))



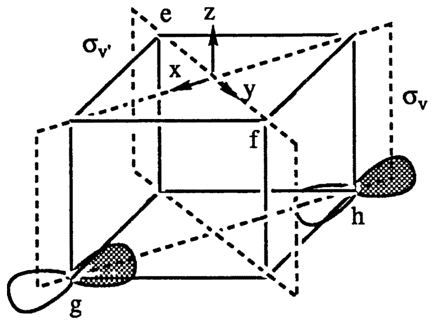
A2(I1)=1/(2)$^{1/2}$(Px(e)-Px(f)+Py(g)-Py(h))



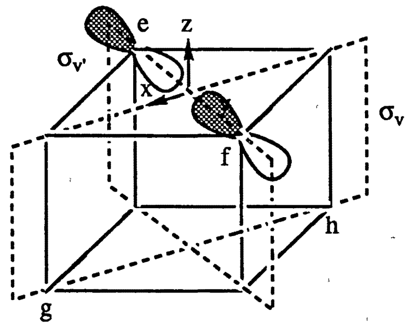
A2(I2)=1/(2)$^{1/2}$(Py(g)-Py(h)-Px(e)+Px(f))



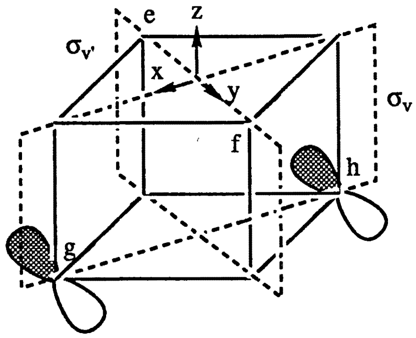
B1(I1)=1/(2)$^{1/2}$(Px(e)+Px(f))



B1(I2)=1/(2)$^{1/2}$(Px(g)+Px(h))

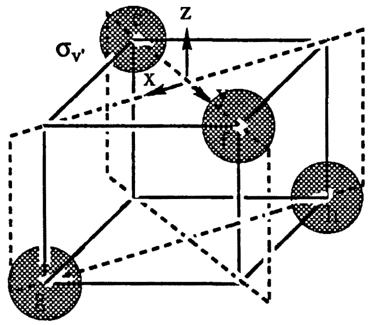


B2(I1)=1/(2)$^{1/2}$(Py(e)+Py(f))

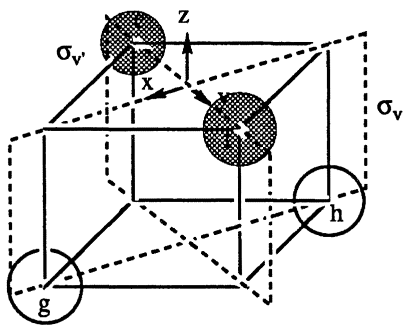


B2(I2)=1/(2)$^{1/2}$(Py(g)+Py(h))

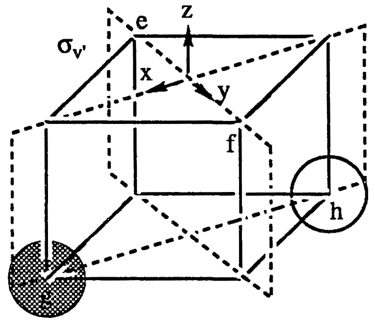
Figure 46. Linear Combinations of Iodide 4p_x and 4p_y Orbitals



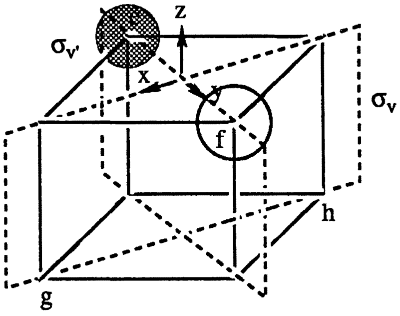
$A1(I3)=1/(2)^{1/2}(S(e)+S(f)+S(g)+S(h))$



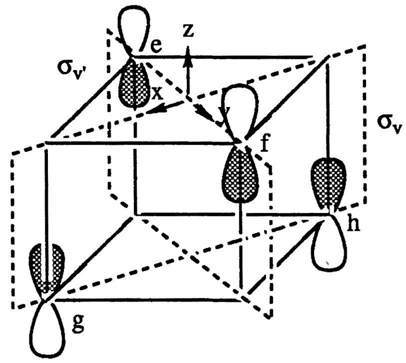
$A1(I4)=1/(2)^{1/2}(S(e)+S(f)-S(g)-S(h))$



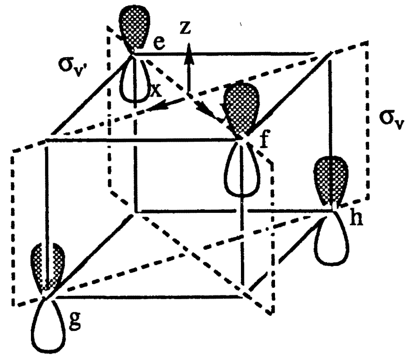
$B1(I3)=1/(2)^{1/2}(S(g)-S(h))$



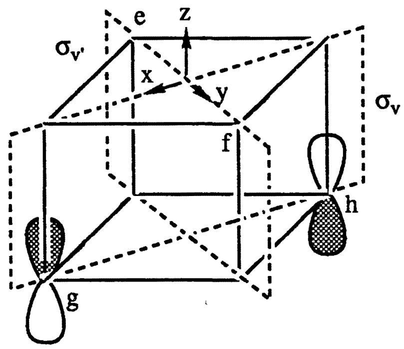
$B2(I3)=1/(2)^{1/2}(S(e)-S(f))$



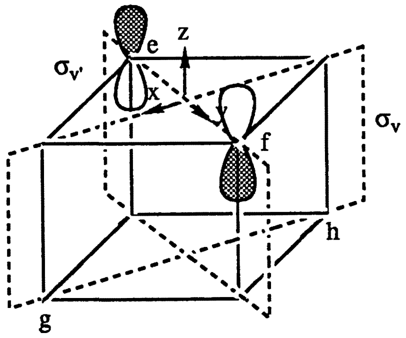
$A1(I5)=1/(2)^{1/2}(Pz(e)+Pz(f)+Pz(g)+Pz(h))$



$A1(I6)=1/(2)^{1/2}(Pz(g)+Pz(h)-Pz(e)-Pz(f))$

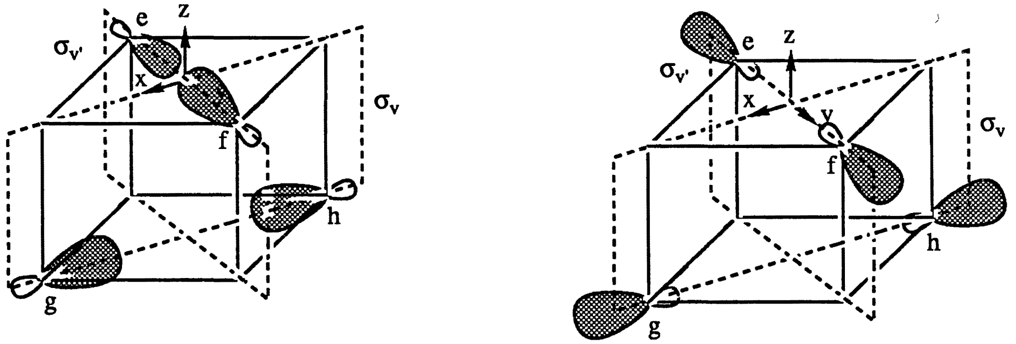


$B1(I4)=1/(2)^{1/2}(Pz(h)-Pz(g))$



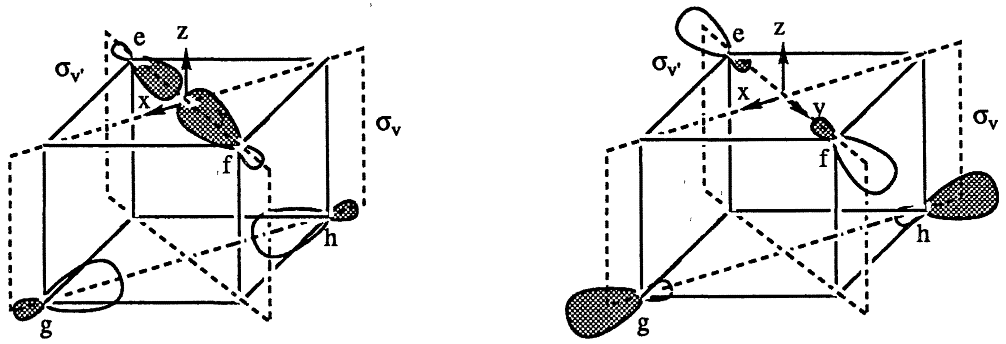
$B2(I4)=1/(2)^{1/2}(Pz(f)-Pz(e))$

Figure 47. Linear Combinations of Iodide 4s and $4p_z$ orbitals



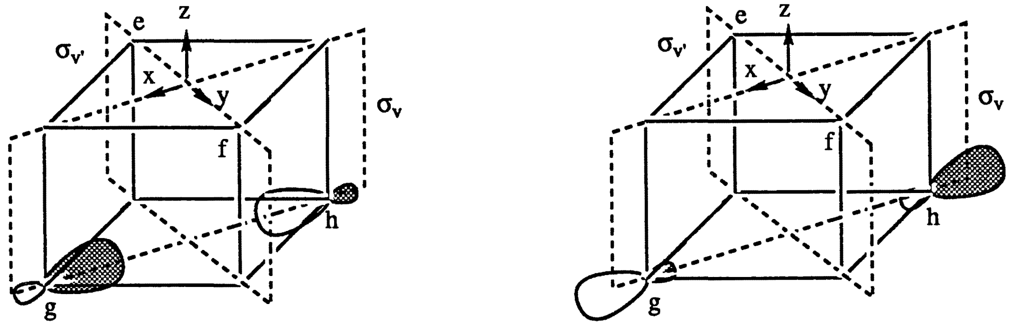
A1(I7)=A1(I1)+A1(I3)

A1(I8)=A1(I3)-A1(I1)



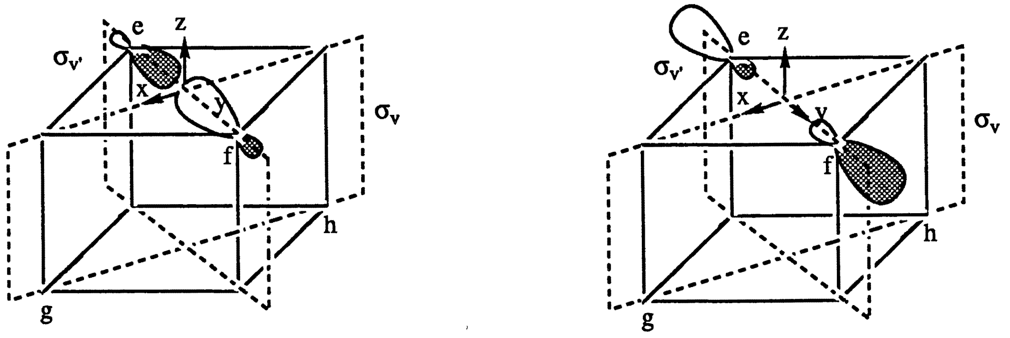
A1(I9)=A1(I2)+A1(I4)

A1(I10)=A1(I2)-A1(I4)



B1(I5)=B1(I2)-B1(I3)

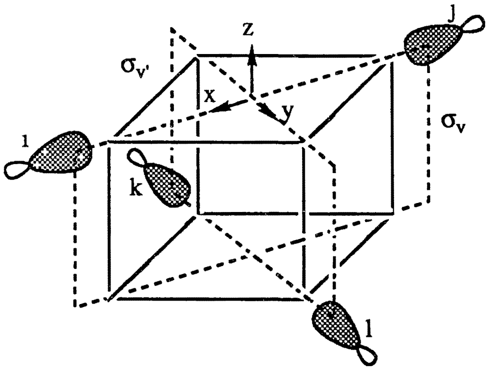
B1(I6)=B1(I2)-B1(I3)



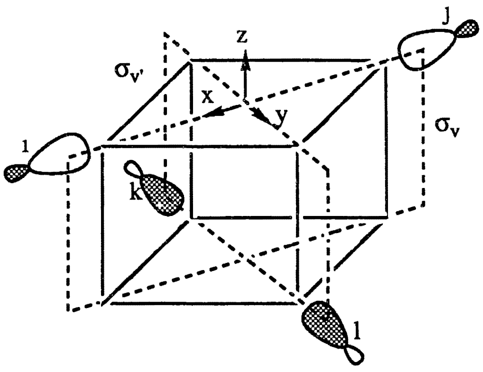
B2(I5)=B2(I3)-B2(I1)

B2(I6)=B2(I1)+B2(I3)

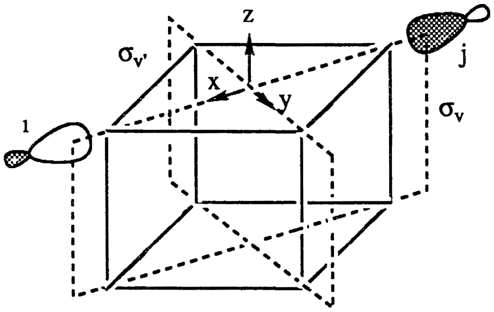
Figure 48. 4s and 4p Mixing of Iodide Orbitals



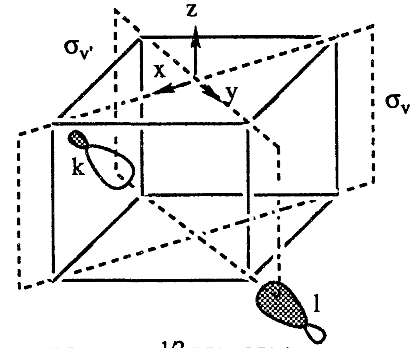
$A1(N1)=1/(2)^{1/2}(N(i)+N(j)+N(k)+N(l))$



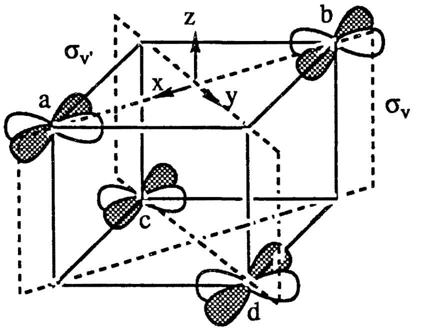
$A1(N2)=1/(2)^{1/2}(N(k)+N(l)-N(i)-N(j))$



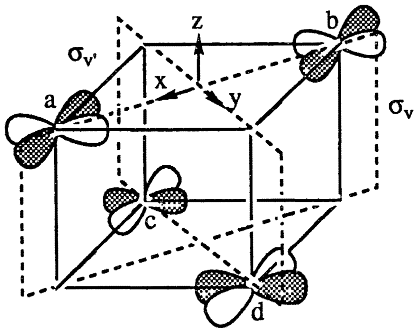
$B1(N1)=1/(2)^{1/2}(N(j)-N(i))$



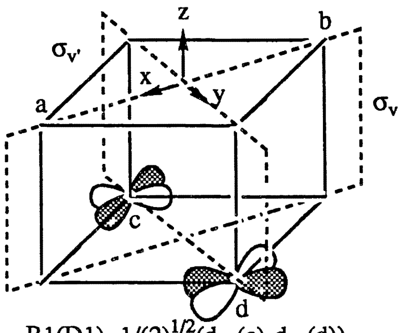
$B2(N1)=1/(2)^{1/2}(N(l)-N(k))$



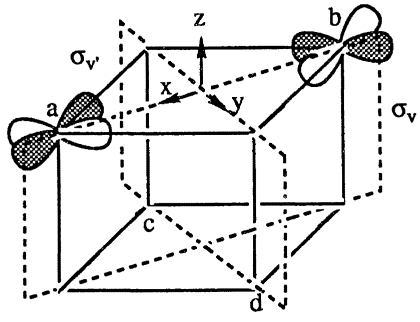
$A2(D1)=1/(2)^{1/2}(d_{xy}(a)+d_{xy}(b)+d_{xy}(c)+d_{xy}(d))$



$A2(D2)=1/(2)^{1/2}(d_{xy}(a)+d_{xy}(b)-d_{xy}(c)-d_{xy}(d))$

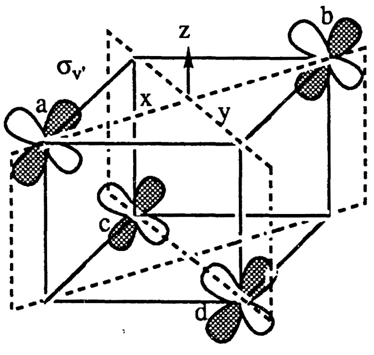


$B1(D1)=1/(2)^{1/2}(d_{xy}(c)-d_{xy}(d))$

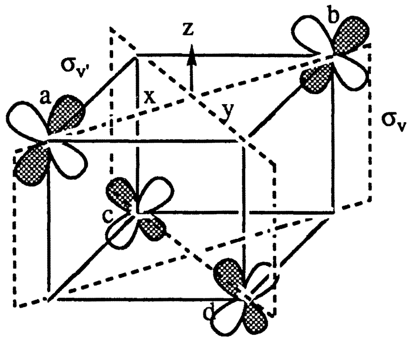


$B2(D1)=1/(2)^{1/2}(d_{xy}(a)-d_{xy}(b))$

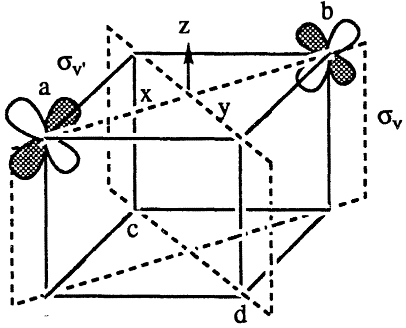
Figure 49. Linear Combinations of Nitrogen sp^3 Orbitals and Copper d_{xy} Orbitals



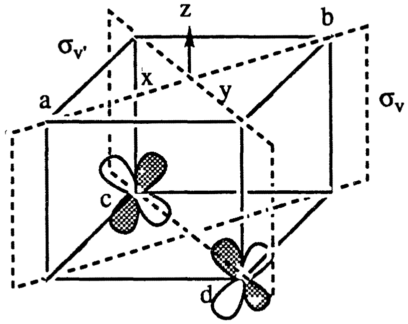
$B1(D2)=1/(2)^{1/2}(d_{xz}(a)+d_{xz}(b)+d_{xz}(c)+d_{xz}(d))$



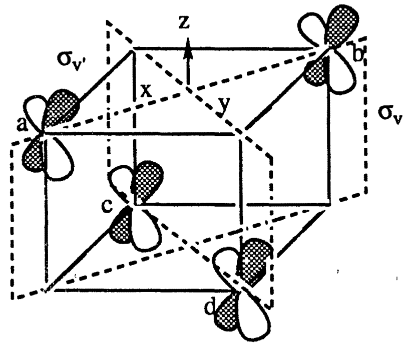
$B1(D3)=1/(2)^{1/2}(d_{xz}(a)+d_{xz}(b)-d_{xz}(c)-d_{xz}(d))$



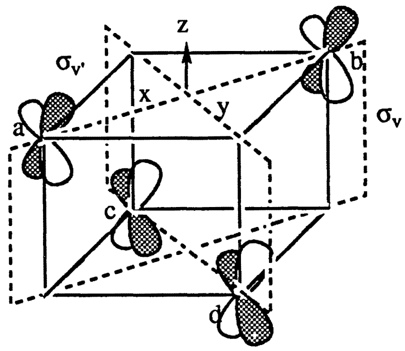
$A1(D1)=1/(2)^{1/2}(d_{xz}(a)-d_{xz}(b))$



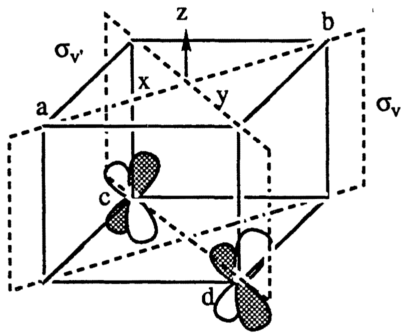
$A2(D3)=1/(2)^{1/2}(d_{xz}(c)-d_{xz}(d))$



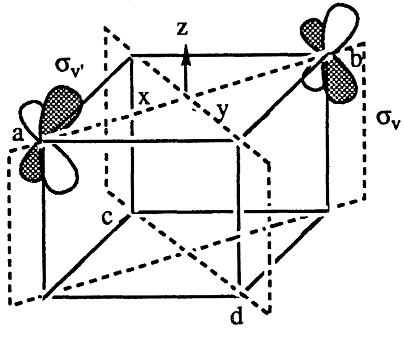
$B2(D2)=1/(2)^{1/2}(d_{yz}(a)+d_{yz}(b)+d_{yz}(c)+d_{yz}(d))$



$B2(D3)=1/(2)^{1/2}(d_{yz}(a)+d_{yz}(b)-d_{yz}(c)-d_{yz}(d))$

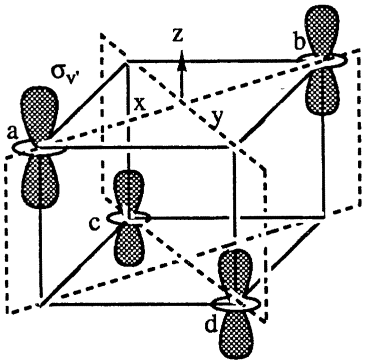


$A1(D2)=1/(2)^{1/2}(d_{yz}(c)-d_{yz}(d))$

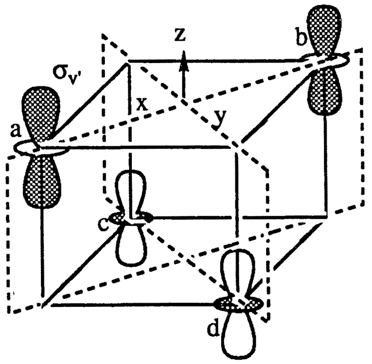


$A2(D4)=1/(2)^{1/2}(d_{yz}(a)-d_{yz}(b))$

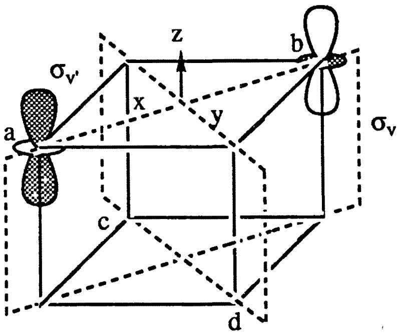
Figure 50. Linear Combinations of Copper d_{xz} and d_{yz} Orbitals



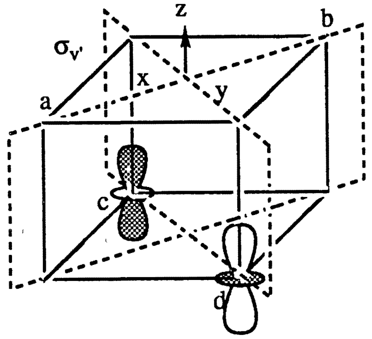
$A1(D3)=1/(2)^{1/2}(d_{z2}(a)+d_{z2}(b)+d_{z2}(c)+d_{z2}(d))$



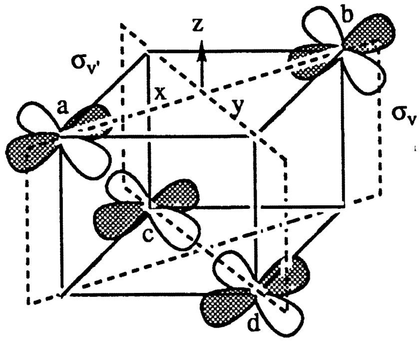
$A1(D4)=1/(2)^{1/2}(d_{z2}(a)+d_{z2}(b)-d_{z2}(c)-d_{z2}(d))$



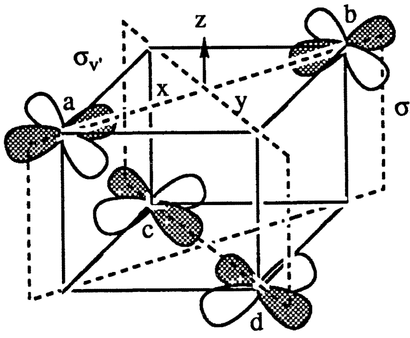
$B1(D4)=1/(2)^{1/2}(d_{z2}(a)-d_{z2}(b))$



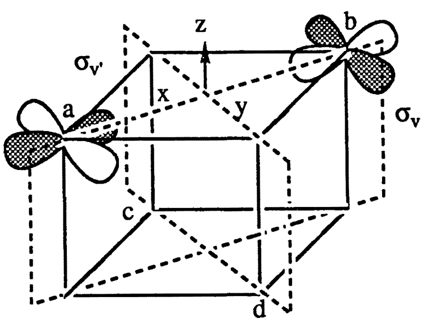
$B2(D4)=1/(2)^{1/2}(d_{z2}(c)-d_{z2}(d))$



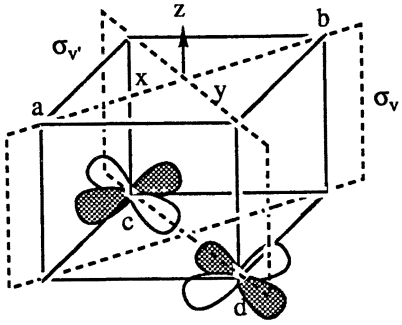
$A1(D5)=1/(2)^{1/2}(d_{x2-y2}(a)+d_{x2-y2}(b)$
$+d_{x2-y2}(c)+d_{x2-y2}(d))$



$A1(D6)=1/(2)^{1/2}(d_{x2-y2}(a)+d_{x2-y2}(b)$
$-d_{x2-y2}(c)-d_{x2-y2}(d))$

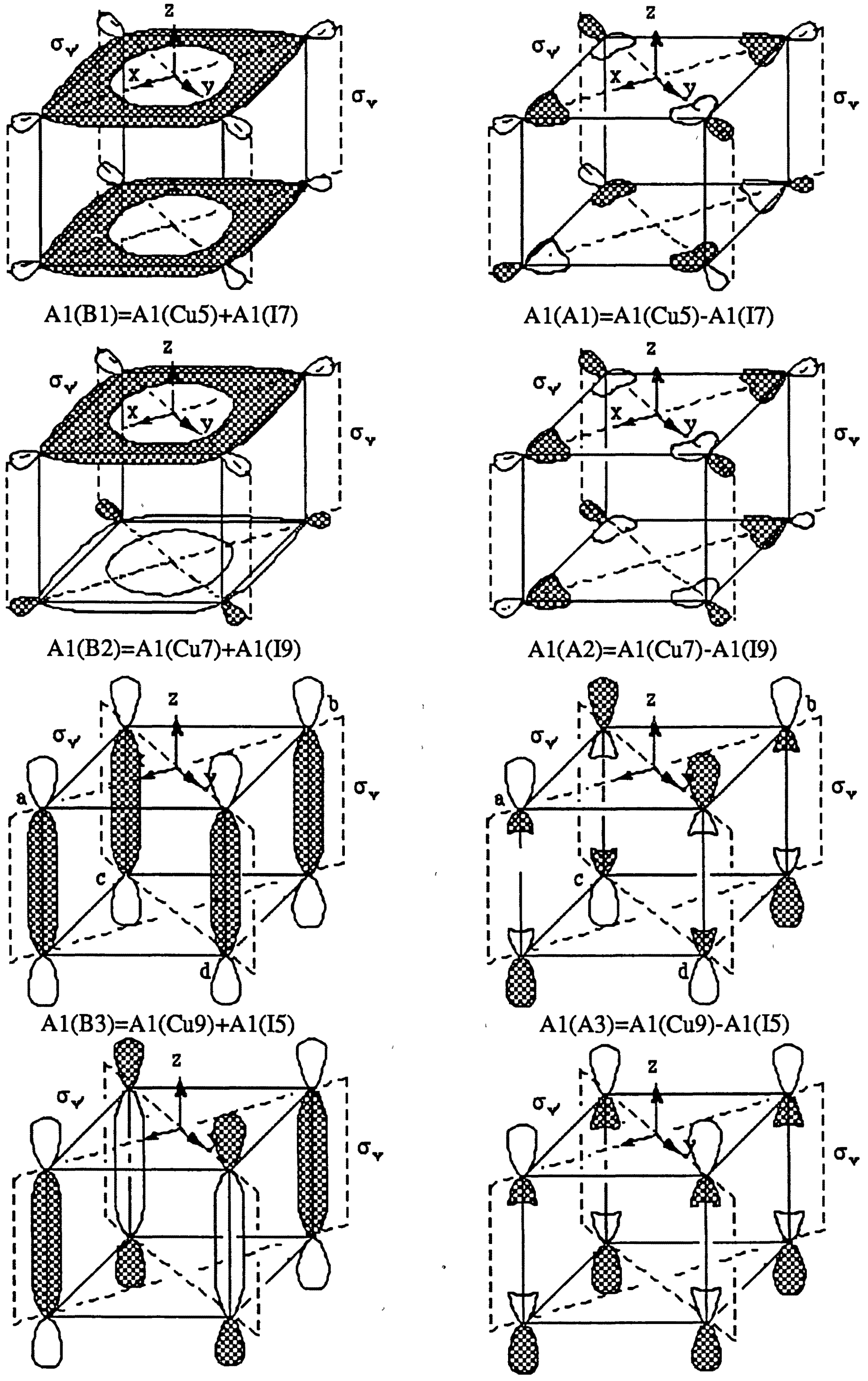


$B1(D5)=1/(2)^{1/2}(d_{x2-y2}(a)-d_{x2-y2}(b))$



$B2(D5)=1/(2)^{1/2}(d_{x2-y2}(c)-d_{x2-y2}(d))$

Figure 51. Linear Combinations of Copper d_{z2} and d_{x2-y2} Orbitals



A1(B1)=A1(Cu5)+A1(I7)

A1(A1)=A1(Cu5)-A1(I7)

A1(B2)=A1(Cu7)+A1(I9)

A1(A2)=A1(Cu7)-A1(I9)

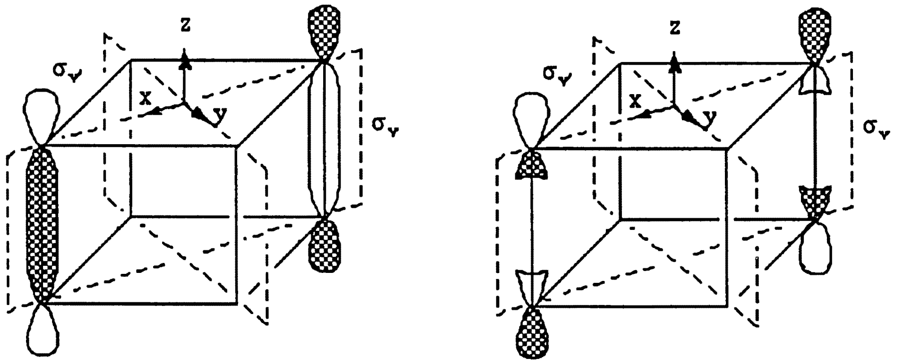
A1(B3)=A1(Cu9)+A1(I5)

A1(A3)=A1(Cu9)-A1(I5)

A1(B4)=A1(Cu10)+A1(I6)

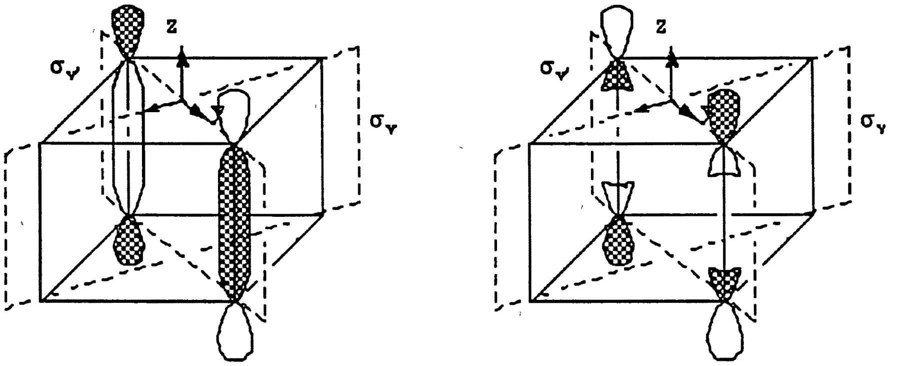
A1(A4)=A1(Cu10)-A1(I6)

Figure 52. Bonding and Antibonding Moleculer Orbitals



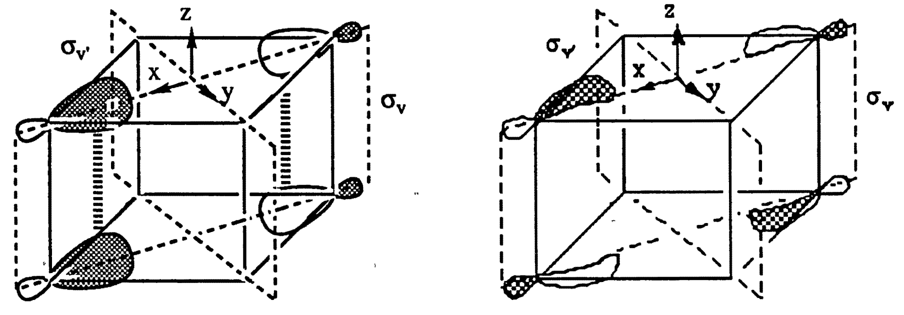
B1(B1)=B1(Cu6)+B1(I4)

B1(A1)=B1(Cu6)-B1(I4)



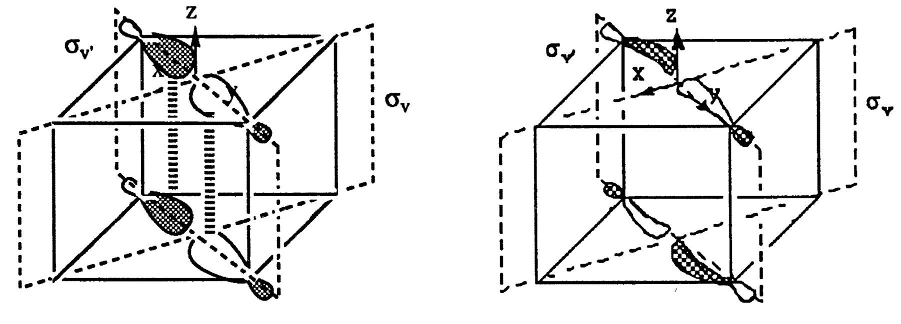
B2(B1)=B2(Cu6)+B2(I4)

B2(A1)=B2(Cu6)-B2(I4)



B1(B3)=B1(Cu4)+B1(I5)

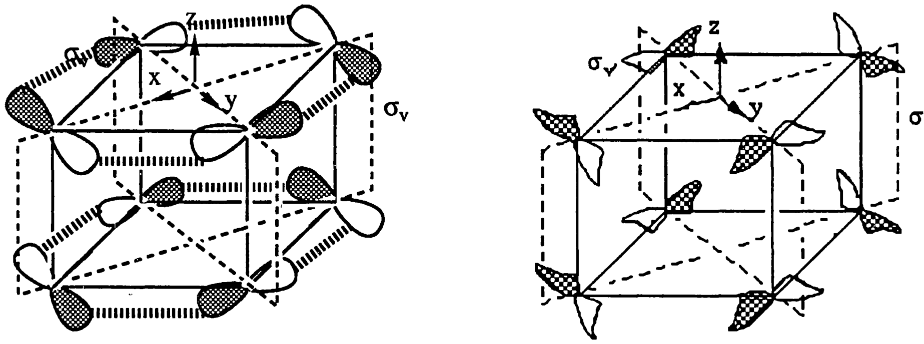
B1(A3)=B1(Cu4)-B1(I5)



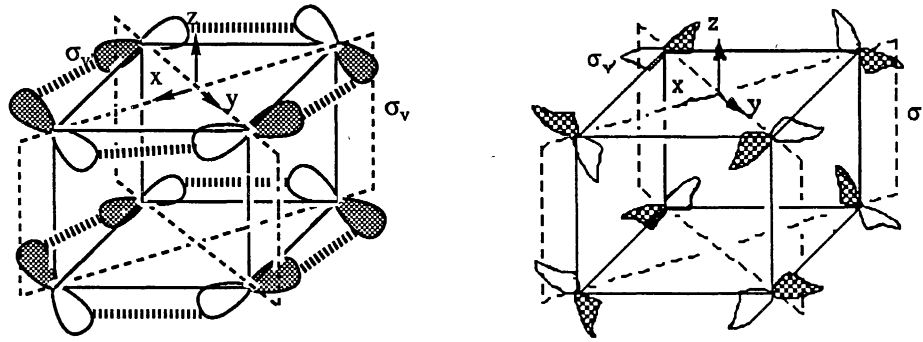
B2(B3)=B2(Cu4)+B2(I5)

B2(A3)=B2(Cu4)-B2(I5)

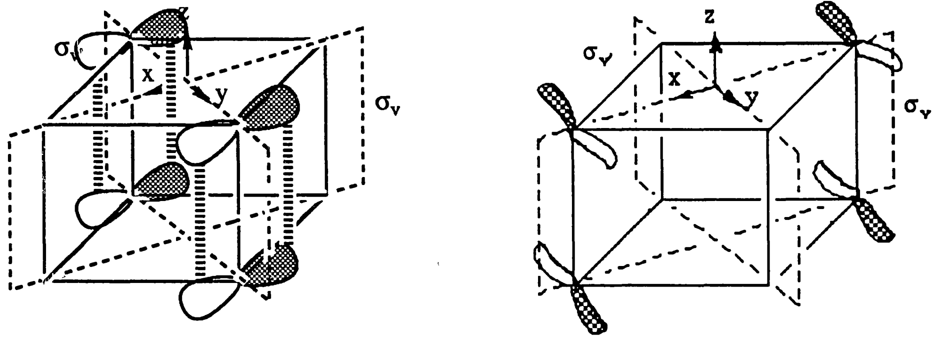
Figure 53. Bonding and Antibonding Molecular Orbitals



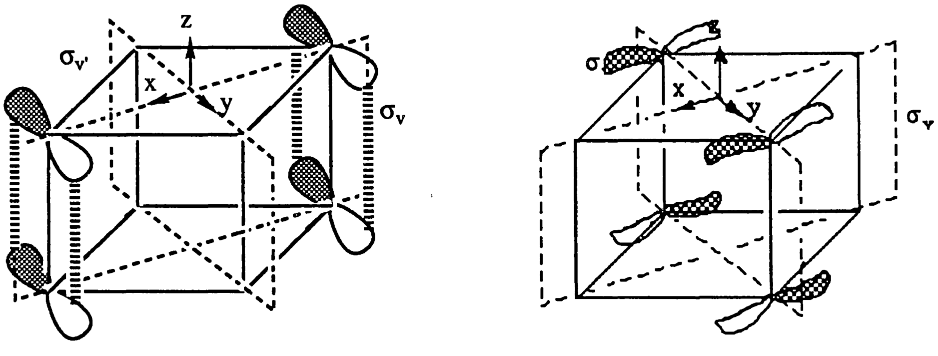
A2(B1)=A2(Cu1)+A2(I1)   A2(A1)=A2(Cu1)-A2(I1)



A2(B2)=A2(Cu2)+A2(I2)   A2(A2)=A2(Cu2)-A2(I2)

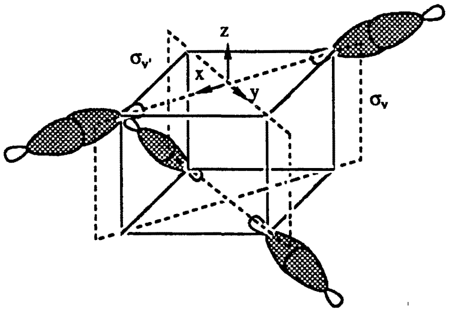


B1(B2)=B1(Cu2)+B1(I1)   B2(A2)=B2(Cu1)-B2(I1)

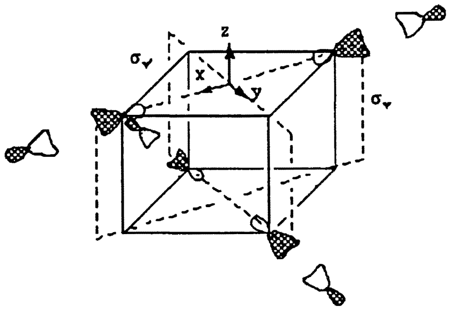


B2(B2)=B2(Cu1)+B2(I1)   B1(A2)=B1(Cu2)-B1(I1)

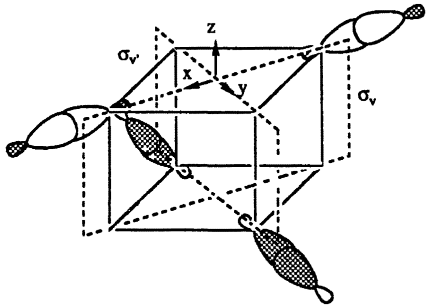
Figure 54. Bonding and Antibonding Molecular Orbitals



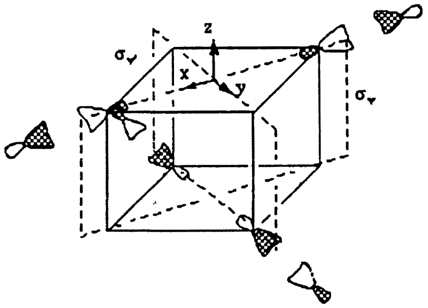
A1(B5)=A1(Cu6)+A1(N1)



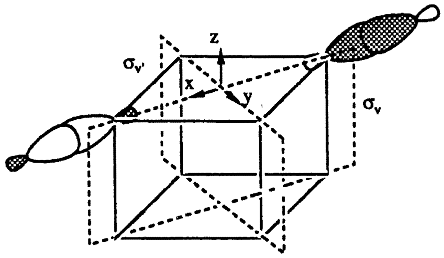
A1(A5)=A1(Cu6)-A1(N1)



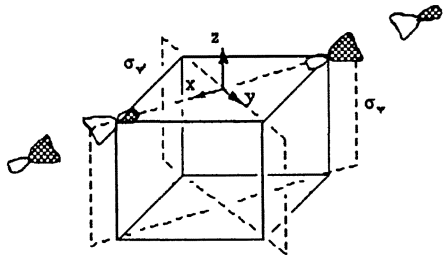
A1(B6)=A1(Cu8)+A1(N2)



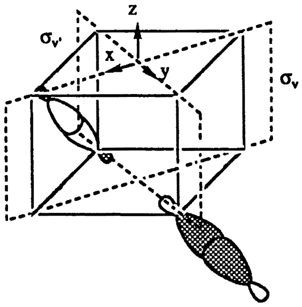
A1(A6)=A1(C8)-A1(N2)



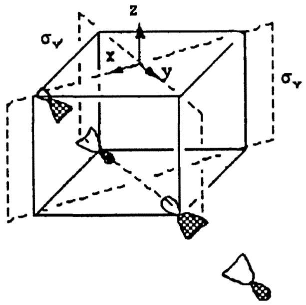
B1(B3)=B1(Cu5)+B1(N1)



B1(A3)=B1(Cu5)-B1(N1)



B2(B3)=B2(Cu5)+B2(N1)



B2(A3)=B2(Cu5)-B2(N1)

Figure 55. Bonding and Antibonding Molecular Orbitals

be treated in a similar way as described before. However, because orbitals p_x and p_y as well as d_{xz} and d_{yz} transform to each other under the symmetry of S_4 and S_4^3, these orbitals need to be considered together. For example, the transformations of the p_x orbital of copper atom (a) to p_x or p_y orbitals of the other three copper atoms are shown in Table 6.

Table 6. Transformation of p_x Orbital of Atom (a) under S_4 Group

	E	S_4	C_2	S_4^3
A	Px(a)	-Py(c)	-Px(b)	Py(d)
B	Px(a)	Py(c)	-Px(b)	-Py(d)
E	Px(a)	-iPy(c)	Px(b)	-iPy(d)
	Px(a)	iPy(c)	Px(b)	iPy(d)

From Table 6, one can obtain four linear combinations of copper $4p_x$ and $4p_y$ orbitals after normalization:

A(Cu1)=1/2(Px(a)-Px(b)-Py(c)+Py(d))

B(Cu1)=1/2(Px(a)-Px(b)+Py(c)-Py(d))

E(Cu1)=1/2(Px(a)+Px(b)-iPy(c)-iPy(d))

E(Cu2)=1/2(Px(a)+Px(b)+iPy(c)+iPy(d))

Similarly, if one starts with the p_y orbital of copper atom (a), one can get another four linear combinations of $4p_x$ and $4p_y$ orbitals:

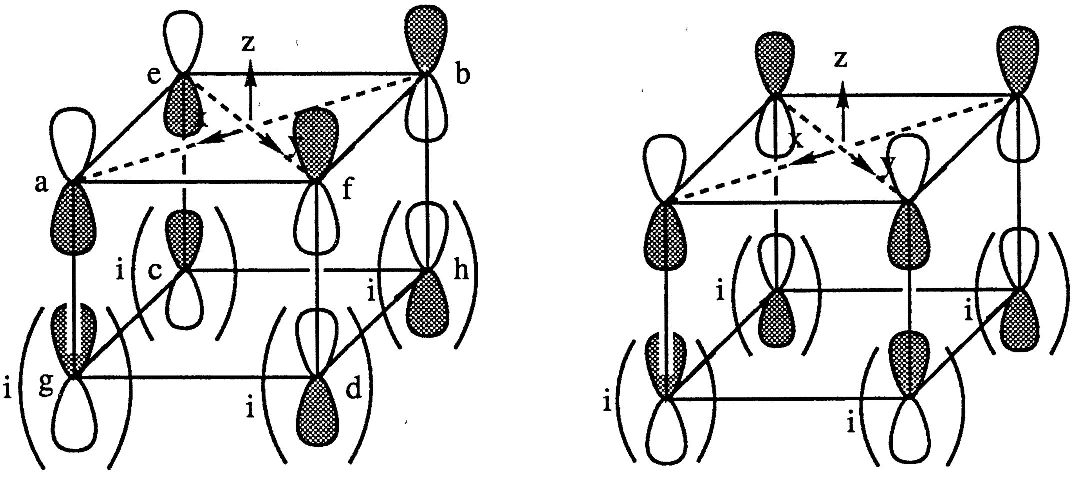
A(Cu2)=1/2(Py(a)-Py(b)+Px(c)-Px(d))

B(Cu2)=1/2(Py(a)-Py(b)-Px(c)+Px(d))

E(Cu3)=1/2(Py(a)+Py(b)+iPx(c)+iPx(d))

E(Cu4)=1/2(Py(a)+Py(b)-iPx(c)-iPx(d))

Linear combinations of the 4s, 4p and 3d orbitals of copper and the 4s, 4p and 3d orbitals of iodide atoms and sp^3 orbitals of nitrogen as well as the bonding and antibonding molecular orbitals are given in Figures 56 - 68. Another problem of the S_4 group is the two complex form characters (Table 5) which makes discussion of the relative order of the orbital energies difficult. Since the nodal plane criterion can not be applied to the characters of complex form, an alternative based on the properties of the orbitals in a cubic structure is needed to permit discussion of the relative energy level of the orbitals. Using a pair of E bonding orbitals as an example:



$\psi(E_a)$ $\psi(E_b)$

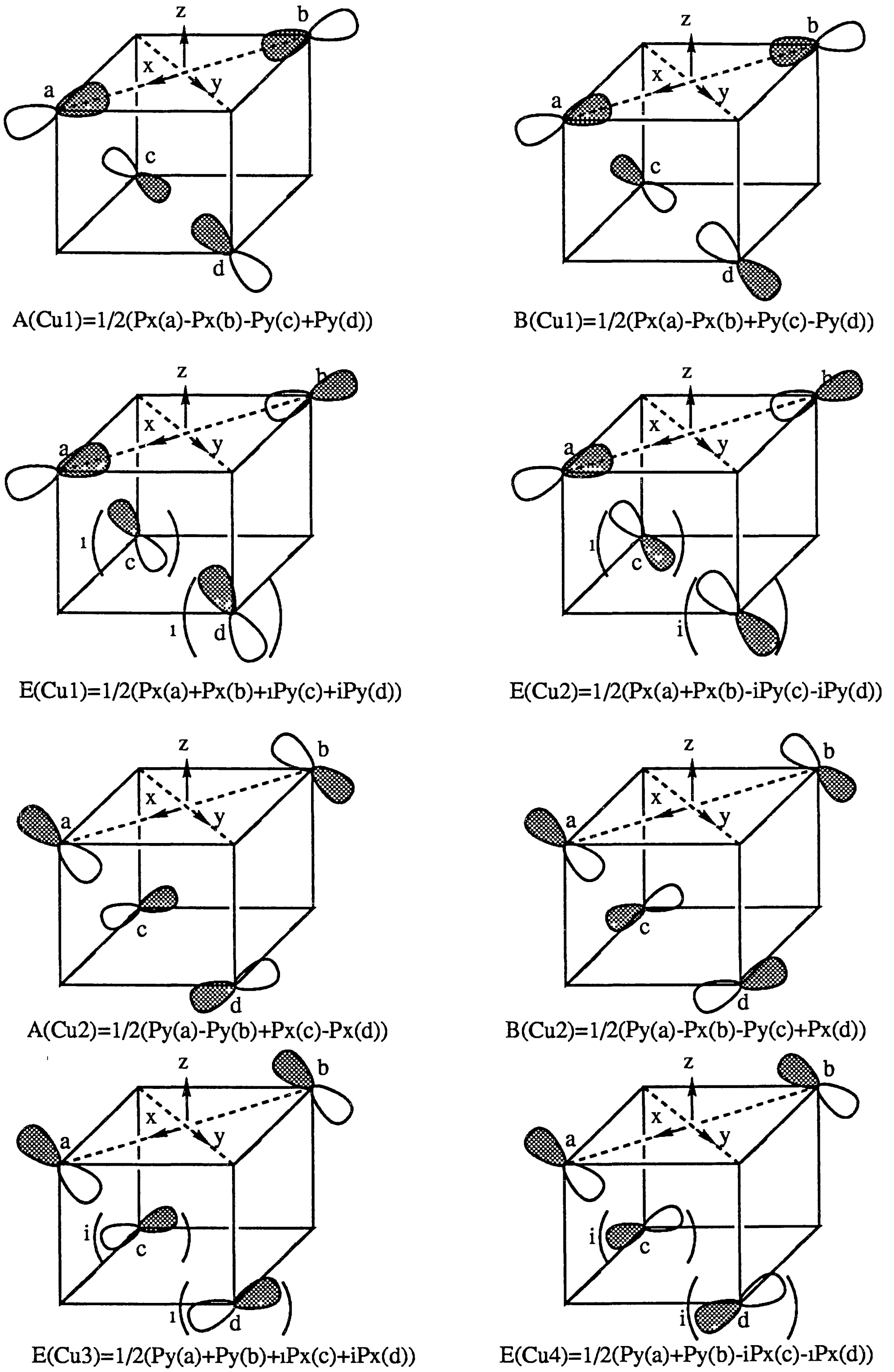
Figure 69. Two Bonding Molecular Orbitals Formed by Combination of Pz Orbitals

Figure 69. shows a pair of degenerate bonding molecular orbitals formed by the linear combination of p_z orbitals between copper and iodide atoms:

$$\psi(E_a)=\frac{1}{2\sqrt{2}}(Pz(a)-Pz(b)+Pz(e)-Pz(f)-iPz(c)+iPz(d)-iPz(g)+iPz(h))$$

$$\psi(E_b)=\frac{1}{2\sqrt{2}}1/2(Pz(a)-Pz(b)+Pz(e)-Pz(f)+iPz(c)-iPz(d)+iPz(g)-iPz(h))$$

From the above functions, we can see that $\psi(E_b)$ is the complex conjugate of $\psi(E_a)$. The energy of the two degenerated molecular orbitals can be obtained from the energy integrals:



A(Cu1)=1/2(Px(a)-Px(b)-Py(c)+Py(d))

B(Cu1)=1/2(Px(a)-Px(b)+Py(c)-Py(d))

E(Cu1)=1/2(Px(a)+Px(b)+iPy(c)+iPy(d))

E(Cu2)=1/2(Px(a)+Px(b)-iPy(c)-iPy(d))

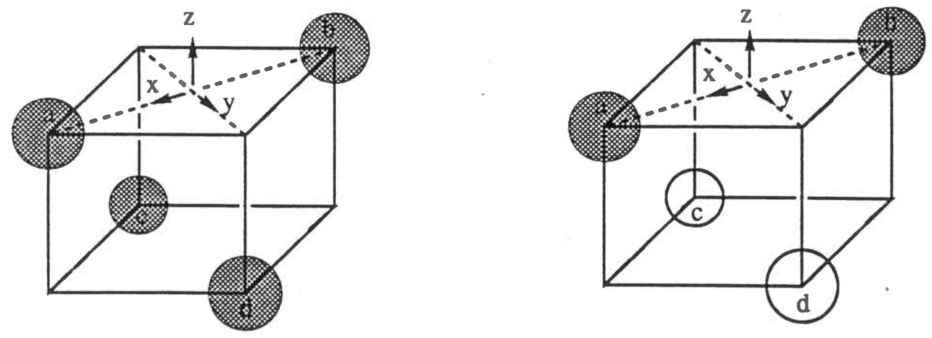
A(Cu2)=1/2(Py(a)-Py(b)+Px(c)-Px(d))

B(Cu2)=1/2(Py(a)-Px(b)-Py(c)+Px(d))

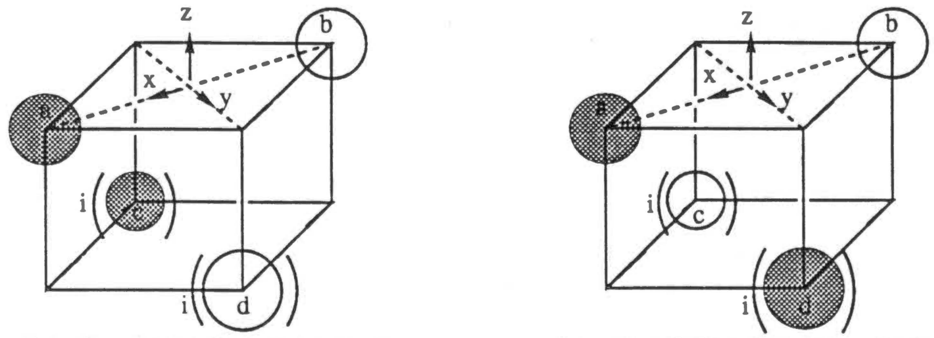
E(Cu3)=1/2(Py(a)+Py(b)+iPx(c)+iPx(d))

E(Cu4)=1/2(Py(a)+Py(b)-iPx(c)-iPx(d))

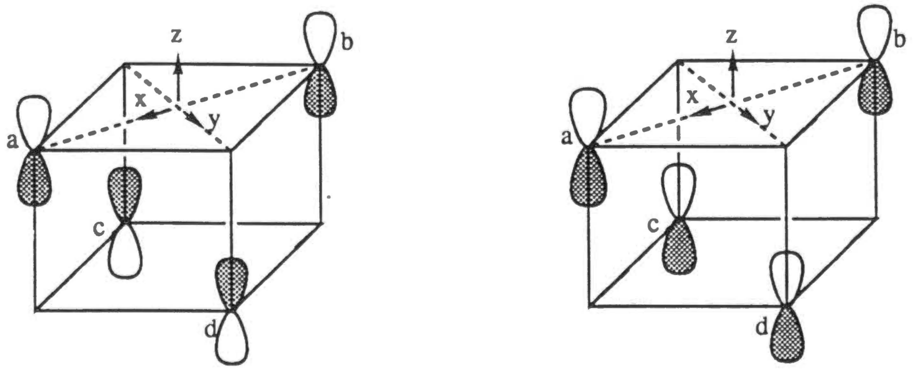
Figure 56. Linear Combinations of Copper $4p_x$ and $4p_y$ Orbitals



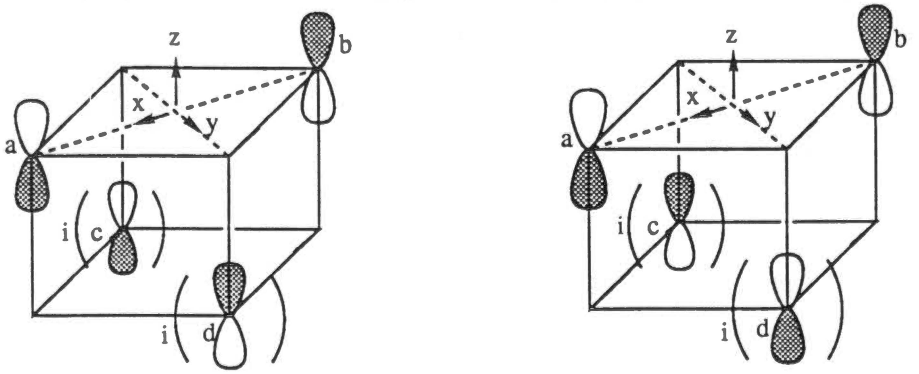
A(Cu3)=1/2(S(a)+S(b)+S(c)+S(d)) B(Cu3)=1/2(S(a)+S(b)-S(c)-S(d))



E(Cu5)=1/2(S(a)-S(b)+iS(c)-iS(d)) E(Cu6)=1/2(S(a)-S(b)-iS(c)+iS(d))

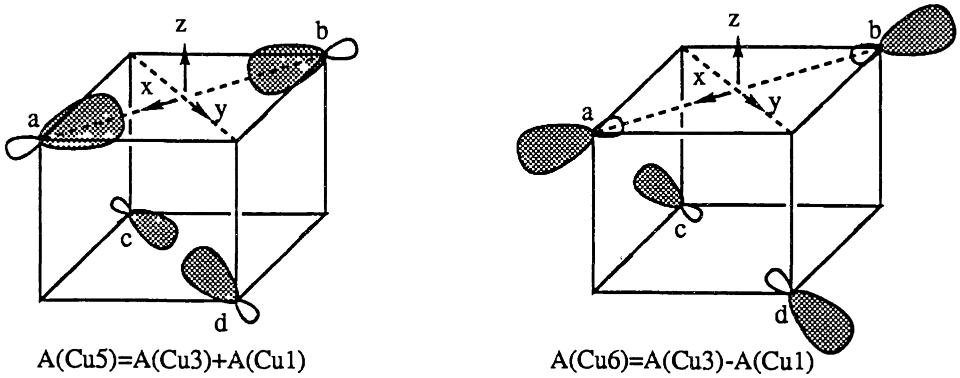


B(Cu4)=1/2(Pz(a)+Pz(b)-Pz(c)-Pz(d)) A(Cu4)=1/2(Pz(a)+Pz(b)+Pz(c)+Pz(d))

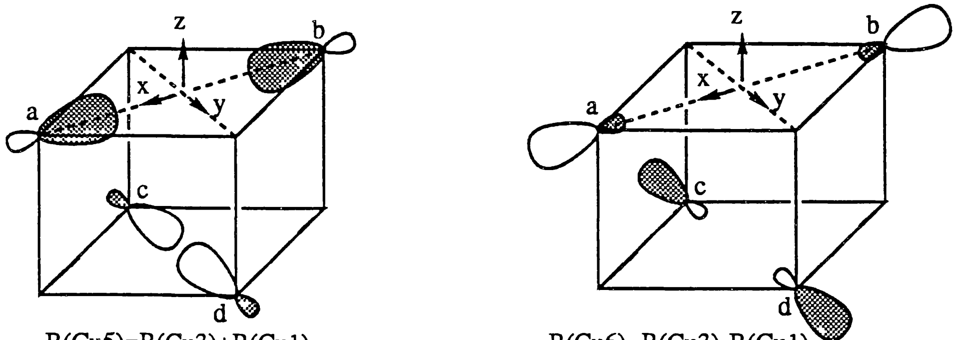


E(Cu7)=1/2(Pz(a)-Pz(b)+iPz(c)-iPz(d)) E(Cu8)=1/2(Pz(a)-Pz(b)-iPz(c)+iPz(d))

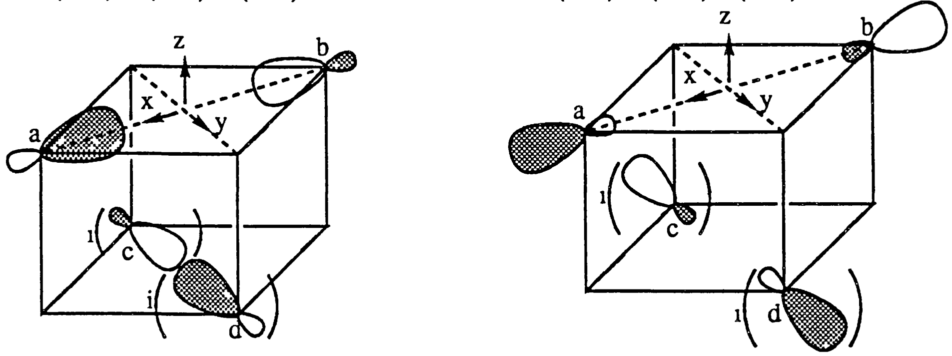
Figure 57. Linear Combinations of Copper 4s and $4p_z$ Orbitals



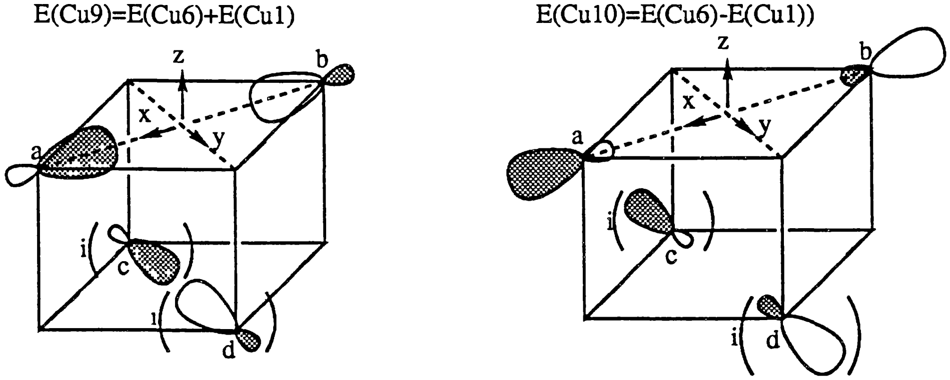
A(Cu5)=A(Cu3)+A(Cu1) A(Cu6)=A(Cu3)-A(Cu1)



B(Cu5)=B(Cu3)+B(Cu1) B(Cu6)=B(Cu3)-B(Cu1)

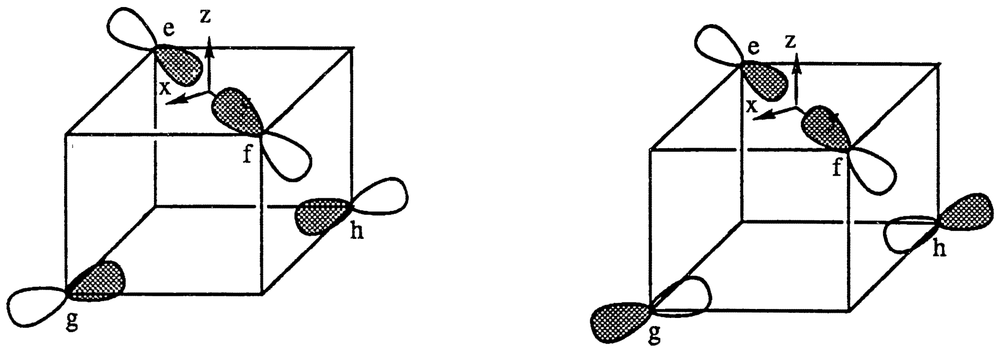


E(Cu9)=E(Cu6)+E(Cu1) E(Cu10)=E(Cu6)-E(Cu1))



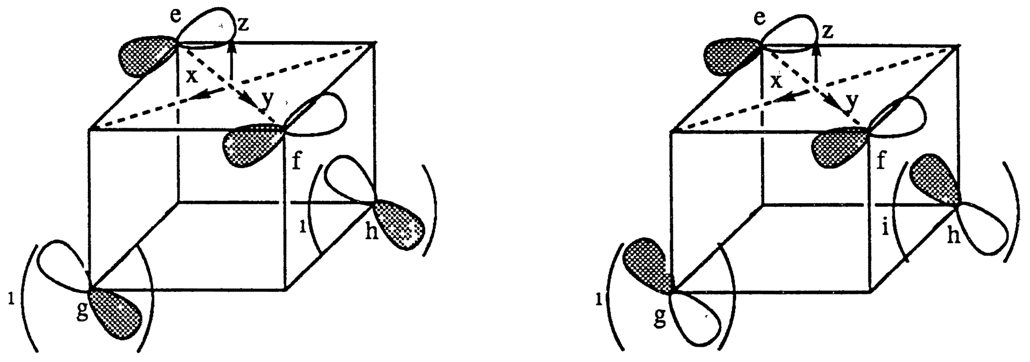
E(Cu11)=E(Cu5)+E(Cu2) E(Cu12)=E(Cu5)-E(Cu2)

Figure 58. 4s and 4p Mixing of Copper Orbitals



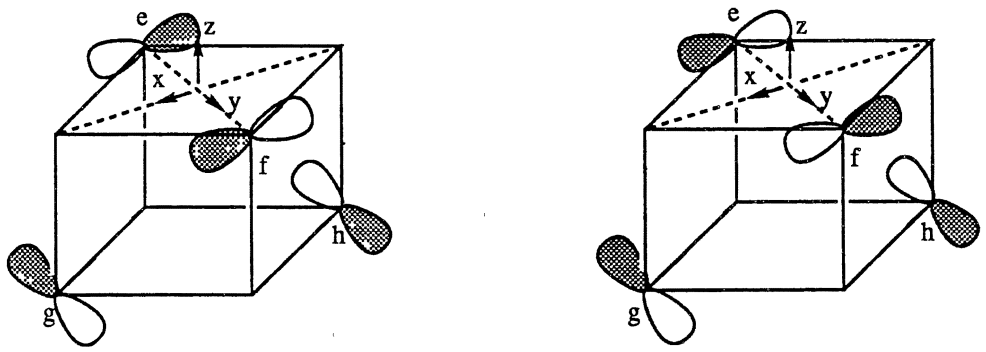
A(I1)=1/2(Px(e)-Px(f)+Py(g)-Py(h))

B(I1)=1/2(Px(e)-Px(f)-Py(g)+Py(h))



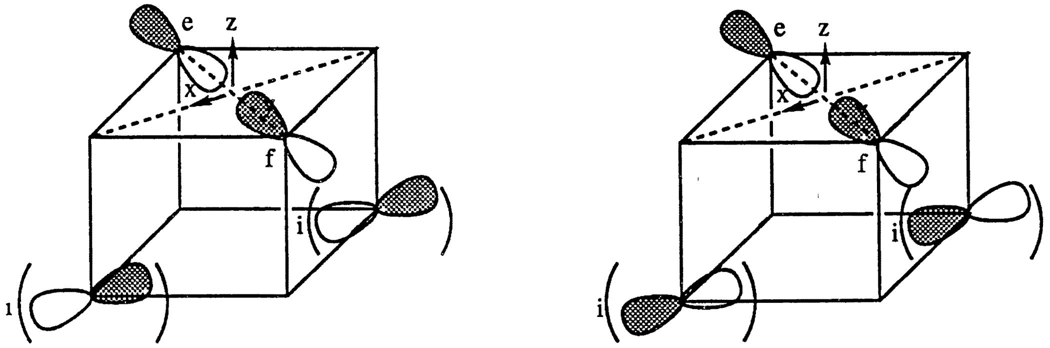
E(I1)=1/2(Px(e)+Px(f)-iPy(g)-iPy(h))

E(I2)=1/2(Px(e)+Px(f)+iPy(g)+iPy(h))



A(I2)=1/2(Py(e)-Py(f)-Px(g)+Px(h))

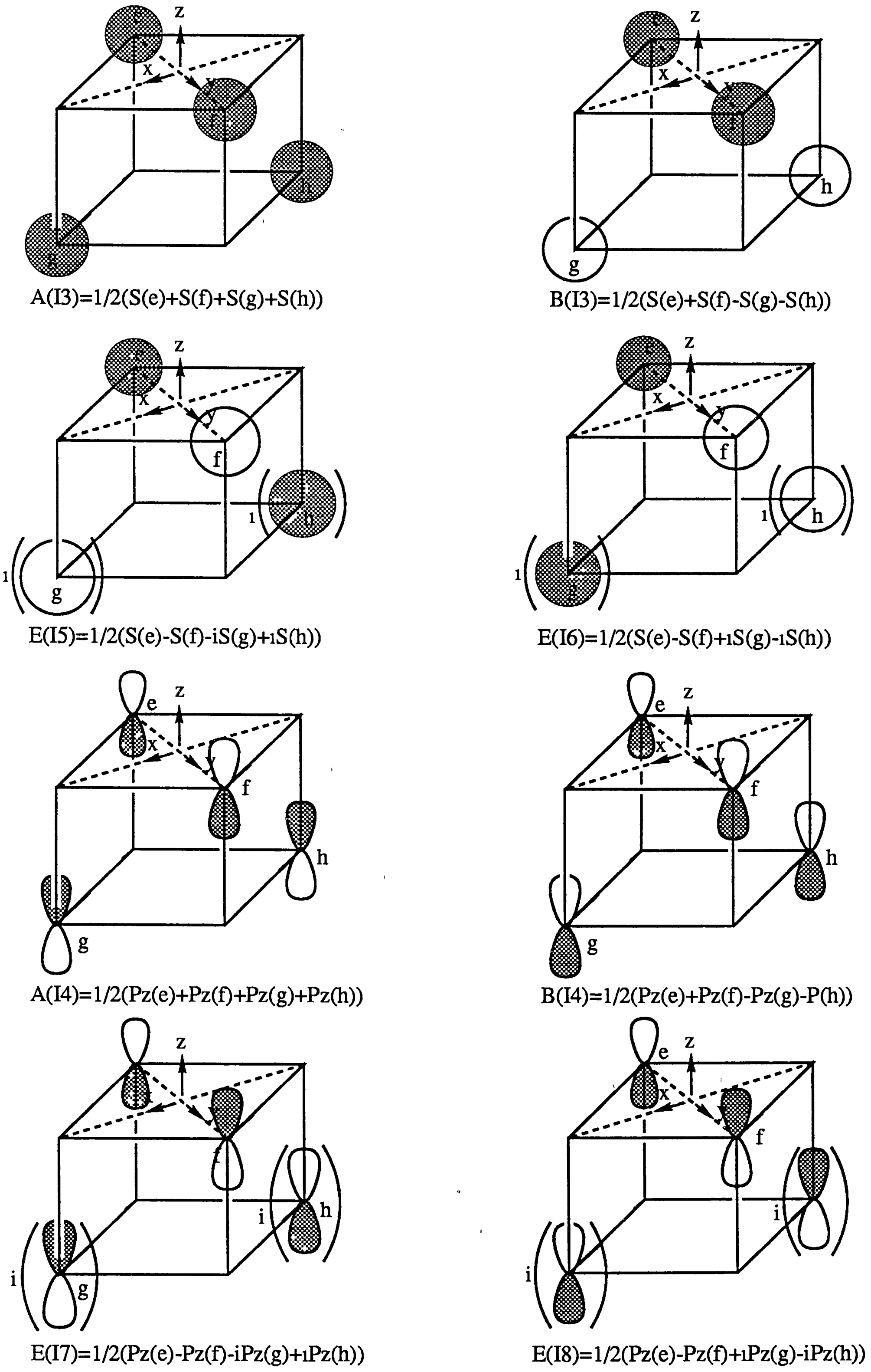
B(I2)=1/2(Py(e)-Py(f)+Px(g)-Px(h))



E(I3)=1/2(Py(e)+Py(f)+iPx(g)+iPx(h))

E(I4)=1/2(Py(e)+Py(f)-iPx(g)-iP(h))

Figure 59. Linear Combinations of Iodide $4p_x$ and $4p_y$ Orbitals



A(I3)=1/2(S(e)+S(f)+S(g)+S(h))

B(I3)=1/2(S(e)+S(f)-S(g)-S(h))

E(I5)=1/2(S(e)-S(f)-iS(g)+iS(h))

E(I6)=1/2(S(e)-S(f)+iS(g)-iS(h))

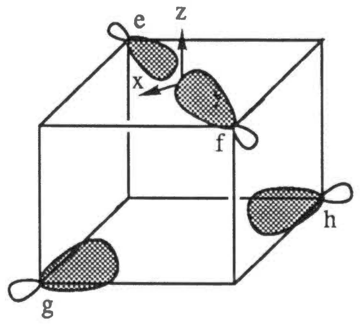
A(I4)=1/2(Pz(e)+Pz(f)+Pz(g)+Pz(h))

B(I4)=1/2(Pz(e)+Pz(f)-Pz(g)-P(h))

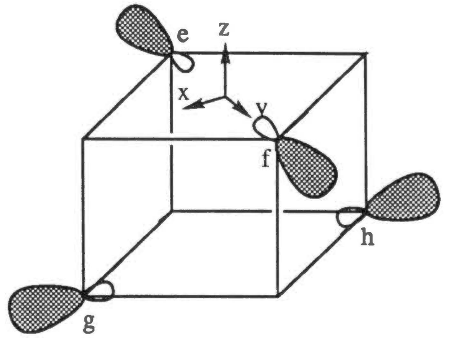
E(I7)=1/2(Pz(e)-Pz(f)-iPz(g)+iPz(h))

E(I8)=1/2(Pz(e)-Pz(f)+iPz(g)-iPz(h))

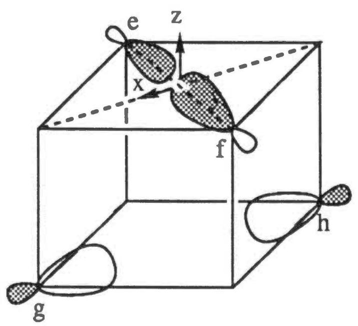
Figure 60. Linear Combinations of Iodide 4s and $4p_z$ Orbitals



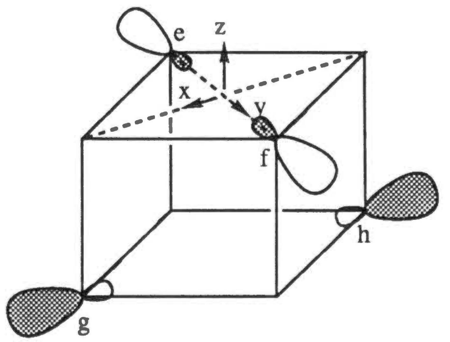
A(I5)=A(I3)+A(I1)



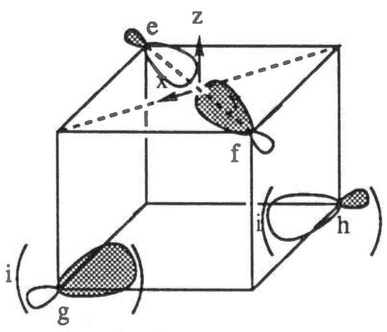
A(I6)=A(I3)-A(I1)



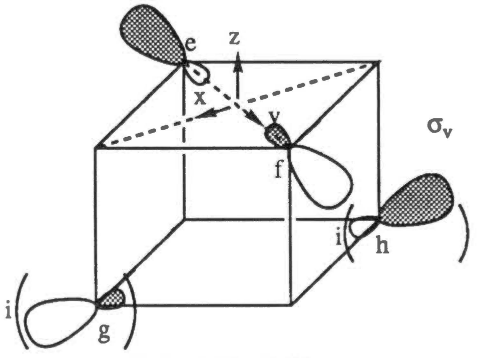
B(I5)=B(I1)+B(I3)



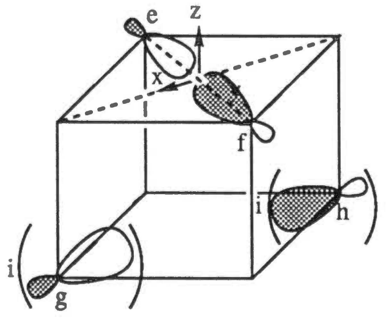
B(I6)=B(I1)-B(I3)



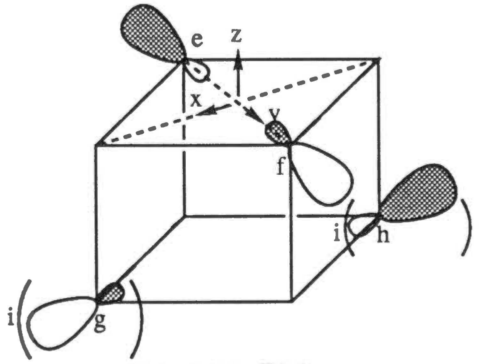
E(I9)=E(I3)-E(I5)



E(I10)=E(I3)+E(I5)

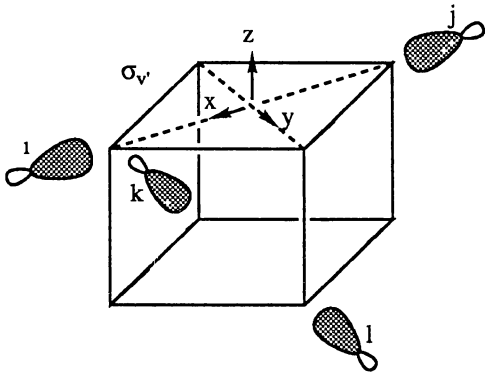


E(I11)=E(I4)-E(I6)

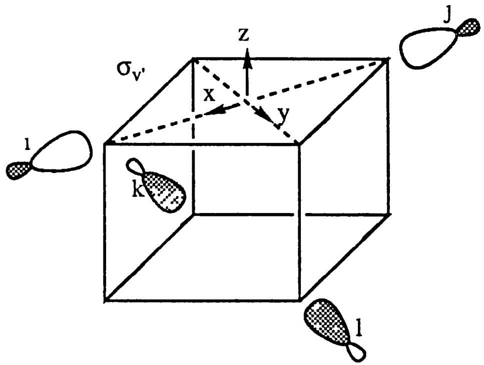


E(I12)=E(I4)+E(I6)

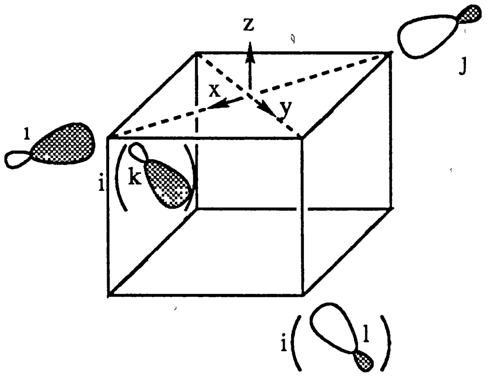
Figure 61. 4s and 4p Mixing of Iodide Orbitals



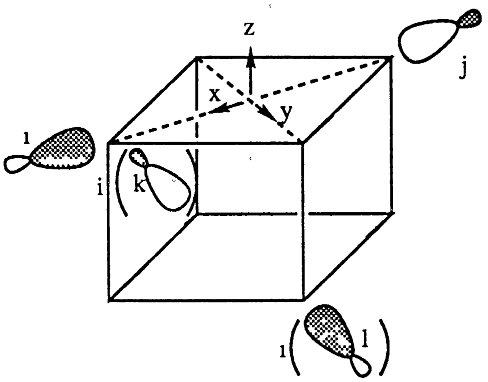
$A1(N1)=1/2(N(i)+N(j)+N(k)+N(l))$



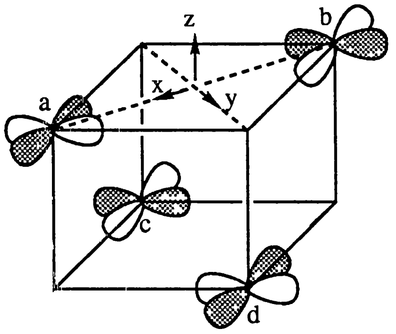
$B1(N1)=1/2(N(k)+N(l)-N(i)+N(j))$



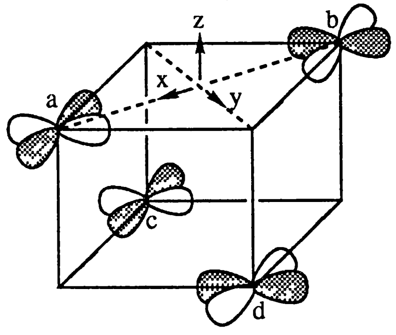
$E(N1)=1/2(N(i)-N(j)+iN(k)-iN(l))$



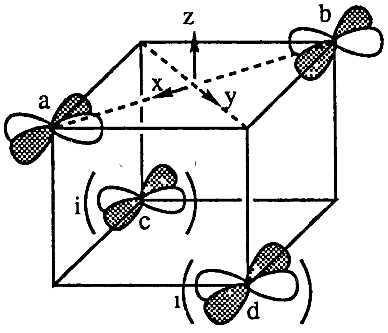
$E(N2)=1/2(N(i)-N(j)-iN(k)+iN(l))$



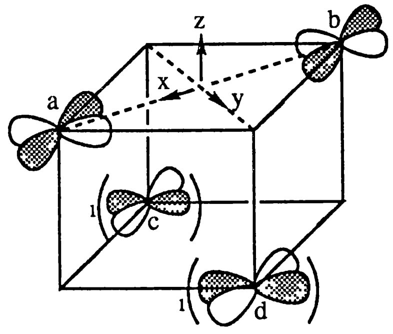
$A(D1)=1/2(d_{xy}(a)-d_{xy}(b)-d_{xy}(c)+d_{xy}(d))$



$B(D1)=1/2(d_{xy}(a)-d_{xy}(b)+d_{xy}(c)-d_{xy}(d))$

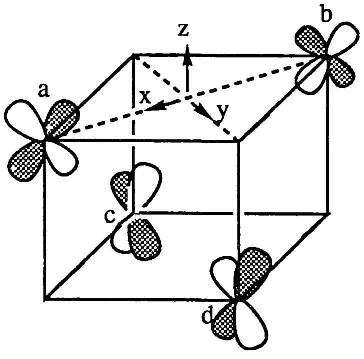


$E(D1)=1/2(d_{xy}(a)+d_{xy}(b)-id_{xy}(c)-id_{xy}(d))$

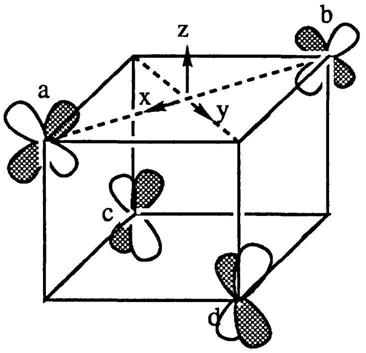


$E(D2)=1/2(d_{xy}(a)+d_{xy}(b)+id_{xy}(c)+id_{xy}(d))$

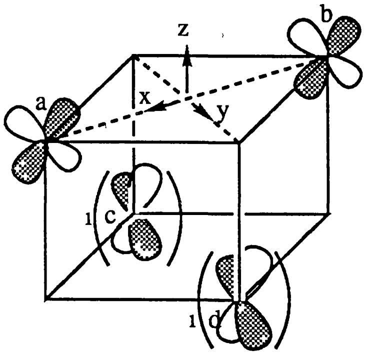
Figure 62. Linear Combinations of Nitrogen sp^3 Orbitals and Copper d_{xy} Orbitals



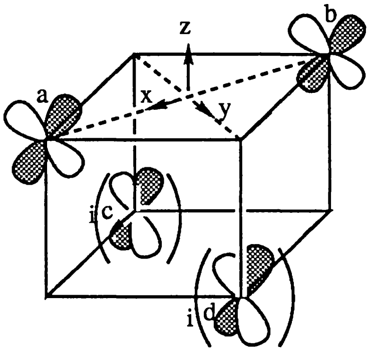
$A(D2)=1/2(d_{xz}(a)-d_{xz}(b)-d_{yz}(c)+P_{yz}(d))$



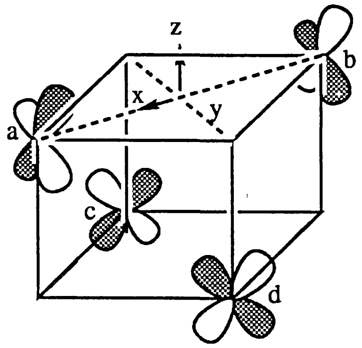
$B(D2)=(P_{xz}(a)-P_{xz}(b)+P_{yz}(c)-P_{yz}(d))$



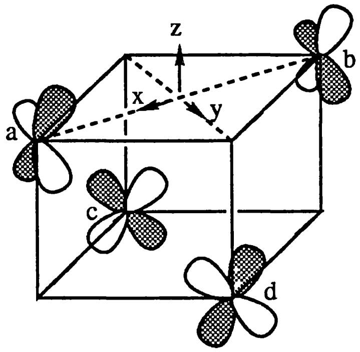
$E(D3)=1/2(P_{xz}(a)+P_{xz}(b)-iP_{yz}(c)-iP_{yz}(d))$



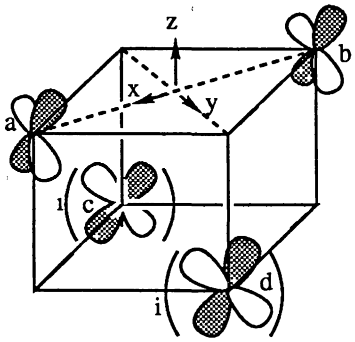
$E(D4)=(P_{xz}(a)+P_{xz}(b)+iP_{yz}(c)+iP_{yz}(d))$



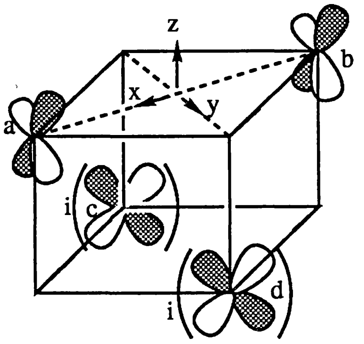
$A(D3)=1/2(P_{yz}(a)+P_{yz}(b)-P_{xz}(c)-P_{xz}(d))$



$B(D3)=(P_{yz}(a)-P_{yz}(b)-P_{xz}(c)+P_{xz}(d))$

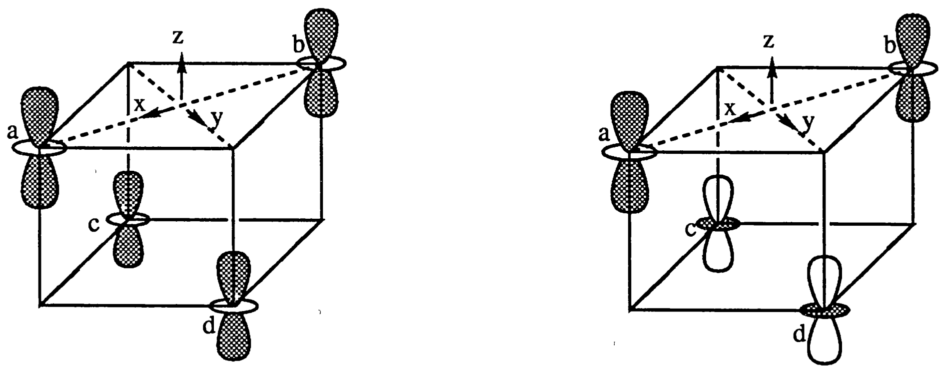


$E(D5)=1/2(P_{yz}(a)+P_{yz}(b)+iP_{xz}(c)+iP_{xz}(d))$

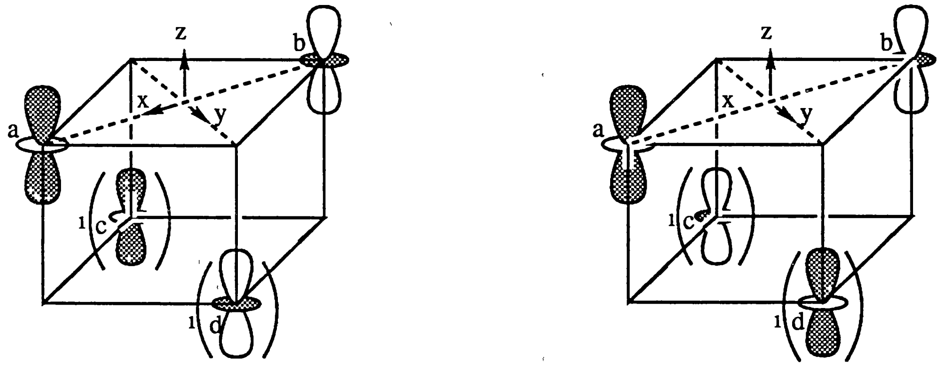


$E(D6)=(P_{yz}(a)+P_{yz}(b)-iP_{xz}(c)-iP_{xz}(d))$

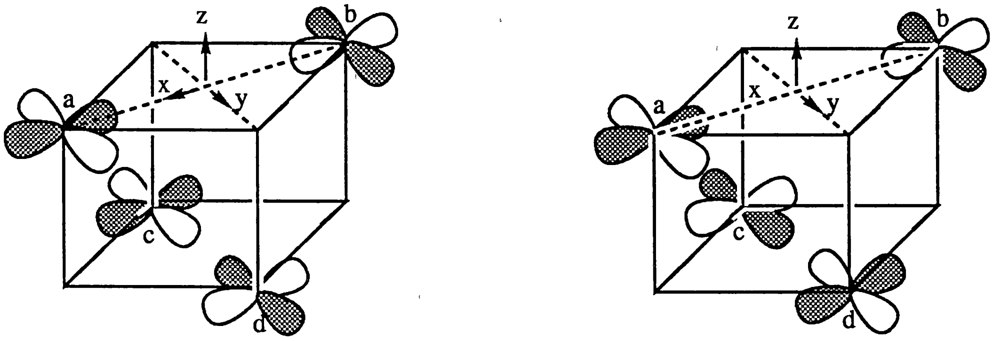
Figure 63. Linear Combinations of Copper d_{xz} and d_{yz} Orbitals



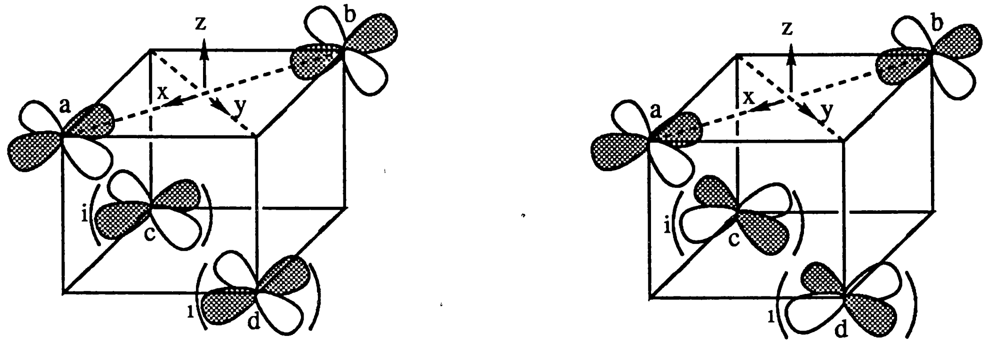
$A(D4)=1/2(d_{z2}(a)+d_{z2}(b)+d_{z2}(c)+d_{z2}(d))$ $B(D4)=1/2(d_{z2}(a)+d_{z2}(b)-d_{z2}(c)-d_{z2}(d))$



$E(D7)=1/2(d_{z2}(a)-d_{z2}(b)+id_{z2}(c)-id_{z2}(d))$ $E(D8)=1/2(d_{z2}(a)-d_{z2}(b)-id_{z2}(c)+id_{z2}(d))$

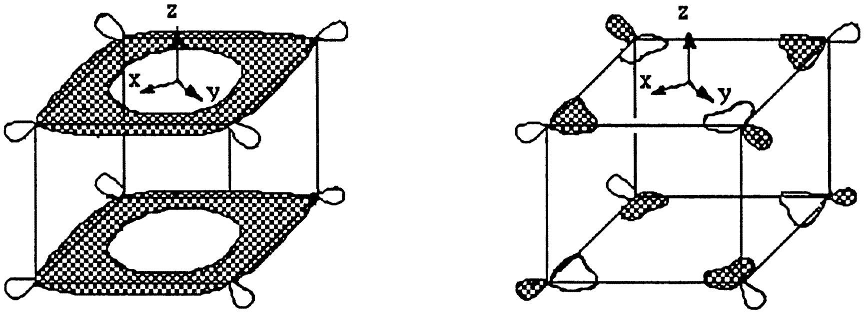


$A(D5)=1/2(d_{x2-y2}(a)-d_{x2-y2}(b)-d_{x2-y2}(c)+d_{X2-y2}(d))$ $B(D5)=1/2(d_{x2-y2}(a)-d_{x2-y2}(b)+d_{x2-y2}(c)-d_{x2-y2}(d))$



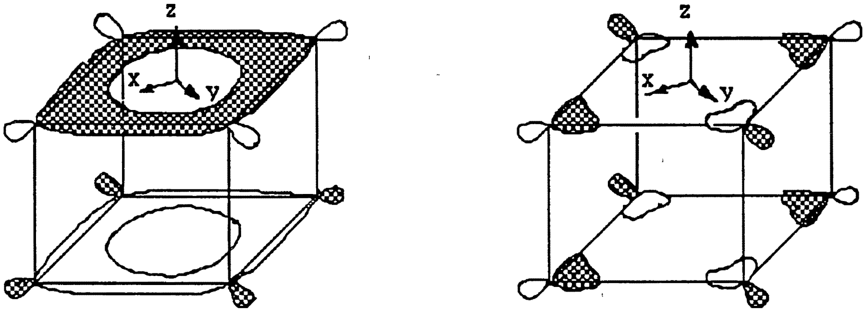
$E(D9)=1/2(d_{x2-y2}(a)+d_{x2-y2}(b)+id_{x2-y2}(c)+id_{X2-y2}(d))$ $E(D10)=1/2(d_{x2-y2}(a)+d_{x2-y2}(b)-id_{x2-y2}(c)-id_{x2-y2}(d))$

Figure 64. Linear Combinations of Copper d_{z2} and d_{x2-y2} Orbitals



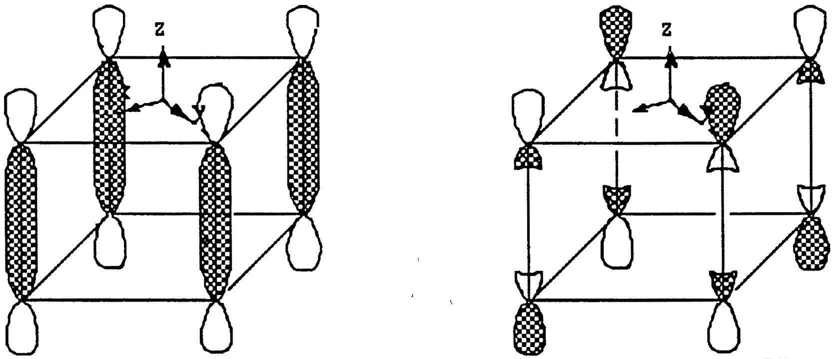
A(B1)=A(Cu5)+A(I5)

A(A1)=A(Cu5)-A(I5)



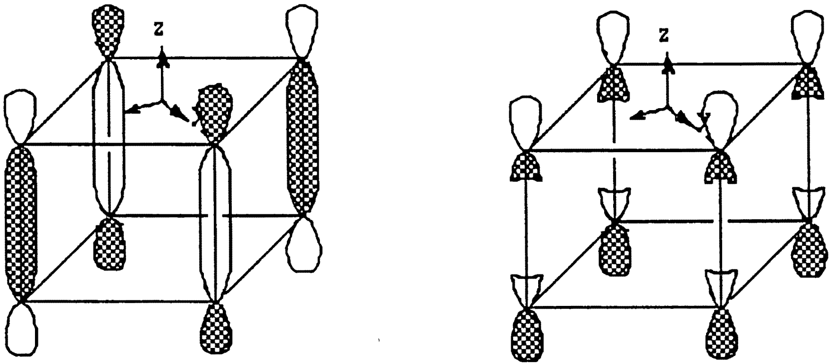
B(B1)=B(Cu5)+B(I5)

B(A1)=B(cu5)-B(I5)



A(B2)=A(Cu4)+A(I4)

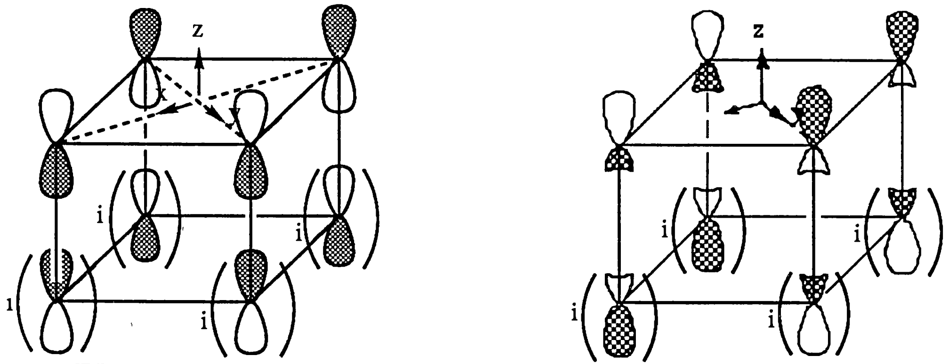
A(A2)=A(Cu4)-A(I4)



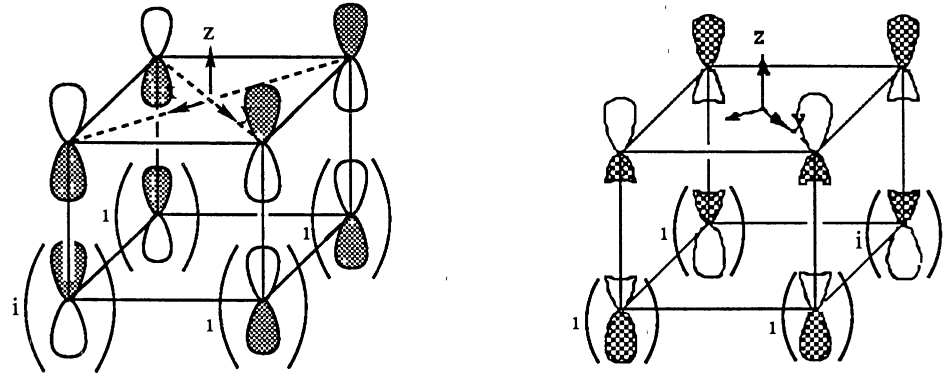
B(B2)=B(Cu4)+B(I4)

B(A2)=B(Cu4)-B(I4)

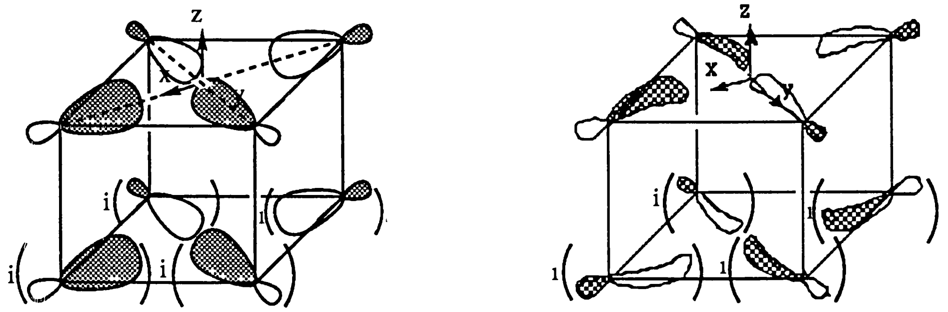
Figure 65. Bonding and Antibonding Molecular Orbitals



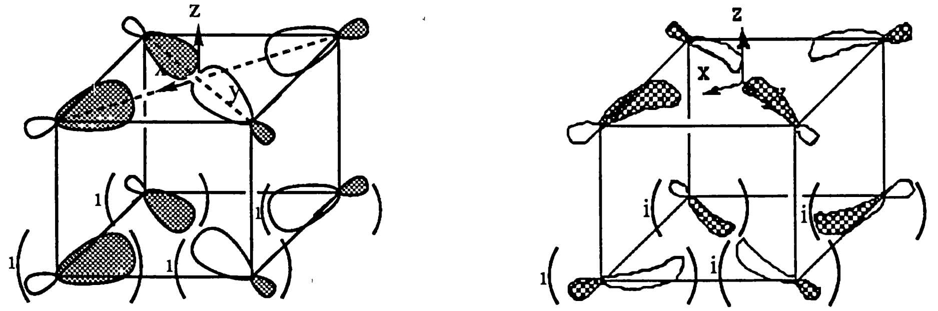
E(B1)=E(Cu7)-E(I8) E(A1)=E(Cu7)+E(I8)



E(B2)=E(Cu8)+E(I7) E(A2)=E(Cu8)-E(I7)

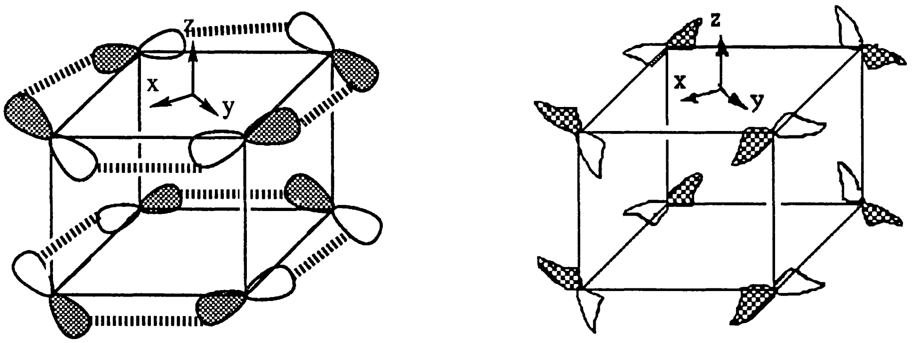


E(B3)=E(Cu9)+E(I9) E(A3)=E(Cu9)-E(I9)

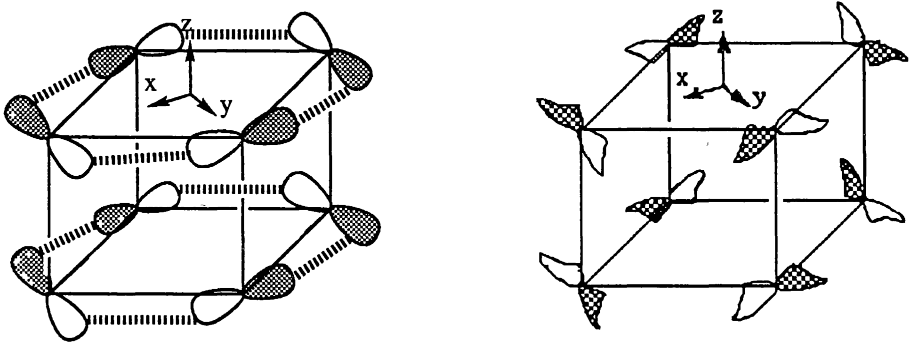


E(B4)=E(Cu11)-E(I11) E(A4)=E(Cu11)+(EI11)

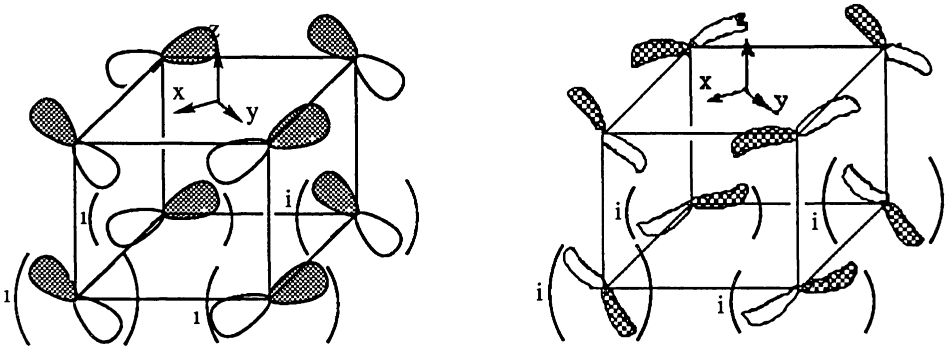
Figure 66. Bonding and Antibonding Molecular Orbitals



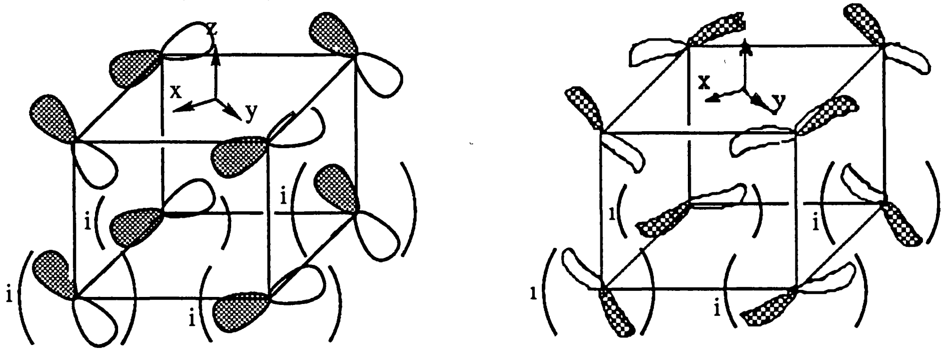
A(B3)=A(Cu2)-A(I2) A(A3)=A(Cu2)+A(I2)



B(B3)=B(Cu2)+B(I2) B(A3)=B(Cu2)-B(I2)

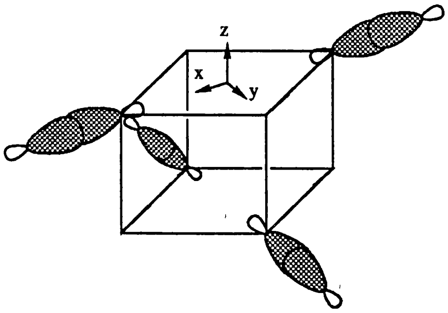


E(B5)=E(Cu3)-E(I1) E(A5)=E(Cu3)+E(I1)

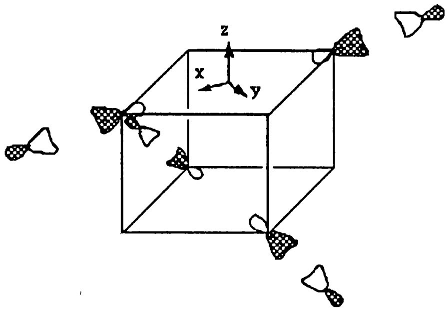


E(B6)=E(Cu4)+E(I2) E(A6)=E(Cu4)-E(I2)

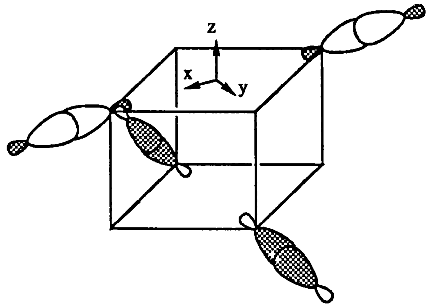
Figure 67. Bonding and Antibonding Molecular Orbitals



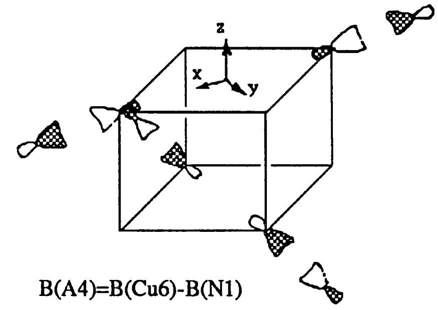
A(B4)=A(Cu6)+A(N1)



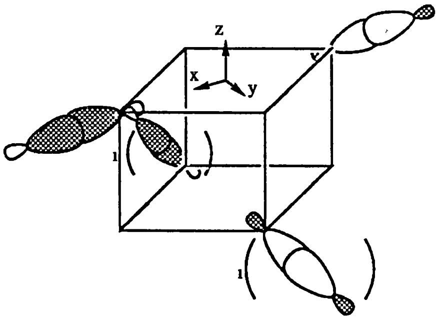
A(A4)=A(Cu6)-A(N1)



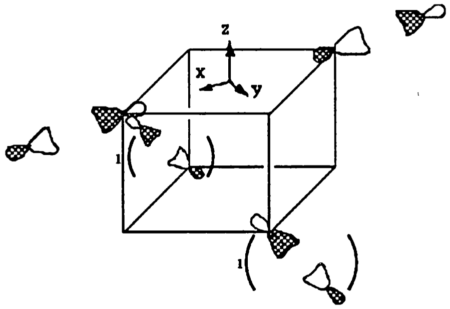
B(B4)=B(Cu6)+B(N1)



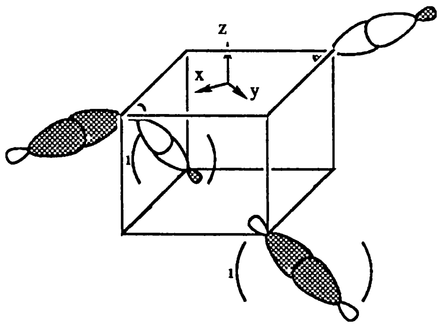
B(A4)=B(Cu6)-B(N1)



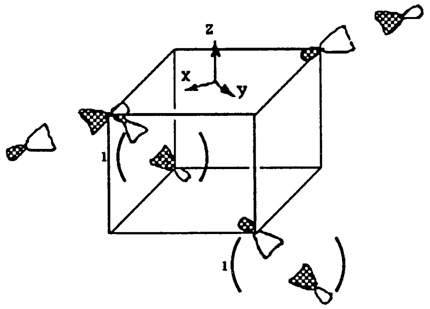
E(B7)=E(Cu12)+E(N1)



E(A7)=E(Cu12)-E(N1)



E(B8)=E(Cu10)+E(N2)



E(A8)=E(Cu10)-E(N2)

Figure 68. Bonding and Antibonding Molecular Orbitals

$$\int \psi(E_a)\mathcal{H}\psi(E_a)^* dv = \int \psi(E_a)\mathcal{H}\psi(E_b) dv$$

Based on the cubic structure of the molecule in which the atoms are arranged in two parallel rhombohedra, one can make the following approximation:

a) before interaction, the copper orbitals have energy, α, and the iodide and nitrogen orbitals have energy, α'. For orbitals a and e one has, then,

$$\int a\mathcal{H}a\ dv = \alpha$$

$$\int e\mathcal{H}e\ dv = \alpha'$$

b) The energy of the π interaction between adjacent orbitals is called β. That is, the interaction between a and e in $\psi(E_a)$ is

$$\int a\mathcal{H}e\ dv = \int e\mathcal{H}a\ dv = \beta$$

c) The energy of σ interaction between adjacent orbitals is called γ. For instance,

$$\int a\mathcal{H}g\ dv = \int g\mathcal{H}a\ dv = -\gamma$$

The sign is negative because only two orbitals with opposite sign can have a positive σ interaction.

d) Orbitals which are not adjacent do not have a π interaction. For instance,

$$\int a\mathcal{H}e\ dv = \int e\mathcal{H}a\ dv = 0$$

Under these approximations, we have the orbital energies of $\psi(E_a)$ and $\psi(E_b)$ as:

$$\int \psi(E_a)\mathcal{H}\psi(E_a)^* dv = \int \psi(E_a)\mathcal{H}\psi(E_b) dv = 1/8(\ 4\alpha\ + 4\alpha' + 8\beta\ ) = 1/2\alpha + 1/2\ \alpha' + \beta$$

Now let us treat an imaginary bonding orbital $\psi(E_i)$ in which all terms are simple integers with the same magnitude and arrangement of p_z orbitals of copper and iodide atoms as that in $\psi(E_a)$ with the same approximation given above. The linear combination of this orbital will be,

$$\psi(E_i) = \frac{1}{2\sqrt{2}}(Pz(a)-Pz(b)+Pz(e)-Pz(f)-Pz(c)+Pz(d)-Pz(g)+Pz(h))$$

The energy of $\psi(E_i)$ is,

$$\int \psi(E_i)\mathcal{H}\psi(E_i) dv = 1/2\alpha + 1/2\ \alpha' + \beta + \gamma$$

Because the average Cu - I bond distance is about 2.68 Å, one knows that the π interactions (β) between copper and iodide orbitals will be very insignificant. Therefore, the energy of interaction is mainly the result of the σ bonds between copper and iodide atoms (γ). From Figure 65, it can be seen that orbitals A(B2) and B(B2) have the same number of σ interactions as $\psi(E_i)$ does. So, one knows that the energies of interaction for A(B2) and B(B2) are similar to that for $\psi(E_i)$, in turn , they are greater than that for $\psi(E_a)$ and $\psi(E_b)$. This approach is not suitable for evaluating the orbital energy sequence of the molecular orbitals with A and B symmetry. Therefore the relative sequence of orbital energies for molecular orbitals obtained from combination between A and B combinations must be judged by the nodal plane criterion.

Figure 70 gives the schematic bonding orbital energy diagram of compound 10, $(Cu_4I_4(piperidine)_4)$. Because transition between HOMO and LUMO is forbidden based on the selection rule as mentioned earlier, emission arises from decay between the lowest antibonding orbital with A symmetry and the HOMO from which the electron originated. This explains why the solid state emission of $Cu_4I_4(piperidine)_4$ takes place at considerably higher energy than that observed for $Cu_4I_4(morpholine)_4$ (Figure 28.).

Compounds 12 $(Cu_nI_n(morpholine)_{2n})$ and 13 $(Cu_nI_n(4(\text{-}2\text{-}aminoethyl)\text{-}morpholine)_{2n}$ crystalize in a polymeric chain $\left[\!-\mathrm{Cu(L_2)} - \mathrm{I} - \mathrm{Cu(L_2)} - \mathrm{I}-\!\right]_n$ motif in which coordination at the copper atoms is tetrahedral with each copper bonded to two iodide and two molecules of ligand. The projection view of the two molecules is shown in Figures 71- 72 respectively.

Compound 14, $(Cu(C_6H_{12}N_2)_2{}^+I^-)$ is an ionic complex which was obtained unexpectedly from copper(I)iodide and pyrrolidine in acetonitrile as solvent. The synthetic method used first produces colorless powdery crystals of $Cu_4I_4(pyrrolidine)_4$ which emit orange under UV light. Before crystals large enough for X-ray analysis were formed, these crystals disappeared and large cubic crystals were formed. These crystals do not emit either at room temperature or at 10 K under UV light. A projection view of the crystalline

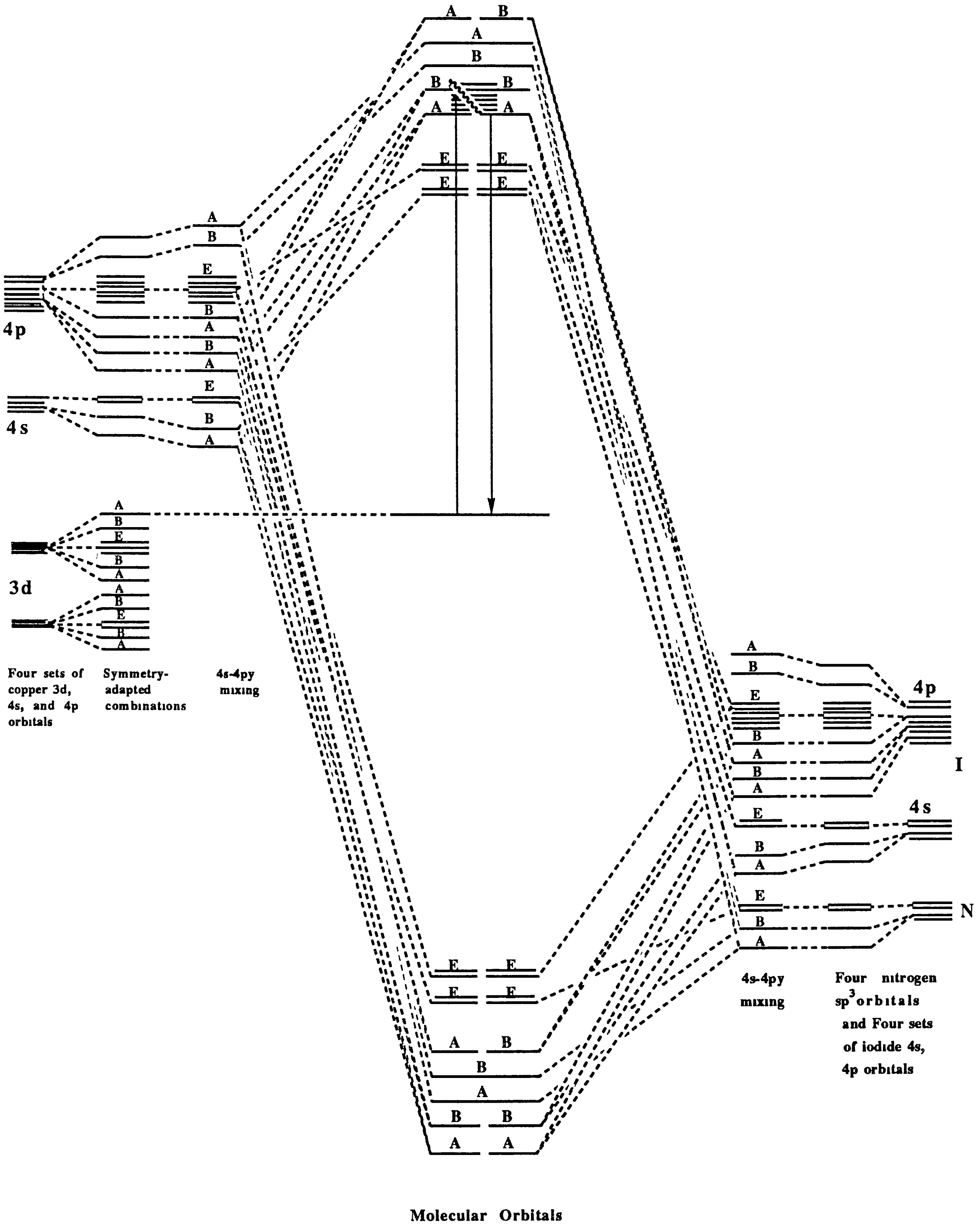


Figure 70. Schematic Molecular Orbital Energy Level Diagram of Compound Cu_4I_4(piperidine)$_4$

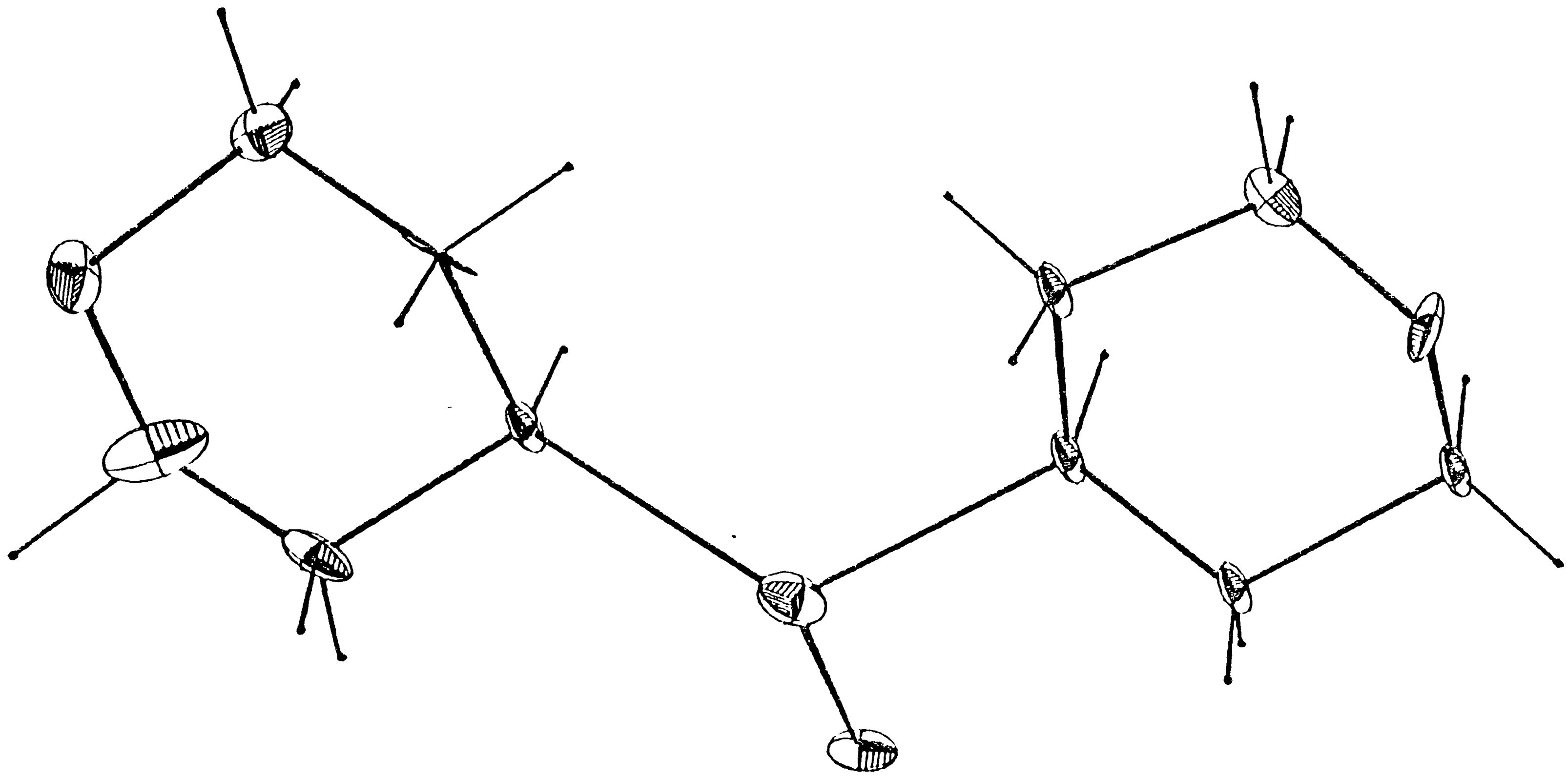


Figure 71. Projection View of $Cu_nI_n(morpholine)_{2n}$

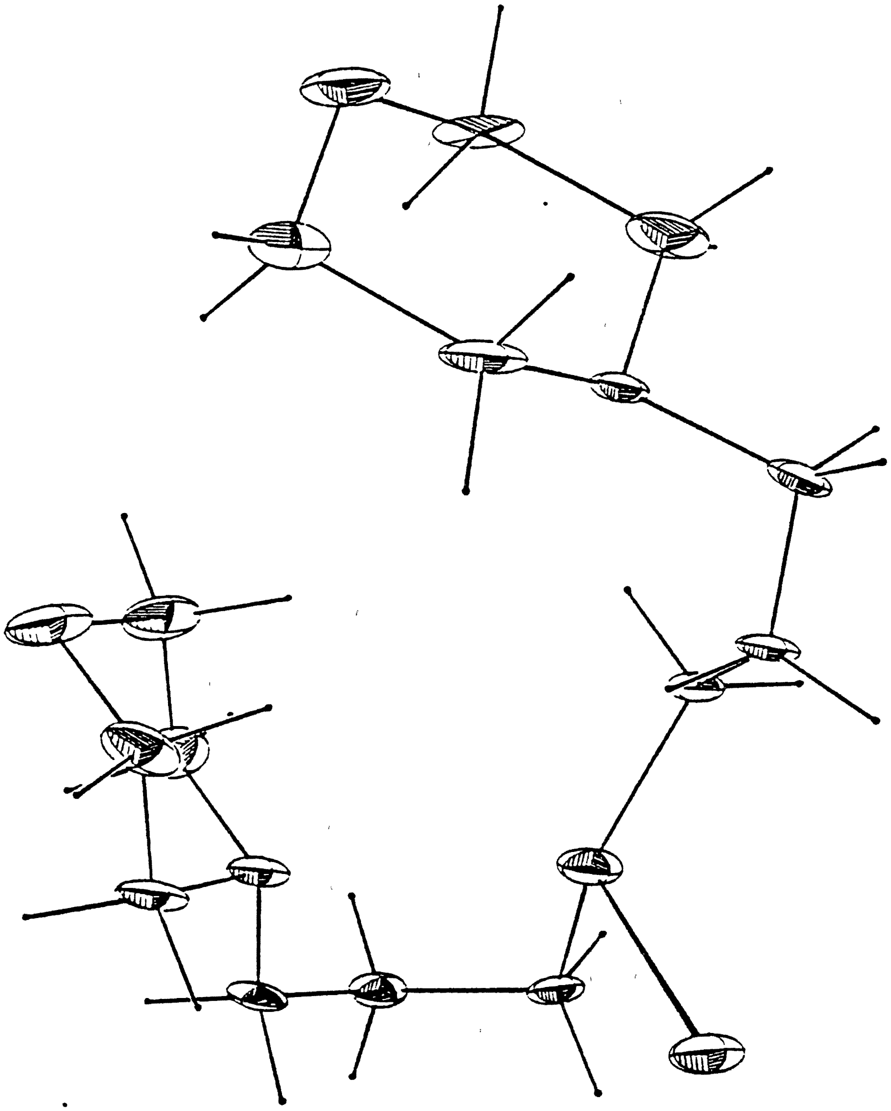


Figure 72. Projection View of Cu_nI_n(4-(2-aminoethyl)-morpholine)$_{2n}$

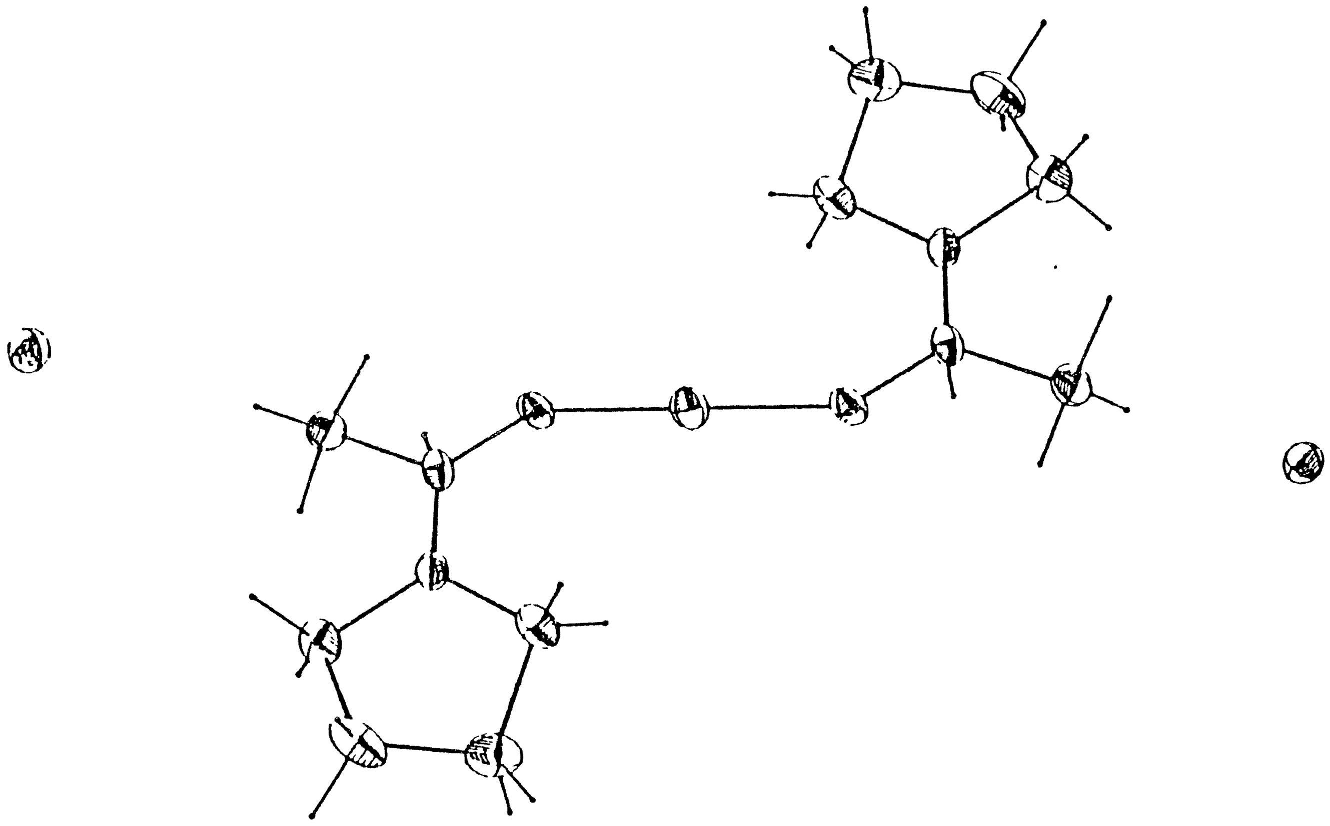
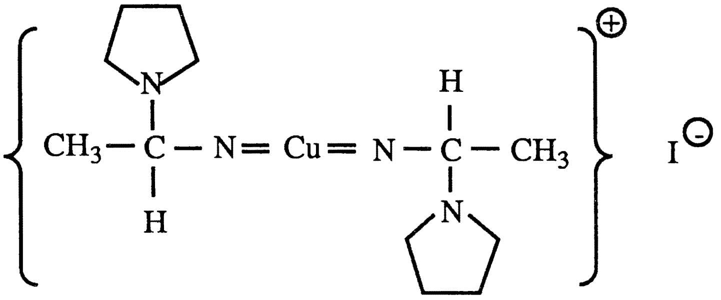


Figure 73. Projection View of $(CuI(C_6H_{12}N_2)_2)^+I^-$

compound is shown in Figure 73. From the molecular structure of the molecule, one can propose that the final product was formed from reaction:

$$CuI + 2C_4H_9N + 2CH_3CN \longrightarrow$$



The projection view of compounds, CuI(2-(2-aminoethyl)pyridine) (15) and CuI(2-(2-piperidinoethyl)pyridine) (16) are shown in Figures 74 and 75. In both compounds, coordination at the copper atoms is trigonal with each copper bonded to one iodide and a bidentate ligand.

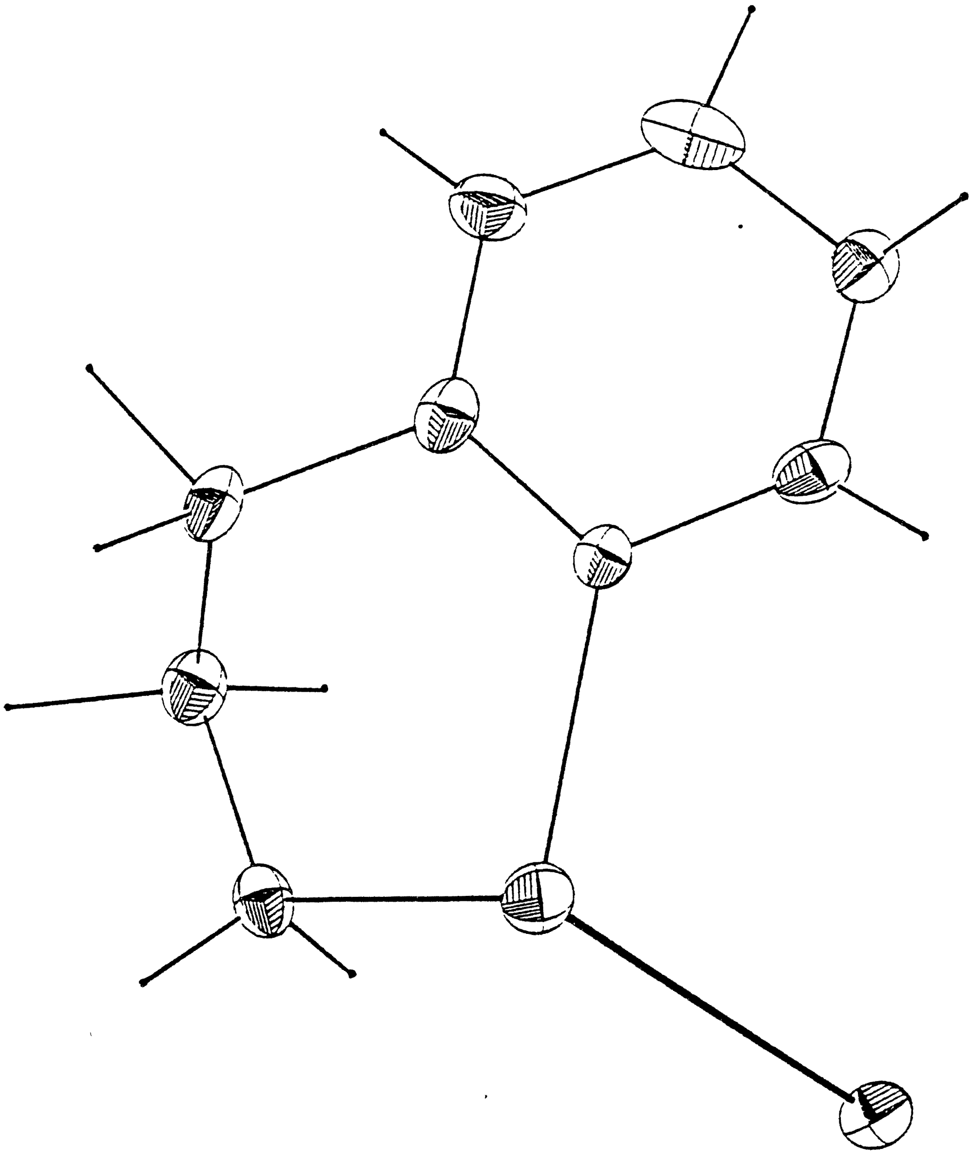


Figure 74. Projection View of CuI(2-(2-aminoethyl)-pyridine)

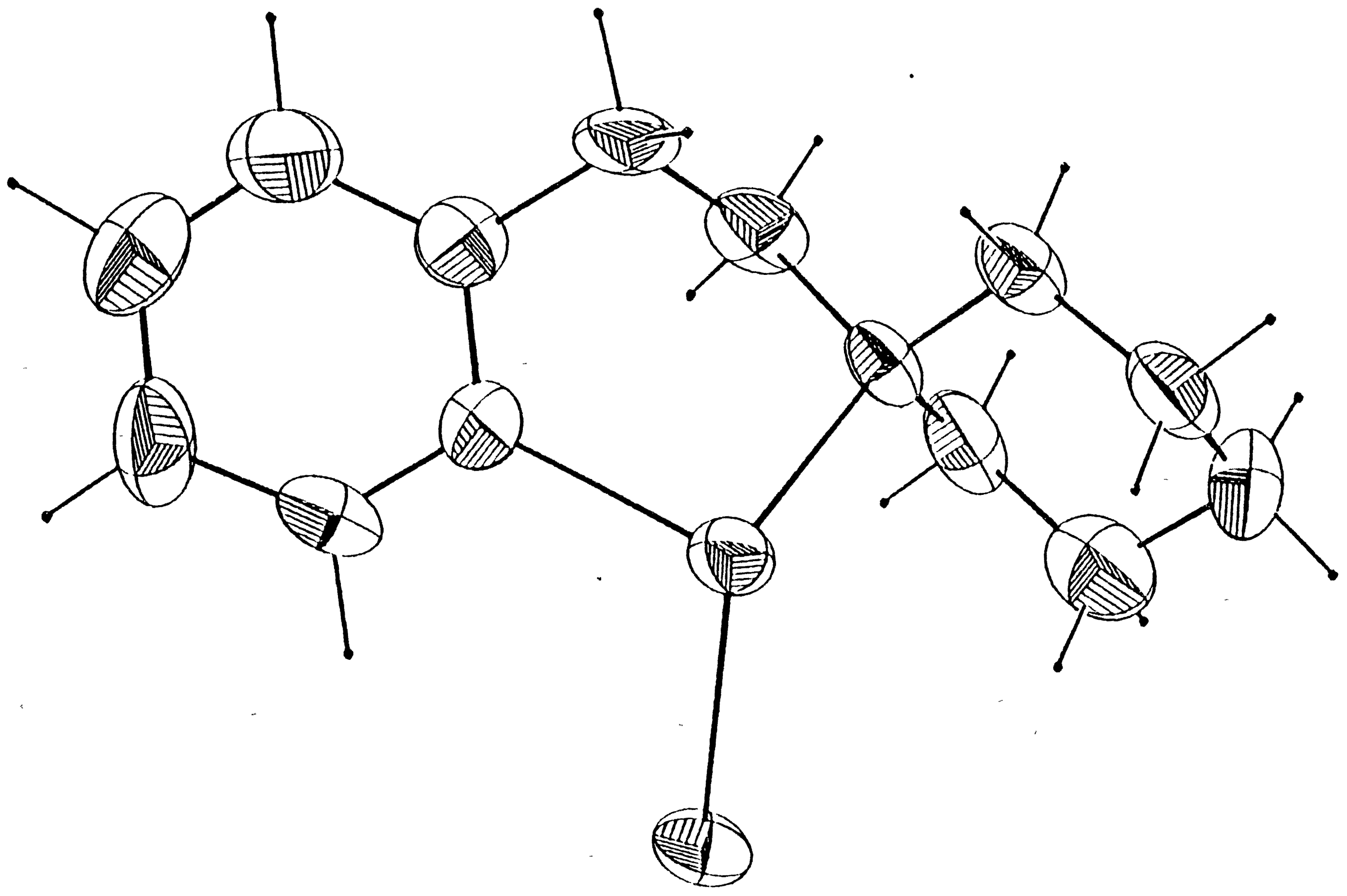


Figure 75. Projection View of CuI(2-(2-piperidinoethyl)-pyridine)

PART II

COPPER(I) HALIDE π COMPLEXES

CHAPTER VI

COPPER(I) HALIDE π COMPLEXES

Copper(I) halides (halide = iodide, bromide or chloride) have been observed to form neutral complexes of wide variation in structural motif and stoichiometry with Lewis base ligands which bond through donation of an unshared electron pair (39 - 41). The solid state structures of many of these complexes derive from a rhombohedral motif of alternating copper and iodine atoms which exist in isolation or combined by the sharing of edges or faces to form polymeric pleated sheets, chairs, or cubes (42). Copper normally achieves tetrahedral coordination (and thus an eighteen electron configuration) via further bonding to the Lewis base ligands. However with increased bulk of the ligand, three coordinate (trigonal planar) copper is also observed.

The structures of copper halide complexes with alkenes in which the ligand donates the π electrons of an unsaturated bond are less well known (43). Some of these display structures based on the Cu_2X_2 rhombohedron. $[CuCl(1,5\text{-cyclooctadiene})]_2$ crystallizes with a rhomb of alternating copper(I) and chloride atoms. The copper atoms are each bound to two double bonds of a boat shaped 1,5-cyclooctadiene ring (Cu...Cu) 2.944Å (44). A similar rhombohedron is found in CuCl(trans-1-cyanobuta-1,3-diene) with each copper atom coordinated to the nitrogen of a cyano group and π bound to a terminal double bond of a second organic molecule.(45). A rhombohedron has been observed with two different modes of binding at copper atoms. $(CuCl)_2(\text{trans-cyclooctene})_3$ crystallizes with a $(CuCl)_2$ rhombohedron in which one copper atom is bound to the double bonds of two different trans-cyclooctene molecules while the second copper atom binds to only one olefin molecule (46). Copper(I) atoms display both 16 and 18 electron totals in this complex.

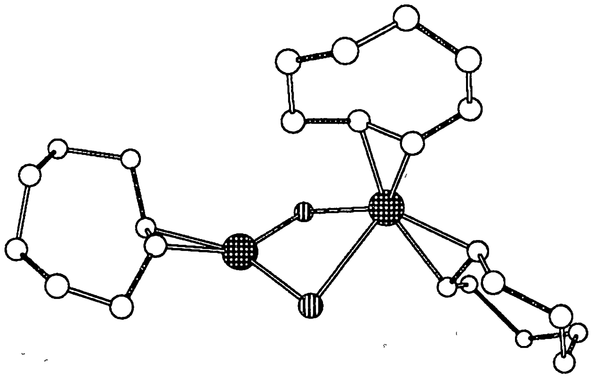


Figure 76. Crystal Structure of $(CuCl)_2$(trans-cyclooctene)$_3$.

A number of structures involve two edge sharing Cu_2Cl_2 rhombohedra in a chair conformation. Solid state [CuCl(allylalcohol)]$_4$ displays an isolated chair in which two of the four π bound allyl alcohols display additional Cu-O binding to copper atoms and (47). Copper-chloride distances in this structure range from 2.276(2)-2.750(3)Å.

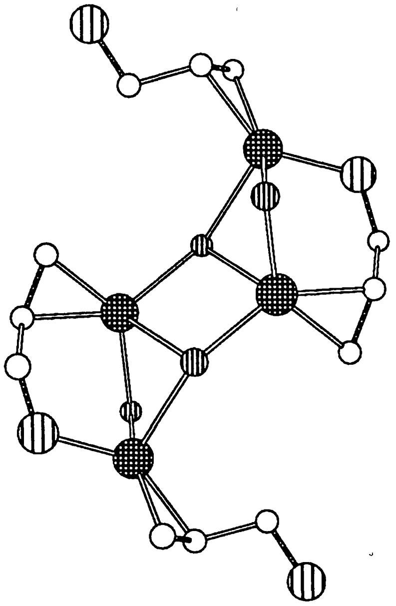


Figure 77. Crystal Structure of (CuCl(allylalcohol))$_4$.

A similar configuration of Cu_4X_4, chairs (X=Cl, Br) cross linked by a Cu-X bond was observed in Cu_2X_2allylcyanide (48) in which two of the four copper atoms are π bound to an allyl group whereas the remaining two are bound to the nitrogen atom of a bridging cyano group. CuCl-1,5-hexadiene (49) shows chairlike units linked into a folded, polymeric sheet and cross linked by 1,5-cyclohexadiene molecules.

In addition to structures based on rhombohedra, others have been observed with one dimensional $[Cu-X]_x$ arrays, both cyclic and polymeric. The $(CuClcyclooctatetraene)_x$ solid state structure consists of a continuous $(CuCl)_x$ chain with one double bond of the olefin bound to each copper atom. The carbon atoms of the double bond are approximately coplanar with the $CuCl_2$ unit (50).

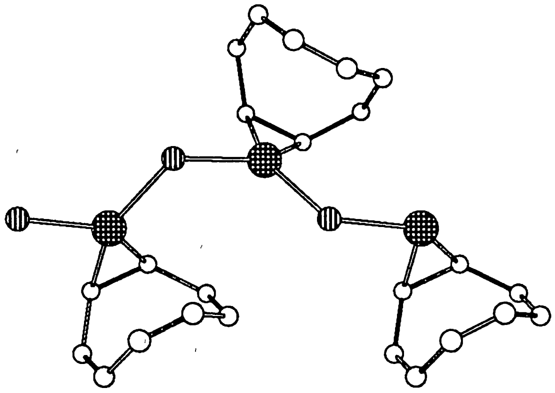


Figure 78. Crystal Structure of $(CuClcyclooctatetraene)_x$.

Cu_2Cl_2(diallylether) (49) shows a similar chain cross linked by π bound diallylether molecules. CuClacrylamide (51) and CuClacrylic acid (52) crystallize with CuCl chains π bound to the double bond of the acrylic moiety. Interchain hydrogen bonding of amide and carboxyl functions links chains together.

Two six membered rings of alternating copper and chlorine atoms with close stacking of rings: 2.757(3)Å separation (Cu-Cl) between rings, and with stacked ring pairs cross linked by p-divinylbenzene molecules form the structure of Cu_2Cl_2(p-divinylbenzene) (53).

Eight membered rings may adopt tub or step configurations. A tetranuclear structure has been observed for [CuCl(1,5-norbornadiene)$]_4$ in which copper atoms related by a 4 symmetry element are bridged by chloride atoms to form an eight membered tub shaped ring. Each copper atom in three coordinate, being additionally bound to one double bond of the olefin. The carbon atoms of the olefin lie in the plane of the $CuCl_2$ group (54). An eight membered step shaped ring has been observed for [CuCl(dibenzocyclooctatetraene)$]_4$ with each copper atom involved in two π bonds to a single cyclooctatetraene molecule (55).

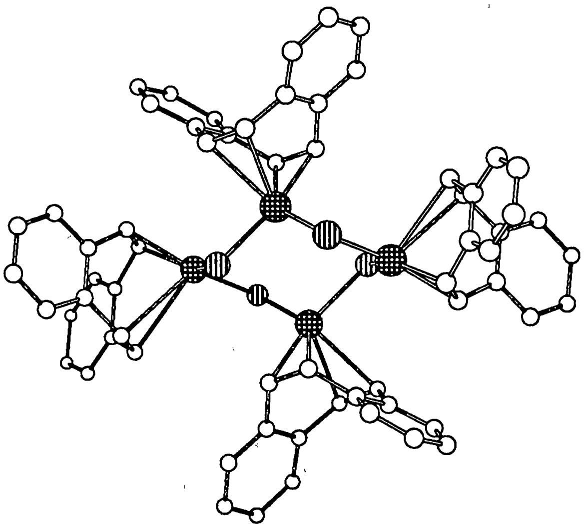


Figure 79. Crystal Structure of (CuCl(dibenzocyclooctatetraene)$)_4$.

The existence of (CuBr-1,5-cyclooctadiene$)_2$ and CuBr(cyclooctatetraene) complexes have been reported (44, 50) but their solid state structures are unknown.

Previous work in this laboratory has shown that the identity of the halide is not a definitive factor in the observation of emission or nonemission from solid state complexes of copper(I) halides. CuX complexes in which X = Cl, Br and I have shown emission. The preparation of similar complexes with change of halide has allowed probing of the influence of halide identity upon wavelength of maximum emission. A number of anionic Cu_yX_z systems have been prepared with X = Cl, Br and I. $CsCu_2X_3$, X=Cl, Br and I, crystallize in isostructural format. All three emit at 591 nm, independent of halide identity. Thus, in this system, mechanisms involving the halide may be ruled out. $Cs_3Cu_2X_5$, X = Cl, Br and I, which are isostructural, show a shift of the solid state emission maximum to longer wavelength with increased electronegativity of the halide suggesting an excitation mechanism which is influenced by electron density on copper or which involves the halide. (56) Nine $Cu_4X_6^{=}$ complexes have been prepared with X = I and Br. If bromide replaces iodide in clusters of similar symmetry, emission is normally shifted to longer wavelength. (57).

Experimental

(CuBr(norbornene))$_4$ To a suspension of Cu(I) bromide (0.72 g, 5 mmol) in ethylene glycol dimethylether (20 ml) was added 0.47 g (5 mmol) of norbornene. The mixture was heated under reflux with stirring for 6 h, filtered to remove undissolved solids and allowed to cool to room temperature. Colorless cubic crystals formed after 24 h.

((CuCl)$_5$(norbonene)$_4$) To a suspension of Cu(I) chloride (0.50 g, 5 mmol) in ethylene glycol dimethylether(20 ml) was added 0.47 g (5 mmol) of norbornene. The mixture was heated under reflux with stirring for 6 h, filtered and allowed to cool to room temperature. Crystallization produced a colorless needle shaped solid after 24 h. These crystals decomposed in air. X-ray measurements were carried out on a crystal mounted in a capillary in an inert atmosphere.

(Cu$_2$Br$_2$(1,5-cyclooctadiene)$_2$) To a suspension of Cu(I) bromide (0.72 g, 5 mmol) in ethylene glycol dimethylether(20 ml) was added 0.54 g (5 mmol) of 1,5-cyclooctadiene. The mixture was heated under reflux with stirring for 6 h, filtered and allowed to cool to room temperature. Crystallization produced a colorless needle shaped solid after 24 h.

Results and discussion

Three new copper(I) halide complexes (58) with alkenes in which the ligand donates the π electrons of an unsaturated bond, Cu_5Cl_5(norbornene)$_4$, Cu_4Br_4(norbornene)$_4$, and Cu_2Br_2(1,5-cyclooctadiene)$_2$, were synthesized and structurally characterized by single crystal X-ray diffraction techniques. The complete crytallographic data for the three complexes can be found at the end of this thesis (Tables 72 to 86).

In the unique complex Cu_5Cl_5(norbornene)$_4$, an eight membered ring of alternating copper and chlorine atoms (Figure 80.) displays an additional copper atom bridging two opposing chlorine atoms (Cu_{ring}-Cl_{ring}, av. 2.32(2)Å ; $Cu_{bridging}$ - Cl_{ring}, av. 2.45(2)Å) and further bound to a terminal chlorine atom.($Cu_{bridging}$ -$Cl_{terminal}$, 2.26(1)Å) The copper atoms of the ring are each bound to the π electrons of a norbornene molecule (Cu - C average 2.05(8)Å), twist angles average 19.84°; the bridging copper atom is coplanar with its three bound chlorine atoms.

Packing of complexes in the unit cell (Figure 81.) places the terminal chlorine atom of one motif 2.7Å from the four copper atoms of the eight membered ring of an adjacent motif. This can be considered a weakly interactive distance since the sum of the Van der Waals radii for Cu^+ and Cl^- is 2.77Å. It should also be noted that $(CuCl)_2$(trans-cyclooctene)$_3$ (45) includes one Cu-Cl distance of 2.928(7)Å, (CuCl(allylalcohol))$_4$ (46) includes two Cu-Cl distances of 2.750(3)Å. The 'long bonds' appear an integral part of the structural motifs despite their length. Thus the intermotif Cu-Cl distance of 2.7Å found in this work appears significant. The length of the interactive distance is consistent with the terminal chloride contributing an electron pair to one bound Cu while contributing three unshared pairs to an interaction with four other copper atoms. The 3.1Å separating this chlorine atom from vinylic hydrogen atoms of the norbornene molecules ligated to these copper atoms appears insignificant.

Cu_4Br_4(norbornene)$_4$ crystallizes with an eight membered ring of alternating copper and bromide atoms having each copper atom further bound to a norbornene molecule via π dornation of the electrons of the double bond (Figure 82.).

Cu_2Br_2(1,5-cyclooctadiene)$_2$ crytallizes with a rhombohrdron of alternating copper(I) and brobide atoms. The copper atoms are each bound to two double bonds of a boat shaped 1,5-cyclooctadiene ring. A projection view of the complex is shown in Figure 83.

The structures of copper(I) iodide complexes with alkene ligands are unknown, suggesting that copper(I) acceptance of π electrons in a sigma mode requires the presence of other ligands of high electronegativity (X=Br or Cl). Iodide is apparently not sufficiently electronegative to allow formation of stable complexes.

These π bound bromide and chloride complexes do not emit in the visible when excited at 300 nm and are thus unlike copper iodide complexes with electron pair donor ligands in which d^{10} electrons undergo excitation leading to emission in the 450-650 nm range (40, 41).

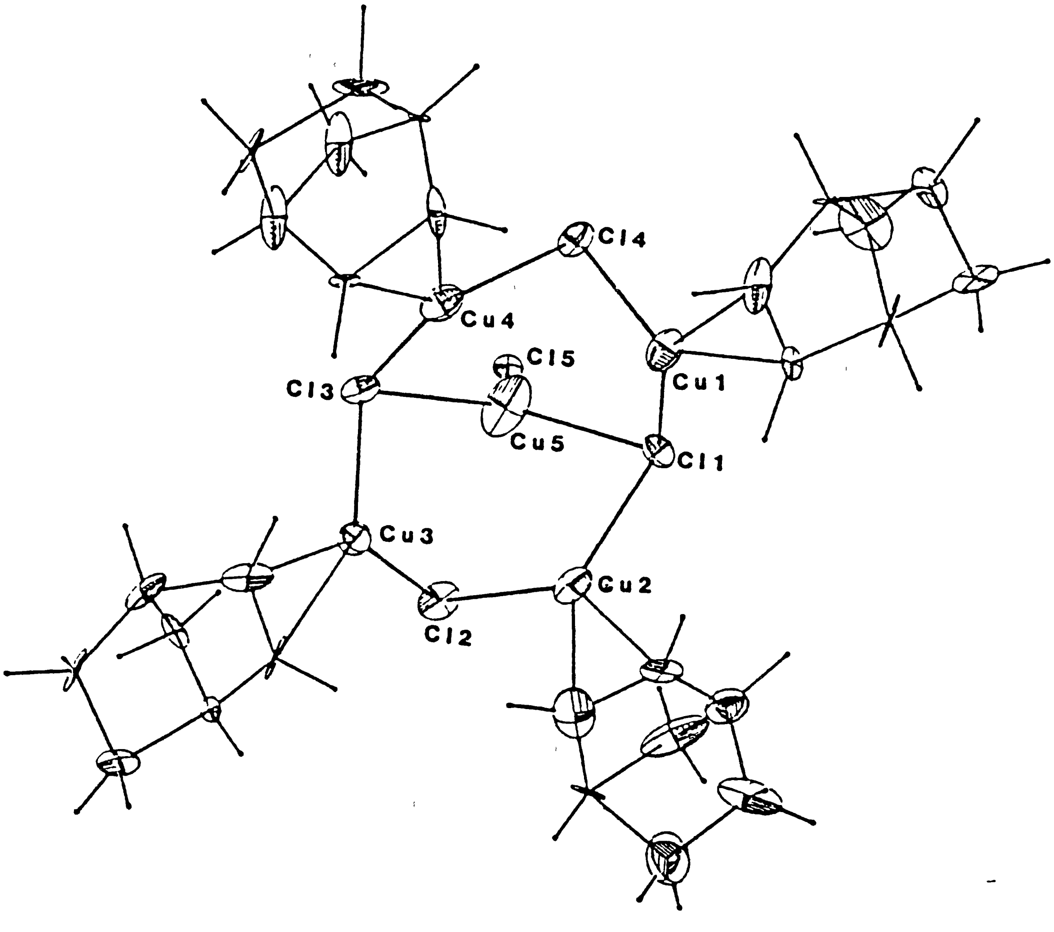


Figure 80. Projection View of $Cu_5Cl_5(norbornene)_4$

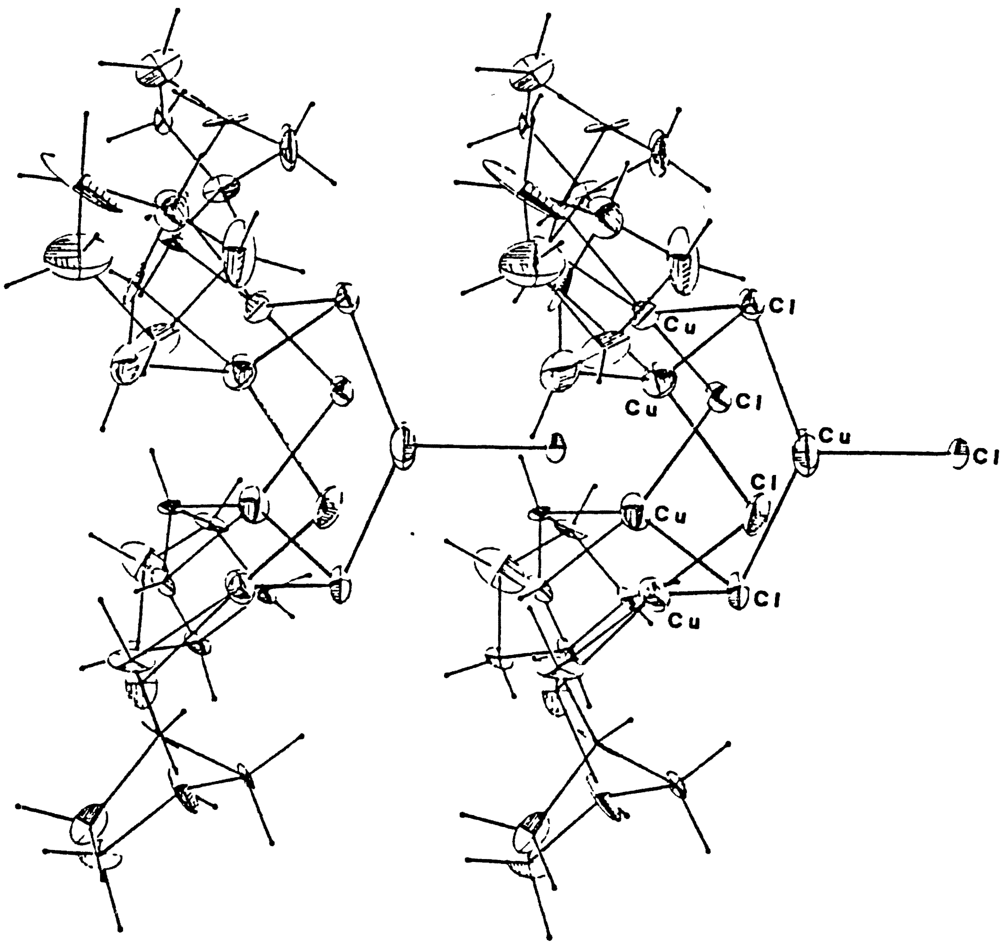


Figure 81. Packing of $Cu_5Cl_5(norbornene)_4$ in The Unit Cell

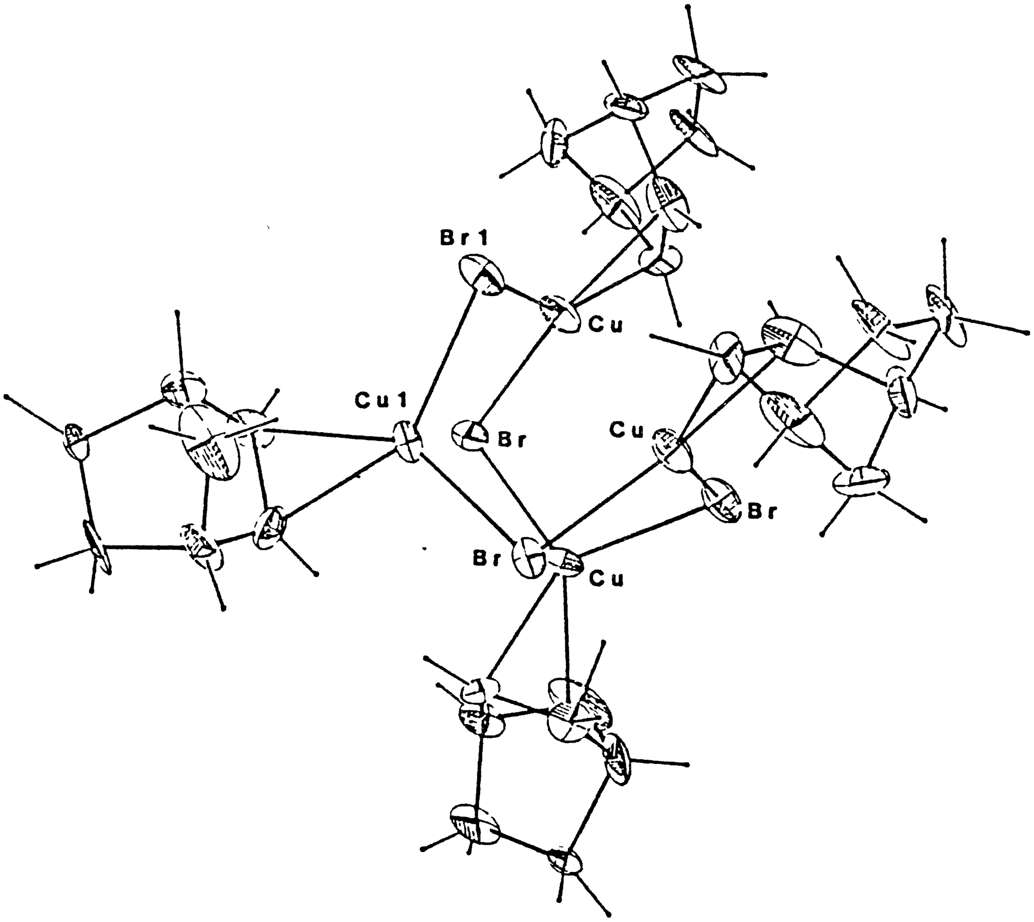


Figure 82. Projection View of $Cu_4Br_4(norbornene)_4$

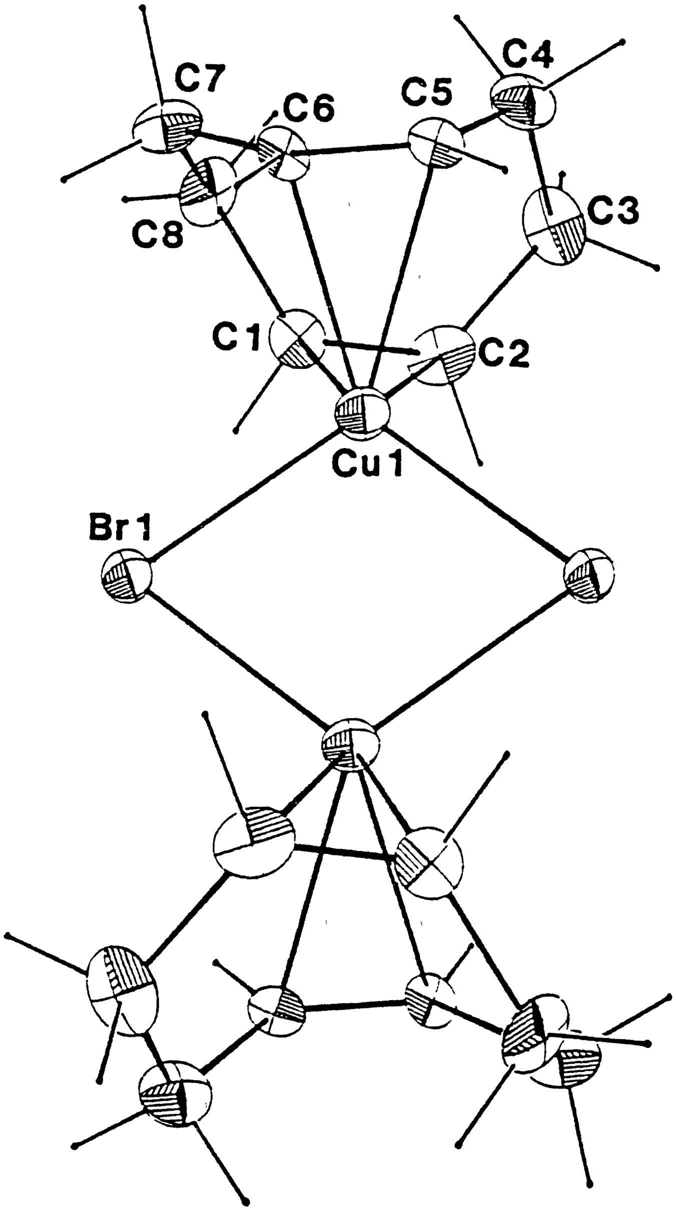


Figure 83. Projection View of Cu_2Br_2(1,5-cyclooctadiene)$_2$

TABLE I

CRYSTAL DATA FOR COPPER IODIDE 1 - METHYLPIPERAZINE

Formula	$(CuI(C_5N_2H_{12})_2)_2$
MWT	781.55
a	9.040(2) Å
b	21.85(1)
c	15.054(6)
α	90.0 °
β	90.0
γ	90.0
V	2974(2)
F (000)	1552
μMoK_α	35.11 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.745 g cm^{-3}
Z	4
Meas. Refl.	2703
Obs. Refl.	1344
R	6.0 %
Space Group	$Pn2_1a$
Octants Meas.	h, k, l

TABLE II

POSITIONAL PARAMETERS FOR COPPER IODIDE 1 - METHYLPIPERAZINE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.1493 (3)	0.2777 (6)	0.0638 (2)
I2	0.5476 (3)	0.3731 (6)	-0.0570 (2)
Cu1	0.2640 (7)	0.3296 (7)	-0.0809 (4)
Cu2	0.4212 (6)	0.3178 (7)	0.0789 (4)
N1	0.288 (3)	0.262 (1)	-0.178 (2)
N2	0.472 (3)	0.196 (1)	-0.307 (2)
N3	0.141 (5)	0.412 (2)	-0.117 (3)
N4	-0.007 (6)	0.529 (3)	-0.118 (5)
N5	0.557 (3)	0.256 (1)	0.148 (2)
N6	0.604 (3)	0.135 (1)	0.088 (2)
N7	0.397 (3)	0.391 (1)	0.179 (1)
N8	0.201 (3)	0.460 (1)	0.300 (1)
C1	0.333 (4)	0.288 (1)	-0.266 (2)
C2	0.374 (4)	0.242 (2)	-0.332 (3)
C3	0.424 (5)	0.168 (1)	-0.226 (3)
C4	0.387 (4)	0.211 (2)	-0.153 (2)
C5	0.498 (5)	0.149 (2)	-0.379 (2)
C6	0.002 (4)	0.424 (2)	-0.067 (3)
C7	-0.068 (6)	0.482 (3)	-0.088 (4)
C8	0.118 (4)	0.514 (2)	-0.169 (3)
C9	0.188 (9)	0.466 (3)	-0.160 (8)
C10	-0.077 (8)	0.578 (3)	-0.135 (5)
C11	0.488 (5)	0.203 (3)	0.185 (3)
C12	0.467 (6)	0.152 (2)	0.125 (3)
C13	0.670 (4)	0.182 (2)	0.045 (2)
C14	0.494 (6)	0.231 (2)	0.112 (3)
C15	0.577 (7)	0.087 (2)	0.029 (4)
C16	0.295 (4)	0.440 (1)	0.147 (2)

TABLE II (Continued)

C17	0.266 (3)	0.489 (1)	0.217 (2)
C18	0.324 (4)	0.418 (2)	0.337 (2)
C19	0.349 (3)	0.369 (1)	0.269 (2)
C20	0.181 (4)	0.505 (1)	0.363 (2)

TABLE III

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE 1 - METHYLPIPERAZINE

ATOM	X	Y	Z
H11	0.2534	0.3167	-0.2880
H12	0.4204	0.3170	-0.2562
H21	0.2796	0.2203	-0.3501
H22	0.4109	0.2609	-0.3874
H31	0.3244	0.1454	-0.2442
H32	0.4866	0.1355	-0.2072
H41	0.3425	0.1910	-0.1037
H42	0.4794	0.2304	-0.1358
H51	0.5812	0.1235	-0.3613
H52	0.4067	0.1186	-0.3690
H53	0.4950	0.1637	-0.4321
H61	-0.0620	0.3852	-0.0732
H62	0.0335	0.4226	-0.0036
H71	-0.1471	0.4678	-0.1376
H72	-0.1367	0.4900	-0.0376
H81	0.0789	0.5153	-0.2332
H82	0.1870	0.5499	-0.1673
H91	0.2377	0.4422	-0.2192
H92	0.2956	0.4665	-0.1263
H101	-0.1412	0.5938	-0.0775
H102	-0.0114	0.6164	-0.1396
H103	-0.1453	0.5790	-0.1802
H111	0.5572	0.1889	0.2394
H112	0.3975	0.2143	0.2169
H121	0.4276	0.1216	0.1589
H122	0.4075	0.1712	0.0832
H131	0.7600	0.1643	0.0178
H132	0.6054	0.1950	-0.0038

TABLE III (Continued)

H141	0.7583	0.2122	0.1582
H142	0.7571	0.2613	0.0809
H151	0.5325	0.1009	-0.0227
H152	0.6721	0.0658	0.0167
H153	0.5134	0.0550	0.0585
H161	0.3383	0.4588	0.0932
H162	0.2039	0.4192	0.1284
H171	0.3512	0.5122	0.2276
H172	0.1851	0.5158	0.1944
H181	0.4206	0.4370	0.3472
H182	0.2956	0.3969	0.3924
H191	0.4191	0.3370	0.2869
H192	0.2533	0.3470	0.2561
H201	0.1142	0.5373	0.3474
H202	0.1203	0.4830	0.4157
H203	0.2656	0.5202	0.3923
H221	0.1884	0.2453	-0.1840
H331	0.1061	0.3806	-0.1642
H551	0.5830	0.2894	0.1909
H771	0.4966	0.4119	0.1893

TABLE IV

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 1 - METHYLPIPERAZINE

ATOM	U11	U22	U33	U12	U13	U23
I1	29 (1)	57 (1)	36 (1)	-8 (1)	3 (1)	-7 (2)
I2	32 (1)	70 (2)	38 (1)	-12 (1)	4 (1)	-3 (2)
CU1	45 (3)	61 (4)	46 (3)	1 (3)	10 (3)	-8 (3)
CU2	36 (3)	51 (3)	44 (3)	4 (3)	7 (2)	-5 (3)
N1	2 (1)	5 (2)	2 (1)	1 (1)	1 (1)	5 (1)
N2	4 (2)	1 (1)	3 (1)	-1 (1	-1 (1)	1 (1)
N3	7 (3)	4 (3)	11 (4)	3 (2)	-2 (3)	-3 (2)
N4	8 (4)	14 (5)	27 (9)	5 (4)	13 (5)	13 (6)
N5	2 (1)	3 (2)	5 (2)	1 (1)	0 (1)	-4 (1)
N6	4 (2)	1 (1)	4 (2)	-1 (1)	-1 (1)	1 (1)
N7	0 (1)	4 (2)	1 (1)	1 (1)	0 (1)	0 (1)
N8	6 (2)	4 (2)	1 (1)	1 (1)	0 (1)	0 (1)
C1	4 (2)	1 (2)	2 (1)	2 (2)	1 (1)	2 (1)
C2	1 (2)	4 (3)	5 (3)	-2 (2)	1 (2)	1 (2)
C3	4 (2)	0 (1)	10 (4)	0 (2)	-1 (2)	1 (2)
C4	1 (2)	6 (3)	3 (2)	1 (2)	2 (2)	1 (2)
C5	5 (3)	5 (3)	4 (2)	3 (2)	-1 (2)	0 (2)
C6	2 (2)	10 (4)	5 (3)	-1 (3)	3 (2)	-3 (3)
C7	7 (4)	8 (4)	10 (5)	8 (4)	2 (4)	2 (4)
C8	3 (2)	2 (2)	10 (4)	1 (2)	-1 (3)	2 (3)
C9	16 (8)	14 (7)	10 (4)	-3 (6)	-6 (3)	4 (9)
C10	18 (7)	5 (4)	14 (6)	7 (5)	-2 (6)	2 (5)
C11	6 (4)	19 (6)	5 (3)	9 (4)	5 (3)	6 (4)
C12	4 (3)	8 (4)	8 (4)	0 (3)	-3 (3)	1 (3)
C13	4 (2)	6 (3)	5 (3)	3 (2)	1 (2)	0 (2)
C14	9 (4)	5 (3)	5 (3)	-5 (3)	-4 (3)	1 (2)
C15	16 (6)	5 (4)	12 (5)	3 (4)	-8 (5)	-3 (3)
C16	4 (2)	1 (2)	5 (3)	-1 (2)	3 (2)	0 (2)

TABLE IV (Continued)

C17	1 (2)	3 (2)	1 (2)	0 (2)	1 (1)	-1 (1)
C18	5 (3)	4 (3)	1 (2)	0 (2)	-1 (2)	0 (2)
C19	3 (2)	3 (2)	2 (2)	0 (2)	-2 (2)	0 (2)
C20	2 (2)	5 (3)	5 (3)	-2 (2)	1 (2)	-1 (2)

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 10^2 for C, N.

TABLE V

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 1 - METHYLPIPERAZINE

I1 - Cu1	2.66 (1)	Cu1 - I1 - Cu2	64.0 (2)
I1 - Cu2	2.62 (1)	Cu1 - I2 - Cu2	62.7 (2)
I2 - Cu1	3.27 (1)	I1 - Cu1 - I2	113.6 (2)
I2 - Cu2	2.75 (1)	I1 - Cu2 - I2	119.5 (2)
Cu1 - N1	2.08 (3)	I1 - Cu1 - N1	108 (1)
Cu1 - N3	2.20 (4)	I2 - Cu1 - N1	103 (1)
Cu2 - N5	2.10 (3)	I1 - Cu1 - N3	110 (1)
Cu2 - N7	2.20 (3)	I2 - Cu1 - N3	102 (1)
N1 - C1	1.49 (4)	N1 - Cu1 - N3	117 (1)
N1 - C4	1.47 (5)	I1 - Cu2 - N5	111 (1)
C1 - C2	1.47 (6)	I2 - Cu2 - N5	115 (1)
C2 - N2	1.38 (5)	I1 - Cu2 - N7	102 (1)
N2 - C3	1.43 (5)	I2 - Cu2 - N7	104 (1)
N2 - C5	1.52 (5)	N5 - Cu2 - N7	100 (1)
C3 - C4	1.48 (6)	Cu1 - N1 - C1	112 (2)
N3 - C6	1.47 (6)	Cu1 - N1 - C4	114 (2)
N3 - C9	1.4 (1)	C1 - N1 - C4	110 (2)
C6 - C7	1.44 (8)	N1 - C1 - C2	113 (2)
C7 - N2	1.25 (9)	C1 - C2 - N2	117 (3)
N4 - C8	1.41 (8)	C2 - N2 - C3	110 (3)
N4 - C10	1.26 (9)	C2 - N2 - C5	112 (3)
C8 - C9	1.21 (9)	C3 - N2 - C5	111 (2)
N5 - C11	1.43 (7)	N2 - C3 - C4	114 (3)
N5 - C14	1.45 (6)	C3 - C4 - N1	115 (3)
C11 - C12	1.44 (8)	Cu - N3 - C6	116 (3)
C12 - N6	1.41 (6)	Cu - N3 - C9	130 (4)
N6 - C13	1.35 (5)	C6 - N3 - C9	110 (5)
N6 - C15	1.39 (6)	N3 - C6 - C7	114 (4)

TABLE V (Continued)

C13 - C14	1.48 (6)	C6 - C7 - N4	126 (5)
N7 - C16	1.48 (4)	C7 - N4 - C8	110 (6)
N7 - C19	1.50 (4)	C7 - N4 - C10	122 (6)
C16 - C17	1.53 (4)	C8 - N4 - C10	119 (6)
C17 - N8	1.49 (4)	N4 - C8 - C9	124 (6)
N8 - C18	1.50 (5)	C8 - C9 - N3	126 (7)
N8 - C20	1.38 (5)	Cu2 - N5 - C11	117 (2)
C18 - C19	1.50 (5)	Cu2 - N5 - C14	123 (2)
Cu1...Cu2	2.803 (8)	C11 - N5 - C14	101 (3)
		N5 - C11 - C12	115 (4)
		C11 - C12 - N6	109 (4)
		C12 - N6 - C13	111 (3)
		C12 - N6 - C15	107 (4)
		C13 - N6 - C15	110 (3)
		N6 - C13 - C14	107 (3)
		C13 - C14 - N5	113 (4)
		Cu2 - N7 - C16	110 (2)
		Cu2 - N7 - C19	114 (2)
		C16 - N7 - C19	110 (2)
		N7 - C16 - C17	112 (2)
		C16 - C17 - N8	109 (2)
		C17 - N8 - C18	108 (2)
		C17 - N8 - C20	109 (2)
		C18 - N8 - C20	107 (2)
		N8 - C18 - C19	106 (2)
		C18 - C19 - N7	114 (3)

TABLE VI

CRYSTAL DATA FOR COPPER IODIDE
3, 3 - DIMETHYLPIPERIDINE

Formula	$(CuI(C_7Nh_{15})_2)_2$
MWT	833.71
a	6.720(3) Å
b	11.728(9)
c	12.018(7)
α	93.46(5)°
β	95.38(4)
γ	107.13(4)
V	897.4(9) Å^3
F (000)	468
μMoK_α	34.57 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.542 g cm^{-3}
Z	1
Meas. Refl.	3162
Obs. Refl.	1877
R	9.5 %
Space Group	P1bar
Octants Meas.	±h, k, ±l

TABLE VIII

POSITIONAL PARAMETERS FOR IODIDE 3, 3 - DIMETHYLPIPERIDINE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.2766 (6)	0.0387 (3)	0.1330 (3)
Cu1	0.1185 (9)	-0.0290 (5)	-0.0794 (5)
N1	0.156 (6)	-0.189 (3)	-0.079 (1)
N2	0.297 (6)	0.110 (3)	-0.173 (3)
C1	0.011 (8)	-0.255 (4)	-0.230 (4)
C2	0.041 (9)	-0.369 (4)	-0.283 (4)
C3	0.051 (9)	-0.454 (5)	-0.185 (4)
C4	0.218 (10)	-0.384 (5)	-0.090 (4)
C5	0.179 (10)	-0.274 (5)	-0.044 (4)
C6	0.255 (10)	-0.338 (6)	-0.334 (5)
C7	-0.131 (10)	-0.433 (6)	-0.366 (5)
C8	0.232 (8)	0.077 (4)	-0.296 (4)
C9	0.363 (9)	0.175 (8)	-0.370 (4)
C10	0.348 (7)	0.299 (4)	-0.324 (4)
C11	0.415 (8)	0.328 (4)	-0.198 (5)
C12	0.291 (8)	0.225 (4)	-0.134 (4)
C13	0.250 (10)	0.142 (6)	-0.490 (5)
C14	0.587 (10)	0.179 (6)	-0.365 (5)

TABLE IX

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE 3,3 - DIMETHYLPIPERIDINE

ATOM	X	Y	Z
H1	0.2977	-0.1723	-0.1626
H2	0.4442	0.1111	-0.1648
H11	-0.1318	-0.2775	-0.2026
H12	0.0033	-0.2006	-0.2885
H31	-0.0869	-0.4792	-0.1529
H32	0.0732	-0.5295	-0.2138
H41	0.2424	-0.4361	-0.0318
H42	0.3592	-0.3604	-0.1242
H51	0.0409	-0.2971	-0.0079
H52	0.2922	-0.2289	0.0167
H61	0.2735	-0.2789	-0.3892
H62	0.3798	-0.2995	-0.2719
H63	0.2921	-0.4071	-0.3669
H71	-0.1141	-0.5082	-0.3966
H72	-0.2622	-0.4539	-0.3330
H73	-0.1398	-0.3822	-0.4256
H81	0.2435	-0.0031	-0.3175
H82	0.0780	0.0686	-0.3116
H101	0.4304	0.3637	-0.3644
H102	0.2000	0.2999	-0.3382
H111	0.5689	0.3381	-0.1825
H112	0.4002	0.4068	-0.1709
H121	0.3368	0.2389	-0.0521
H122	0.1393	0.2231	-0.1414
H131	0.2540	0.0582	-0.5198
H132	0.1078	0.1395	-0.4986
H133	0.3333	0.1974	-0.5381
H141	0.6674	0.2367	-0.4106

TABLE IX (Continued)

H142	0.6554	0.1931	-0.2886
H143	0.6039	0.0987	-0.3945

TABLE X

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 3, 3 - DIMETHYLPIPERIDINE

ATOM	U11	U22	U33	U12	U13	U23
I1	45 (2)	60 (3)	32 (2)	22 (2)	5 (1)	21 (1)
Cu1	64 (5)	40 (5)	41 (4)	19 (4)	17 (4)	18 (3)
N1	6 (3)	4 (2)	1 (2)	1 (2)	1 (2)	1 (2)
N2	6 (3)	4 (3)	2 (2)	1 (2)	2 (2)	2 (2)
C1	10 (4)	3 (3)	3 (3)	1 (3)	2 (3)	1 (3)
C2	9 (4)	3 (3)	1 (2)	-2 (3)	-2 (3)	0 (2)
C3	13 (5)	3 (3)	7 (4)	4 (4)	4 (4)	2 (3)
C4	18 (7)	4 (4)	2 (3)	4 (4)	0 (4)	-1 (3)
C5	16 (6)	7 (4)	1 (2)	6 (4)	2 (3)	2 (3)
C6	21 (8)	12 (6)	7 (4)	8 (6)	10 (5)	5 (4)
C7	14 (6)	8 (5)	6 (4)	5 (5)	2 (4)	3 (4)
C8	7 (4)	3 (3)	6 (4)	2 (3)	3 (3)	3 (3)
C9	9 (5)	6 (4)	4 (3)	0 (3)	1 (3)	4 (3)
C10	4 (3)	5 (4)	4 (3)	0 (3)	1 (2)	2 (3)
C11	8 (4)	3 (4)	8 (4)	1 (3)	1 (3)	2 (3)
C12	7 (4)	1 (3)	4 (3)	1 (3)	1 (3)	-1 (2)
C13	14 (6)	9 (5)	6 (4)	3 (5)	2 (4)	6 (4)
C14	15 (6)	14 (6)	11 (5)	9 (6)	11 (5)	10 (5)

Anisotropic thermal parameters in the form:

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

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

TABLE XI

BOND DISTANCES (Å) AND BOND ANGGLES (°) FOR COPPER IODIDE 3, 3 - DIMETHYLPIPERIDINE

I1 - Cu1	2.650 (6)	I1 - Cu1 - N1	112.5 (9)
Cu1 - N1	2.05 (4)	I1 - Cu1 - N2	104 (1)
Cu1 - N2	2.16 (3)	N1 - Cu1 - N2	108 (1)
N1 - C1	1.44 (5)	Cu1 - N1 - C1	116 (3)
N1 - C5	1.56 (6)	Cu1 - N1 - C5	115 (2)
N2 - C8	1.49 (5)	C1 - N1 - C5	110 (3)
N2 - C12	1.42 (6)	Cu1 - N2 - C8	109 (2)
C1 - C2	1.52 (7)	Cu1 - N2 - C12	112 (2)
C2 - C3	1.60 (7)	C8 - N2 - C12	114 (3)
C2 - C6	1.56 (9)	N1 - C1 - C2	119 (4)
C2 - C7	1.44 (7)	C1 - C2 - C3	106 (3)
C3 - C4	1.53 (7)	C1 - C2 - C6	109 (4)
C4 - C5	1.47 (9)	C1 - C2 - C7	112 (5)
C8 - C9	1.60 (6)	C3 - C2 - C6	108 (5)
C9 - C10	1.55 (7)	C3 - C2 - C7	107 (4)
C9 - C13	1.53 (7)	C6 - C2 - C7	111 (4)
C9 - C14	1.48 (9)	C2 - C3 - C4	108 (3)
C10 - C11	1.52 (6)	C3 - C4 - C5	113 (5)
C11 - C12	1.54 (6)	C4 - C5 - N1	112 (3)
Cu1...Cu1'	2.76 (1)	N2 - C8 - C9	112 (3)
		C8 - C9 - C10	107 (4)
		C8 - C9 - C13	105 (3)
		C8 - C9 - C14	112 (5)
		C10 - C9 - C13	109 (5)
		C10 - C9 - C14	109 (4)
		C13 - C9 - C14	111 (5)
		C9 - C10 - C11	113 (4)
		C10 - C11 - C12	110 (3)
		C11 - C12 - N2	114 (4)

TABLE XII

CRYSTAL DATA FOR COPPER IODEDE 4 - METHYLPIPERIDINE

Formula	$(CuI(C_6NH_{13})_2)_2$
MWT	388.71
a	14.998(4) Å
b	9.046(2)
c	21.875(9)
α	90.0 °
β	90.0
γ	90.0
V	2968(1) Å^3
F (000)	1552
μMoK_α	35.15 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.74
Z	4
Meas. Refl.	2697
Obs. Refl.	1155
R	7.8 %
Space Group	$Pbn2_1$
Octants Meas.	h, k, l

TABLE XIII

POSITIONAL PARAMETERS FOR COPPER IODIDE 4 - METHYLPIPERIDINE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.9431 (2)	0.0472 (4)	0.7500
I2	1.0640 (2)	-0.3505 (4)	0.6550 (2)
Cu1	0.9196 (5)	-0.2369 (9)	0.7074 (5)
Cu2	1.0785 (5)	-0.0783 (8)	0.6961 (5)
N1	0.817 (2)	-0.218 (5)	0.639 (2)
N2	0.882 (4)	-0.359 (5)	0.785 (3)
N3	1.149 (3)	0.064 (5)	0.637 (2)
N4	1.176 (2)	-0.113 (5)	0.772 (2)
C1	0.730 (4)	-0.164 (8)	0.661 (3)
C2	0.659 (3)	-0.130 (4)	0.619 (2)
C3	0.696 (3)	-0.035 (6)	0.573 (2)
C4	0.778 (3)	-0.081 (4)	0.540 (2)
C5	0.849 (3)	-0.116 (4)	0.601 (2)
C6	0.624 (4)	0.007 (7)	0.530 (2)
C7	0.861 (6)	-0.280 (9)	0.839 (3)
C8	0.829 (4)	-0.378 (6)	0.884 (4)
C9	0.877 (6)	-0.505 (8)	0.903 (4)
C10	0.913 (5)	-0.570 (8)	0.859 (4)
C11	0.927 (3)	-0.488 (7)	0.803 (3)
C12	0.875 (5)	-0.559 (8)	0.961 (4)
C13	1.192 (3)	0.001 (7)	0.586 (2)
C14	1.129 (4)	-0.022 (5)	0.535 (2)
C15	1.087 (2)	0.107 (4)	0.512 (2)
C16	1.045 (3)	0.174 (6)	0.562 (3)
C17	1.110 (3)	0.195 (5)	0.613 (2)
C18	1.037 (5)	0.066 (12)	0.465 (3)
C19	1.148 (4)	-0.203 (7)	0.819 (3)
C20	1.218 (3)	-0.243 (6)	0.860 (2)

TABLE XIII (Continued)

C21	1.300 (3)	-0.295 (4)	0.838 (2)
C22	1.334 (3)	-0.168 (6)	0.800 (2)
C23	1.268 (2)	-0.135 (4)	0.743 (2)
C24	1.270 (4)	-0.326 (9)	0.888 (3)

TABLE XIV

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE 4 - METHYLPIPERIDINE

ATOM	X	Y	Z
H1	0.8109	-0.3264	0.6283
H2	0.8243	-0.4153	0.7748
H3	1.1950	0.1185	0.6588
H4	1.1858	-0.0158	0.7932
H11	0.7049	-0.2197	0.6919
H12	0.7423	-0.0594	0.6781
H21	0.6413	-0.2248	0.5993
H22	0.6081	-0.0864	0.6373
H31	0.7112	0.0573	0.5927
H41	0.7653	-0.1729	0.5155
H42	0.7976	-0.0066	0.5108
H51	0.8564	-0.0207	0.6221
H52	0.9072	-0.1424	0.5834
H61	0.6337	-0.0529	0.4919
H62	0.6388	0.1118	0.5163
H63	0.5655	0.0039	0.5405
H71	0.9150	-0.2315	0.8539
H72	0.8177	-0.1982	0.8295
H81	0.8054	-0.3317	0.9203
H82	0.7705	-0.4308	0.8657
H91	0.9358	-0.4585	0.9217
H101	0.9680	-0.6257	0.8629
H102	0.8676	-0.6517	0.8431
H111	0.9883	-0.4667	0.8024
H112	0.9161	-0.5621	0.7672
H121	0.8856	-0.4845	0.9905
H122	0.8181	-0.6048	0.9655
H123	0.9189	-0.6425	0.9734

TABLE XIV (Continued)

H131	1.2442	0.0549	0.5715
H132	1.2157	-0.1012	0.5979
H141	1.1598	-0.0688	0.5008
H142	1.0819	-0.0865	0.5492
H151	1.1313	0.1737	0.4936
H161	1.0230	0.2704	0.5491
H162	0.9966	0.1125	0.5748
H171	1.1589	0.2606	0.6011
H172	1.0800	0.2395	0.6485
H181	1.0781	0.0148	0.4336
H182	0.9956	-0.0119	0.4774
H183	1.0114	0.1478	0.4483
H191	1.1725	-0.3166	0.8011
H192	1.0952	-0.2407	0.8235
H201	1.2288	-0.1548	0.8850
H202	1.1937	-0.3195	0.8896
H211	1.2897	-0.3820	0.8103
H221	1.3386	-0.0805	0.8262
H222	1.3939	-0.1902	0.7844
H231	1.2846	-0.0394	0.7203
H232	1.2657	-0.2105	0.7121
H241	1.3822	-0.2293	0.9093
H242	1.3491	-0.3945	0.9173
H243	1.4274	-0.3577	0.8714

TABLE XV

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 4 - METHYLPIPERIDENE

ATOM	U11	U22	U33	U12	U13	U23
I1	32 (1)	38 (2)	76 (3)	6 (2)	-8 (3)	-15 (2)
I2	33 (1)	35 (2)	54 (2)	3 (2)	1 (2)	-7 (2)
Cu1	35 (4)	67 (5)	69 (5)	11 (4)	-7 (4)	4 (5)
Cu2	39 (4)	41 (4)	54 (5)	2 (3)	-5 (4)	3 (3)
N1	0 (2)	6 (3)	4 (3)	1 (2)	1 (2)	1 (2)
N2	7 (4)	3 (3)	6 (4)	0 (3)	1 (3)	4 (3)
N3	4 (3)	4 (3)	4 (4)	-3 (2)	1 (2)	0 (2)
N4	2 (2)	5 (3)	7 (4)	3 (2)	0 (2)	-1 (2)
C1	4 (3)	13 (6)	1 (3)	-2 (4)	2 (3)	-1 (5)
C2	2 (2)	0 (2)	1 (2)	0 (2)	0 (2)	0 (2)
C3	2 (2)	3 (3)	1 (3)	-1 (3)	-2 (2)	1 (3)
C4	2 (2)	1 (2)	3 (3)	1 (2)	1 (2)	1 (2)
C5	1 (2)	0 (2)	1 (3)	0 (2)	0 (2)	0 (2)
C6	7 (4)	6 (4)	0 (3)	3 (3)	1 (3)	0 (3)
C7	16 (8)	9 (6)	1 (3)	-2 (6)	2 (4)	1 (4)
C8	8 (5)	2 (3)	12 (7)	0 (3)	5 (5)	-3 (4)
C9	14 (8)	5 (5)	6 (6)	0 (5)	1 (5)	5 (4)
C10	11 (7)	6 (5)	13 (8)	-1 (5)	2 (6)	8 (5)
C11	1 (3)	8 (5)	6 (4)	-1 (3)	1 (3)	2 (4)
C12	12 (6)	7 (5)	8 (6)	-2 (5)	0 (5)	-7 (5)
C13	4 (3)	8 (5)	0 (3)	-1 (3)	-1 (2)	0 (3)
C14	11 (5)	0 (2)	1 (3)	-2 (3)	2 (3)	0 (2)
C15	0 (2)	1 (2)	1 (2)	-1 (2)	0 (2)	0 (2)
C16	2 (3)	5 (4)	8 (5)	2 (3)	0 (3)	4 (4)
C17	5 (4)	1 (2)	4 (4)	-2 (3)	-4 (3)	2 (3)
C18	9 (6)	27 (1)	2 (4)	11 (7)	2 (4)	1 (6)
C19	4 (3)	7 (5)	3 (4)	-2 (3)	2 (3)	2 (3)
C20	3 (3)	4 (3)	2 (3)	1 (3)	2 (2)	-2 (3)

TABLE XV (Continued)

C21	1 (2)	0 (2)	1 (2)	0 (2)	0 (2)	0 (2)
C22	3 (3)	5 (4)	3 (4)	3 (3)	-2 (2)	-1 (3)
C23	1 (2)	1 (2)	1 (2)	0 (2)	0 (2)	-1 (2)
C24	3 (3)	13 (7)	7 (6)	-1 (4)	-3 (3)	-2 (5)

Anisotropic thermal parameters in the form:

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

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

TABLE XVI

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

I1 - Cu1	2.755 (9)	Cu1 - I1 - Cu2	62.6 (2)
I1 - Cu2	2.606 (8)	Cu1 - I2 - Cu2	63.7 (2)
I2 - Cu1	2.656 (9)	I1 - Cu1 - I2	113.7 (2)
I2 - Cu2	2.629 (9)	I1 - Cu1 - N1	104 (1)
Cu1 - N1	2.14 (3)	I1 - Cu1 - N2	104 (1)
Cu1 - N2	2.10 (5)	I2 - Cu1 - N1	108 (1)
Cu2 - N3	2.10 (4)	I2 - Cu1 - N2	111 (1)
Cu2 - N4	2.24 (4)	N1 - Cu1 - N2	114 (1)
N1 - C1	1.48 (6)	I1 - Cu2 - I2	119(2)
N1 - C5	1.32 (5)	I1 - Cu2 - N3	113 (1)
C1 - C2	1.43 (7)	I1 - Cu2 - N4	103 (1)
C2 - C3	1.42 (6)	I2 - Cu2 - N3	113 (1)
C3 - C4	1.49 (6)	I2 - Cu2 - N4	100 (1)
C3 - C6	1.47 (7)	N3 - Cu2 - N4	102 (1)
C4 - C5	1.74 (6)	Cu1 - N1 - C1	115 (3)
N2 - C7	1.42 (8)	Cu1 - N1 - C5	103 (2)
N2 - C11	1.40 (9)	C1 - N1 - C5	106 (4)
C7 - C8	1.40 (9)	N1 - C1 - C2	120 (5)
C8 - C9	1.41 (9)	C1 - C2 - C3	107 (4)
C9 - C10	1.2 (1)	C2 - C3 - C4	119 (4)
C9 - C12	1.3 (1)	C2 - C3 - C6	108 (4)
C10 - C11	1.4 (1)	C4 - C3 - C6	111 (4)
N3 - C13	1.41 (7)	C3 - C4 - C5	100 (3)
N3 - C17	1.41 (6)	C4 - C5 - N1	112 (3)
C13 - C14	1.46 (7)	Cu1 - N2 - C7	117 (4)
C14 - C15	1.42 (6)	Cu1 - N2 - C11	122 (4)
C15 - C16	1.39 (7)	C7 - N2 - C11	107 (5)
C15 - C18	1.31 (7)	N2 - C7 - C8	109 (6)
C16 - C17	1.51 (7)	C7 - C8 - C9	122 (6)
N4 - C19	1.36 (7)	C8 - C9 - C10	112 (7)

TABLE XVI (Continued)

N4 - C23	1.53 (5)	C8 - C9 - C12	123 (7)
C19 - C20	1.43 (7)	C9 - C10 - C11	117 (6)
C20 - C21	1.40 (6)	C10 - C9 - C12	123 (7)
C21 - C22	1.50 (6)	C10 - C11 - N2	126 (5)
C21 - C24	1.53 (7)	Cu2 - N3 - C13	117 (3)
C22 - C23	1.62 (6)	Cu2 - N3 - C17	122 (3)
		C13 - N3 - C17	103 (4)
		N3 - C13 - C14	111 (4)
		C13 - C14 - C15	116 (4)
		C14 - C15 - C16	105 (4)
		C14 - C15 - C18	107 (5)
		C16 - C15 - C18	118 (4)
		C15 - C16 - C17	110 (3)
		C16 - C17 - N3	115 (4)
		Cu2 - N4 - C19	115 (3)
		Cu2 - N4 - C23	106 (3)
		C19 - N4 - C23	120 (4)
		N4 - C19 - C20	113 (4)
		C19 [illegible] - C21	120 (4)
		C20 - C21 - C22	103 (3)
		C20 - C21 - C24	114 (4)
		C22 - C21 - C24	108 (4)
		C21 - C22 - C23	111 (3)
		C22 - C23 - N4	104 (3)

TABLE XVII

CRYSTAL DATA FOR COPPER IODIDE HEXAMETHYLENEIMINE

Formula	$(CuIC_6NH_{13})_4$
MWT	1158.50
a	19.332(8) Å
b	7.910(2)
c	11.958(3)
α	102.58 (2) °
β	82.80(2)
γ	98.14(3)
V	1758(1) $Å^3$
F (000)	1104
μMoK_α	58.91 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.181 g cm^{-3}
Z	2
Meas. Refl.	6229
Obs. Refl.	1500
R	8.3%
Space Group	P1 bar
Octants Meas.	

TABLE XVIII

POSITIONAL PARAMETERS FOR COPPER IODIDE HEXAMETHYLENEIMINE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.6413 (2)	0.4023 (6)	0.6976 (4)
I2	0.7214 (2)	0.1183 (6)	0.9409 (4)
I3	0.7869 (2)	-0.0060 (6)	0.5595 (4)
I4	0.8647 (2)	0.5231 (5)	0.7882 (4)
Cu1	0.7313 (5)	0.4144 (11)	0.8539 (7)
Cu2	0.6888 (5)	0.1052 (11)	0.7295 (8)
Cu3	0.7778 (4)	0.3346 (10)	0.6227 (7)
Cu4	0.8275 (4)	0.1845 (10)	0.7724 (7)
N1	0.701 (2)	0.595 (7)	0.989 (4)
N2	0.615 (3)	-0.081 (8)	0.709 (4)
N3	0.801 (2)	0.502 (6)	0.505 (4)
N4	0.898 (2)	0.023 (6)	0.799 (3)
C1	0.624 (3)	0.567 (8)	1.023 (5)
C2	0.596 (5)	0.708 (9)	1.121 (8)
C3	0.625 (6)	0.741 (10)	1.242 (8)
C4	0.697 (10)	0.779 (7)	1.248 (4)
C5	0.720 (7)	0.809 (11)	1.186 (7)
C6	0.739 (4)	0.[illegible] (8)	1.096 (5)
C7	0.590 (5)	-0.111 (9)	0.598 (5)
C8	0.527 (6)	-0.255 (11)	0.557 (7)
C9	0.459 (8)	-0.256 (7)	0.627 (9)
C10	0.441 (4)	-0.249 (11)	0.730 (8)
C11	0.489 (4)	-0.182 (7)	0.824 (6)
C12	0.559 (4)	-0.088 (11)	0.780 (6)
C13	0.863 (6)	0.553 (10)	0.484 (11)
C14	0.904 (5)	0.433 (14)	0.426 (8)
C15	0.894 (4)	0.296 (10)	0.303 (7)
C16	0.831 (4)	0.260 (10)	0.257 (6)

TABLE XVIII (Continued)

C17	0.758 (3)	0.316 (9)	0.330 (5)
C18	0.755 (4)	0.467 (11)	0.418 (6)
C19	0.916 (3)	0.048 (9)	0.913 (7)
C20	0.957 (4)	0.221 (8)	0.955 (5)
C21	1.026 (4)	0.268 (10)	0.905 (6)
C22	1.051 (5)	0.213 (13)	0.800 (11)
C23	1.008 (4)	0.149 (7)	0.694 (5)
C24	0.955 (3)	-0.030 (10)	0.698 (5)

TABLE XIX

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE HEXAMETHYLENEIMINE

ATOM	X	Y	Z
H1	0.7079	0.7153	0.9661
H2	0.6287	-0.1927	0.6969
H3	0.7954	0.6259	0.5536
H4	0.8732	-0.1029	0.7553
H11	0.6034	0.5406	0.9508
H12	0.6212	0.4610	1.0529
H21	0.5919	0.8077	1.0817
H22	0.5358	0.6539	1.1121
H31	0.5771	0.8074	1.2814
H32	0.6038	0.6211	1.2541
H41	0.6740	0.9353	1.2930
H42	0.6891	0.7585	1.3217
H51	0.7250	0.8965	1.1456
H52	0.7696	0.8313	1.2269
H61	0.7910	0.6792	1.0666
H62	0.7362	0.5568	1.1323
H71	0.5521	-0.0056	0.6052
H72	0.6178	-0.0936	0.5370
H81	0.5388	-0.2887	0.4761
H82	0.5475	-0.3527	0.5897
H91	0.4561	-0.0905	0.6199
H92	0.4251	-0.2776	0.5556
H101	0.3939	-0.2306	0.7510
H102	0.4357	-0.3945	0.7057
H111	0.4659	-0.1270	0.8852
H112	0.5058	-0.2948	0.8431
H121	0.5362	0.0147	0.7612
H122	0.5808	-0.0413	0.8466
H131	0.8778	0.5890	0.3914

TABLE XIX (Continued)

H132	0.9000	0.6315	0.5186
H141	0.9547	0.4338	0.4474
H142	0.8843	0.3325	0.4946
H151	0.9252	0.3502	0.2504
H152	0.9058	0.1748	0.2968
H161	0.8309	0.3267	0.1914
H162	0.8173	0.1372	0.2191
H171	0.7239	0.3022	0.2858
H172	0.7500	0.2235	0.3812
H181	0.7630	0.5787	0.3818
H182	0.7046	0.4788	0.4571
H191	0.8767	0.0189	0.9587
H192	0.9512	-0.0417	0.9099
H201	0.9231	0.3093	0.9646
H202	0.9629	0.2226	1.0414
H211	1.0228	0.4004	0.8863
H212	1.0619	0.2959	0.9531
H221	1.0943	0.2453	0.7864
H222	1.0493	0.0791	0.8230
H231	0.9784	0.2450	0.6760
H232	1.0324	0.1135	0.6128
H241	0.9343	-0.0838	0.6288
H242	0.9826	-0.1107	0.7196

TABLE XX

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE HEXAMETHYLENEIMINE

ATOM	U11	U22	U33	U12	U13	U23
I1	40 (3)	91 (4)	49 (3)	20 (2)	0 (2)	21 (2)
I2	43 (3)	83 (3)	51 (3)	12 (2)	3 (2)	28 (2)
I3	53 (3)	58 (3)	49 (3)	23 (2)	3 (2)	4 (2)
I4	47 (3)	43 (3)	50 (3)	0 (2)	-4 (2)	3 (2)
Cu1	67 (6)	69 (6)	47 (5)	24 (5)	-2 (4)	-15 (4)
Cu2	55 (6)	71 (6)	64 (6)	3 (4)	0 (4)	9 (4)
Cu3	59 (6)	49 (5)	69 (6)	16 (4)	4 (5)	22 (4)
Cu4	54 (5)	44 (5)	70 (6)	20 (4)	-4 (4)	10 (4)
N1	2 (3)	13 (5)	3 (3)	-1 (3)	-3 (3)	1 (3)
N2	12 (6)	12 (5)	0 (3)	-9 (4)	-1 (3)	0 (3)
N3	3 (3)	5 (3)	6 (4)	6 (4)	1 (3)	0 (3)
N4	1 (2)	7 (4)	1 (2)	0 (2)	1 (2)	0 (2)
C1	6 (5)	5 (4)	4 (4)	-2 (4)	3 (4)	-4 (3)
C2	13 (8)	5 (5)	9 (7)	6 (5)	5 (6)	-2 (5)
C3	18 (1)	8 (7)	8 (7)	9 (7)	6 (8)	-2 (5)
C4	34 (3)	25 (7)	21 (6)	60 (9)	13 (4)	22 (1)
C5	25 (5)	9 (7)	3 (5)	-5 (7)	-3 (7)	-3 (4)
C6	12 (7)	6 (5)	1 (4)	0 (4)	0 (4)	-1 (3)
C7	15 (8)	7 (6)	3 (4)	0 (5)	5 (5)	1 (4)
C8	14 (9)	13 (8)	4 (6)	-6 (7)	-2 (6)	1 (5)
C9	22 (7)	51 (8)	3 (7)	6 (6)	9 (9)	-2 (1)
C10	5 (5)	15 (8)	10 (8)	0 (5)	-4 (5)	-4 (6)
C11	6 (5)	1 (3)	8 (5)	-2 (3)	-2 (4)	-2 (3)
C12	5 (5)	16 (8)	7 (6)	0 (5)	-5 (5)	-4 (5)
C13	13 (9)	3 (5)	28 (5)	6 (6)	-5 (9)	2 (6)
C14	8 (7)	21 (1)	11 (8)	-7 (7)	-9 (6)	9 (8)
C15	4 (5)	12 (7)	12 (8)	6 (5)	4 (5)	-1 (6)
C16	8 (6)	13 (8)	7 (6)	3 (5)	5 (5)	-5 (5)
C17	2 (4)	10 (6)	4 (4)	2 (4)	-3 (3)	0 (4)

TABLE XX (Continued)

C18	4 (5)	17 (9)	5 (5)	-5 (5)	2 (4)	-2 (5)
C19	0 (3)	8 (6)	12 (7)	1 (3)	-1 (4)	2 (5)
C20	9 (6)	5 (4)	2 (4)	1 (4)	-3 (4)	-1 (3)
C21	6 (6)	15 (7)	4 (5)	-2 (5)	0 (5)	-8 (5)
C22	7 (7)	21 (1)	18 (2)	7 (7)	-5 (7)	15 (9)
C23	10 (6)	1 (3)	3 (4)	-1 (4)	2 (4)	-2 (3)
C24	2 (3)	14 (7)	3 (4)	4 (4)	0 (3)	2 (4)

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

TABLE XXI

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

I1 - Cu1	2.68 (1)	Cu1 - I1 - Cu2	58.2 (2)
I1 - Cu2	2.75 (1)	Cu1 - I1 - Cu3	60.9 (2)
I1 - Cu3	2.763 (9)	Cu2 - I1 - Cu3	59.2 (2)
I2 - Cu1	2.73 (1)	Cu1 - I2 - Cu2	58.7 (2)
I2 - Cu2	2.65 (1)	Cu1 - I2 - Cu4	59.4 (2)
I2 - Cu4	2.764 (9)	Cu2 - I2 - Cu4	60.8 (2)
I3 - Cu2	2.687 (9)	Cu2 - I3 - Cu3	61.4 (2)
I3 - Cu3	2.658 (9)	Cu2 - I3 - Cu4	60.0 (2)
I3 - Cu4	2.802 (9)	Cu3 - I3 - Cu4	58.8 (2)
I4 - Cu1	2.672 (9)	Cu1 - I4 - Cu3	60.7 (2)
I4 - Cu3	2.790 (9)	Cu1 - I4 - Cu4	61.7 (2)
I4 - Cu4	2.463 (8)	Cu3 - I4 - Cu4	59.1 (2)
Cu1 - Cu2	2.64 (1)	I1 - Cu1 - I2	114.8 (3)
Cu1 - Cu3	2.76 (1)	I1 - Cu1 - I3	114.1 (3)
Cu1 - Cu4	2.72 (1)	I2 - Cu1 - I3	111.0 (3)
Cu1 - N1	1.99 (4)	I1 - Cu2 - I2	115.0 (3)
Cu2 - Cu3	2.72 (1)	I1 - Cu2 - I3	111.0 (3)
Cu2 - Cu4	2.74 (1)	I2 - Cu2 - I3	114.9 (3)
Cu2 - N2	1.89 (6)	I1 - Cu3 - I3	111.6 (3)
Cu3 - Cu4	2.68 (1)	I1 - Cu3 - I4	108.1 (2)
Cu3 - N3	2.09 (5)	I3 - Cu3 - I4	116.5 (3)
Cu4 - N4	2.08 (4)	I2 - Cu4 - I3	108.0 (2)
N1 - C1	1.49 (7)	I2 - Cu4 - I4	111.5 (2)
N1 - C6	1.51 (8)	I3 - Cu4 - I4	116.6 (3)
C1 - C2	1.53 (9)	Cu1 - N1 - C1	111 (3)
C2 - C3	1.5 (1)	Cu1 - N1 - C6	125 (4)
C3 - C4	1.3 (3)	C1 - N1 - C6	109 (4)
C4 - C5	1.09 (1)	N1 - C1 - C2	114 (5)
C5 - C6	1.4 (1)	C1 - C2 - C3	119 (7)
N2 - C7	1.42 (9)	C2 - C3 - C4	118 (4)

TABLE XXI (Continued)

N2 - C12	1.29 (2)	C3 - C4 - C5	118 (3)
C7 - C8	1.5 (1)	C4 - C5 - C6	116 (3)
C8 - C9	1.4 (1)	C5 - C6 - N1	122 (7)
C9 - C10	1.2 (1)	Cu2 - N2 - C7	112 (4)
C10 - C11	1.5 (1)	Cu2 - N2 - C12	122 (4)
C11 - C12	1.53 (9)	C7 - N2 - C12	105 (6)
N3 - C13	1.2 (1)	N2 - C7 - C8	124 (6)
N3 - C18	1.42 (9)	C7 - C8 - C9	120 (7)
C13 - C14	1.3 (1)	C8 - C9 - C10	133 (1)
C14 - C15	1.6 (1)	C9 - C10 - C11	125 (9)
C15 - C16	1.3 (1)	C10 - C11 - C12	111 (6)
C16 - C17	1.60 (9)	C11 - C12 - N2	151 (6)
C17 - C18	1.42 (9)	Cu3 - N3 - C13	117 (7)
N4 - C19	1.42 (8)	Cu3 - N3 - C18	113 (4)
N4 - C24	1.55 (6)	C13 - N3 - C18	119 (8)
C19 - C20	1.48 (8)	N3 - C13 - C14	116 (7)
C20 - C21	1.43 (9)	C13 - C14 - C15	128 (9)
C21 - C22	1.2 (1)	C14 - C15 - C16	121 (6)
C22 - C23	1.5 (1)	C15 - C16 - C17	122 (6)
C23 - C24	1.62 (8)	C16 - C17 - C18	123 (5)
		C17 - C18 - N3	119 (6)
		Cu4 - N4 - C19	116 (3)
		Cu4 - N4 - C24	117 (3)
		C19 - N4 - C24	117 (4)
		N4 - C19 - C20	114 (6)
		C19 - C20 - C21	121 (5)

TABLE XXI (Continued)

	C20 - C21 - C22	125 (7)
	C21 - C22 - C23	126 (7)
	C22 - C23 - C24	112 (6)
	C23 - C24 - N4	104 (4)

TABLE XXII

CRYSTAL DATA FOR COPPER IODIDE 3 - PYRROLINE

Formula	$(CuIC_4NH_7)_4$
MWT	259.55
a	7.404(2) Å
b	11.744(4)
c	17.654(6)
α	96.69(2) °
β	102.36(2)
γ	108.31(2)
V	1395.4(9) $Å^3$
F (000)	960
μMoKα	74.10 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	2.47 g cm^{-3}
Z	2
Meas. Refl.	4915
Obs. Refl.	1400
R	9.7 %
Space Group	P1bar
Octants Meas.	±h, k, ±l

TABLE XXIII

POSITIONAL PARAMETERS FOR COPPER IODIDE 3 - PYRROLINE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.6611 (8)	0.0447 (5)	0.1996 (3)
I2	1.1803 (8)	0.2769 (6)	0.1226 (3)
I3	0.9157 (8)	0.4545 (5)	0.3001 (3)
I4	1.2805 (8)	0.2232 (6)	0.3777 (4)
Cu1	1.067 (1)	0.132 (1)	0.224 (1)
Cu2	0.853 (1)	0.269 (1)	0.177 (1)
Cu3	0.906 (1)	0.231 (1)	0.322 (1)
Cu4	1.210 (1)	0.368 (1)	0.276 (1)
N1	1.135 (7)	-0.019 (5)	0.199 (4)
N2	0.683 (10)	0.304 (5)	0.086 (4)
N3	0.785 (11)	0.191 (5)	0.409 (4)
N4	1.461 (7)	0.516 (5)	0.306 (3)
C1	1.014 (9)	-0.086 (8)	0.106 (5)
C2	0.999 (16)	-0.210 (9)	0.106 (5)
C3	1.041 (13)	-0.228 (8)	0.195 (7)
C4	1.093 (12)	-0.111 (11)	0.244 (6)
C5	0.594 (12)	0.218 (8)	0.011 (5)
C6	0.560 (16)	0.289 (11)	-0.046 (6)
C7	0.678 (19)	0.417 (9)	-0.018 (7)
C8	0.742 (17)	0.422 (8)	0.071 (5)
C9	0.761 (13)	0.077 (8)	0.437 (6)
C10	0.770 (17)	0.105 (8)	0.520 (6)
C11	0.820 (18)	0.214 (14)	0.546 (5)
C12	0.864 (9)	0.270 (8)	0.488 (6)
C13	1.497 (8)	0.577 (7)	0.388 (4)
C14	1.600 (15)	0.715 (12)	0.385 (6)
C15	1.555 (19)	0.733 (9)	0.310 (9)
C16	1.452 (8)	0.604 (8)	0.254 (4)

TABLE XXIV

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE 3 - PYRROLINE

ATOM	X	Y	Z
H1	1.2704	0.0189	0.1966
H2	0.5500	0.2958	0.1071
H3	0.6463	0.1965	0.3907
H4	1.5432	0.4729	0.2926
H11	0.8878	-0.0759	0.0861
H12	1.0919	-0.0581	0.0657
H21	0.9840	-0.2741	0.0799
H31	1.0070	-0.2950	0.2209
H41	1.0318	-0.0889	0.2849
H42	1.2474	-0.0879	0.2873
H51	0.7256	0.1933	0.0101
H52	0.5023	0.1461	0.0129
H61	0.4730	0.2311	-0.1002
H71	0.6905	0.4554	-0.0596
H81	0.8954	0.4606	0.0836
H82	0.0737	0.4888	0.0913
H91	0.6237	0.0018	0.3958
H92	0.8552	0.0350	0.4135
H101	0.7354	0.0305	0.5458
H111	0.8461	0.2239	0.6096
H121	0.8121	0.3361	0.5011
H122	1.0097	0.3092	0.5037
H131	1.3916	0.5588	0.4084
H132	1.6097	0.5587	0.4202
H141	1.6357	0.7923	0.4342
H151	1.6084	0.8194	0.2931
H161	1.3426	0.5948	0.2211
H162	1.5563	0.5957	0.2200

TABLE XXV

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIE 3 - PYRROLINE

ATOM	U11	U22	U33	U12	U13	U23
I1	53 (3)	37 (4)	51 (4)	7 (2)	11 (3)	7 (3)
I2	58 (3)	56 (4)	40 (4)	19 (3)	18 (3)	15 (3)
I3	63 (3)	32 (3)	49 (4)	17 (3)	14 (3)	3 (3)
I4	56 (3)	53 (4)	45 (4)	22 (3)	4 (2)	14 (3)
Cu1	55 (6)	52 (7)	76 (8)	24 (5)	19 (5)	8 (6)
Cu2	48 (6)	65 (7)	73 (8)	21 (5)	16 (5)	19 (6)
Cu3	60 (6)	66 (8)	69 (7)	29 (6)	31 (5)	22 (6)
Cu4	42 (5)	45 (6)	70 (7)	5 (4)	9 (5)	7 (5)
N1	3 (3)	2 (4)	5 (4)	-2 (3)	0 (3)	2 (3)
N2	11 (6)	1 (4)	5 (4)	2 (4)	0 (4)	1 (3)
N3	14 (7)	1 (4)	4 (4)	1 (4)	3 (3)	2 (3)
N4	4 (7)	2 (4)	5 (4)	2 (3)	4 (3)	1 (3)
C1	1 (3)	5 (6)	9 (7)	2 (4)	0 (4)	-2 (5)
C2	16 (1)	2 (6)	4 (6)	-4 (6)	1 (6)	-2 (5)
C3	9 (7)	1 (5)	10 (9)	0 (5)	3 (6)	3 (6)
C4	6 (6)	119 (3)	10 (9)	7 (7)	5 (6)	8 (8)
C5	11 (7)	6 (6)	4 (5)	8 (6)	0 (5)	-1 (5)
C6	1 (1)	16 (1)	9 (8)	12 (9)	7 (7)	9 (8)
C7	22 (4)	1 (5)	10 (9)	0 (6)	0 (8)	3 (6)
C8	21 (1)	2 (6)	1 (5)	5 (6)	0 (5)	0 (4)
C9	11 (7)	1 (5)	7 (8)	1 (5)	4 (6)	3 (5)
C10	18 (1)	2 (5)	4 (6)	1 (6)	6 (7)	3 (5)
C11	15 (1)	14 (4)	1 (5)	0 (1)	-1 (6)	-2 (7)
C12	1 (4)	7 (7)	2 (7)	-2 (4)	-1 (4)	2 (6)
C13	0 (3)	5 (6)	4 (5)	1 (3)	0 (3)	0 (4)
C14	10 (8)	13 (2)	5 (7)	9 (8)	-2 (6)	3 (7)

TABLE XXV (Continued)

C15	16 (1)	3 (7)	14 (7)	6 (7)	16 (3)	4 (9)
C16	0 (3)	6 (6)	5 (5)	0 (3)	0 (3)	1 (5)

Anisotropic thermal parameters in the form:

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

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

TABLE XXVI

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

I1 - Cu1	2.76 (1)	Cu1 - I1 - Cu2	58.5 (3)
I1 - Cu2	2.68 (1)	Cu1 - I1 - Cu3	57.7 (3)
I1 - Cu3	2.73 (1)	Cu2 - I1 - Cu3	57.6 (3)
I2 - Cu1	2.69 (1)	Cu1 - I2 - Cu2	58.4 (3)
I2 - Cu2	2.76 (1)	Cu1 - I2 - Cu4	57.5 (3)
I2 - Cu4	2.72 (1)	Cu2 - I2 - Cu4	57.5 (3)
I3 - Cu2	2.74 (1)	Cu2 - I3 - Cu3	57.7 (3)
I3 - Cu3	2.68 (1)	Cu2 - I3 - Cu4	57.3 (3)
I3 - Cu4	2.76 (1)	Cu3 - I3 - Cu4	58.6 (3)
I4 - Cu1	2.72 (1)	Cu1 - I4 - Cu3	57.9 (3)
I4 - Cu3	2.76 (1)	Cu1 - I4 - Cu4	57.5 (3)
I4 - Cu4	2.69 (1)	Cu3 - I4 - Cu4	58.5 (3)
Cu1 - Cu2	2.66 (1)	I1 - Cu1 - I2	112.1 (4)
Cu1 - Cu3	2.65 (1)	I1 - Cu1 - I4	115.2 (4)
Cu1 - Cu4	2.60 (1)	I1 - Cu1 - N1	104 (1)
Cu2 - Cu3	2.61 (1)	I2 - Cu1 - I4	114.2 (3)
Cu2 - Cu4	2.64 (1)	I2 - Cu1 - N1	107 (1)
Cu3 - Cu4	2.67 (1)	I4 - Cu1 - N1	101 (1)
Cu1 - N1	2.01 (6)	I1 - Cu2 - I2	112.3 (4)
Cu2 - N2	1.98 (6)	I1 - Cu2 - I3	114.0 (4)
Cu3 - N3	1.96 (7)	I1 - Cu2 - N2	108 (1)
Cu4 - N4	2.02 (4)	I2 - Cu2 - I3	115.2 (3)
N1 - C1	1.65 (9)	I2 - Cu2 - N2	101 (2)
N1 - C4	1.4 (1)	I3 - Cu2 - N2	103 (1)
N2 - C5	1.44 (9)	I1 - Cu3 - I3	114.3 (4)
N2 - C8	1.3 (1)	I1 - Cu3 - I4	115.0 (5)
N3 - C9	1.4 (1)	I1 - Cu3 - N3	101 (1)
N3 - C12	1.4 (1)	I3 - Cu3 - I4	112.2 (3)
N4 - C13	1.46 (9)	I3 - Cu3 - N3	109 (2)

TABLE XXVI (Continued)

N4 - C16	1.4 (1)	I4 - Cu3 - N3	103 (2)
C1 - C2	1.4 (1)	I2 - Cu4 - I3	115.7 (3)
C2 - C3	1.3 (1)	I2 - Cu4 - I4	114.3 (4)
C3 - C4	1.4 (1)	I2 - Cu4 - N4	103 (1)
C5 - C6	1.4 (1)	I3 - Cu4 - I4	111.8 (4)
C6 - C7	1.4 (1)	I3 - Cu4 - N4	105 (1)
C7 - C8	1.5 (1)	I4 - Cu4 - N4	104 (1)
C9 - C10	1.4 (1)	Cu1 - N1 - C1	107 (4)
C10 - C11	1.2 (1)	Cu1 - N1 - C4	119 (6)
C11 - C12	1.3 (1)	C1 - N1 - C4	106 (5)
C13 - C14	1.5 (1)	Cu2 - N2 - C5	121 (5)
C14 - C15	1.3 (2)	Cu2 - N2 - C8	117 (4)
C15 - C16	1.5 (1)	C5 - N2 - C8	108 (6)
		Cu3 - N3 - C9	122 (6)
		Cu3 - N3 - C12	121 (4)
		C9 - N3 - C12	95 (6)
		Cu4 - N4 - C13	109 (4)
		Cu4 - N4 - C16	111 (3)
		C13 - N4 - C16	109 (5)
		N1 - C1 - C2	93 (6)
		C1 - C2 - C3	119 (8)
		C2 - C3 - C4	104 (9)
		C3 - C4 - N1	109 (8)
		N2 - C5 - C6	105 (7)
		C5 - C6 - C7	111 (8)
		C6 - C7 - C8	101 (9)
		C7 - C8 - N2	109 (6)
		N3 - C9 - C10	105 (7)
		C9 - C10 - C11	112 (9)
		C10 - C11 - C12	106 (9)
		C11 - C12 - N3	114 (8)

TABLE XXVI (Continued)

	N4 - C13 - C14	102 (6)
	C13 - C14 - C15	110 (7)
	C14 - C15 - C16	107 (9)
	C15 - C16 - N4	104 (7)

TABLE XXVII

CRYSTAL DATA FOR COPPER IODIDE MORPHOLINE ACETONITRILE

Formula	$Cu_4I_4(C_2NH_3)_2(C_4ONH_9)_2$
MWT	1018.15
a	15.959(6) Å
b	21.454(6)
c	7.681(2)
α	90.0 °
β	100.13(2)
γ	90.0
V	2589(1)
F (000)	1852
μMoK_α	79.89 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.611 g cm^{-3}
Z	4
Meas. Refl.	4941
Obs. Refl.	2414
R	7.2 %
Space Group	$P2_1 / n$
Octants Meas.	±h, k, l

TABLE XXVIII

POSITIONAL PARAMETERS FOR COPPER IODIDE MORPHLINE ACETONITRILE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.6197 (1)	0.1237 (1)	0.7351 (3)
I2	0.7452 (1)	0.0215 (1)	0.3360 (3)
I3	0.7330 (1)	0.2268 (1)	0.3186 (3)
I4	0.9041 (1)	0.1324 (1)	0.7645 (2)
Cu1	0.7509 (3)	0.1912 (2)	0.6587 (6)
Cu2	0.7611 (3)	0.0629 (2)	0.6729 (5)
Cu3	0.8346 (2)	0.1282 (2)	0.4286 (4)
Cu4	0.6609 (2)	0.1225 (2)	0.4140 (5)
O1	1.098 (1)	0.127 (1)	0.383 (3)
O2	0.374 (1)	0.118 (1)	0.093 (4)
N1	0.768 (2)	0.265 (1)	0.808 (4)
N2	0.789 (2)	-0.011 (1)	0.833 (3)
N3	0.919 (1)	0.127 (1)	0.254 (3)
N4	0.553 (1)	0.118 (1)	0.225 (3)
C1	0.783 (2)	0.306 (1)	0.901 (4)
C2	0.805 (2)	0.357 (1)	1.021 (5)
C3	0.808 (2)	-0.053 (1)	0.917 (4)
C4	0.835 (2)	-0.106 (1)	1.034 (4)
C5	0.974 (2)	0.181 (1)	0.249 (5)
C6	1.047 (2)	0.180 (1)	0.397 (5)
C7	1.042 (2)	0.070 (1)	0.402 (6)
C8	0.975 (2)	0.072 (1)	0.251 (4)
C9	0.500 (2)	0.064 (1)	0.248 (5)
C10	0.424 (2)	0.061 (2)	0.105 (6)
C11	0.424 (2)	0.170 (1)	0.064 (5)
C12	0.498 (2)	0.175 (1)	0.207 (5)

TABLE XXIX

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE MORPHOLINE ACETONITRILE

ATOM	X	Y	Z
H13	0.8828	0.1290	0.1380
H14	0.5719	0.1140	0.1093
H21	0.8359	0.3314	1.1167
H22	0.8461	0.3893	0.9855
H23	0.7600	0.3818	1.0594
H41	0.8810	-0.1149	0.9744
H42	0.8530	-0.0950	1.1602
H43	0.7928	-0.1395	1.0292
H51	0.9984	0.1833	0.1400
H52	0.9419	0.2216	0.2526
H61	1.0683	0.2212	0.4499
H62	1.0416	0.1527	0.4945
H71	1.0680	0.0334	0.4511
H72	1.0429	0.1020	0.4988
H81	0.9978	0.0721	0.1427
H82	0.9401	0.0354	0.2558
H91	0.5333	0.0266	0.2524
H92	0.4813	0.0690	0.3645
H101	0.4399	0.0542	-0.0115
H102	0.3847	0.0270	0.1231
H111	0.4486	0.1659	-0.0477
H112	0.3930	0.2100	0.0523
H121	0.5329	0.2137	0.1924
H122	0.4767	0.1828	0.3197

TABLE XXX

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE MORPHOLINE ACETONITRILE

ATOM	U11	U22	U33	U12	U13	U23
I1	70(1)	57(1)	52(1)	1(1)	25(1)	3(1)
I2	57(1)	29(1)	47(1)	47(1)	3(1)	-4(0)
I3	56(1)	30(1)	46(1)	-3(0)	0(1)	6(1)
I4	57(1)	79(1)	31(1)	0(1)	-4(0)	0(1)
Cu1	93(3)	50(2)	53(2)	-10(2)	8(2)	-18(2)
Cu2	76(2)	52(2)	48(2)	10 (2)	5(2)	19(2)
Cu3	54(2)	49(2)	36(1)	1(1)	7(1)	-1(2)
Cu4	50(2)	39(2)	50(2)	0(1)	-8(1)	1(2)
O1	3(1)	10(2)	9(2)	4(1)	1(1)	-1(2)
O2	4(1)	9(2)	13(2)	1(1)	-2(1)	-2(2)
N1	9(2)	4(2)	5(2)	-1(1)	0(2)	-1(1)
N2	10(2)	4(2)	4(1)	0(1)	1(1)	0(1)
N3	6(1)	5(1)	2(1)	-1(1)	0(1)	0(1)
N4	3(1)	4(1)	5(1)	0(1)	0(1)	0(1)
C1	7(2)	2(2)	6(2)	0(1)	-1(2)	0(2)
C2	9(2)	4(2)	7(2)	0(2)	2(2)	0(2)
C3	5(2)	3(2)	4(2)	0(1)	0(1)	1(1)
C4	9(2)	2(2)	6(2)	1(1)	2(2)	1(1)
C5	8(3)	5(2)	5(2)	2(2)	2(2)	1(2)
C6	9(3)	5(2)	8(3)	-4(2)	5(2)	-2(2)
C7	7(2)	3(2)	15(4)	1(2)	-5(3)	-2(2)
C8	6(2)	4(2)	5(2)	2(1)	2(2)	-1(2)
C9	3(1)	3(2)	12(3)	0(1)	-3(2)	-2(2)
C10	5(2)	5(2)	13(4)	-1(2)	2(2)	-3(2)
C11	7(2)	6(2)	5(2)	-2(2)	3(2)	0(2)
C12	5(2)	4(2)	10(3)	0(1)	-2(2)	0(2)

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 XXXI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE MORPHOLINE ACETONITRILE

I1 - Cu1	2.693 (5)	Cu1 - I1 - Cu2	61.2 (1)
I1 - Cu2	2.720 (5)	Cu1 - I1 - Cu4	58.3 (1)
I1 - Cu4	2.661 (4)	Cu2 - I1 - Cu4	58.9 (1)
I2 - Cu2	2.705 (4)	Cu2 - I2 - Cu3	61.1 (1)
I2 - Cu3	2.725 (4)	Cu2 - I2 - Cu4	59.0 (1)
I2 - Cu4	2.673 (4)	Cu3 - I2 - Cu4	61.4 (1)
I3 - Cu1	2.688 (4)	Cu1 - I3 - Cu3	61.3 (1)
I3 - Cu3	2.707 (4)	Cu1 - I3 - Cu4	58.2 (1)
I3 - Cu4	2.677 (4)	Cu3 - I3 - Cu4	61.6 (1)
I4 - Cu1	2.743 (5)	Cu1 - I4 - Cu2	60.7 (1)
I4 - Cu2	2.712 (4)	Cu1 - I4 - Cu3	61.6 (1)
I4 - Cu3	2.624 (3)	Cu2 - I4 - Cu3	62.3 (1)
Cu1 - Cu2	2.75 (5)	I1 - Cu1 - I3	114.2 (1)
Cu1 - Cu3	2.75 (6)	I1 - Cu1 - I4	112.0 (1)
Cu1 - Cu4	2.61 (5)	I3 - Cu1 - I4	110.7 (1)
Cu2 - Cu3	2.76 (5)	I1 - Cu1 - N1	110.1 (9)
Cu2 - Cu4	2.65 (5)	I3 - Cu1 - N3	108.6 (8)
Cu3 - Cu4	2.75 (5)	I4 - Cu1 - N1	100.0 (8)
Cu1 - N1	1.95 (2)	I1 - Cu2 - I2	112.6 (1)
Cu2 - N2	2.01 (2)	I1 - Cu2 - I4	112.1 (1)
Cu3 - N3	2.05 (2)	I2 - Cu2 - I4	111.2 (1)
Cu4 - N4	2.04 (1)	I1 - Cu2 - N2	111.9 (8)
N1 - C1	1.12 (4)	I2 - Cu2 - N2	107.3 (7)
C1 - C2	1.42 (4)	I4 - Cu2 - N2	100.9 (7)
N2 - C3	1.11 (3)	I2 - Cu3 - I3	108.4 (1)
C3 - C4	1.47 (4)	I2 - Cu3 - I4	113.3 (1)
N3 - C5	1.46 (4)	I2 - Cu3 - N3	101.2 (6)
N3 - C8	1.49 (3)	I3 - Cu3 - N3	103.0 (6)
C5 - C6	1.46 (4)	I4 - Cu3 - N3	115.5 (5)

TABLE XXXI (Continued)

C6 - O1	1.42 (4)	I1 - Cu4 - I2	115.5 (1)
O1 - C7	1.52 (4)	I1 - Cu4 - I3	115.6 (1)
C7 - C8	1.43 (4)	I2 - Cu4 - I3	110.9 (1)
N4 - C9	1.44 (3)	I1 - Cu4 - N4	110.0 (6)
N4 - C12	1.49 (3)	I2 - Cu4 - N4	101.1 (6)
C9 - C10	1.49 (4)	I3 - Cu4 - N4	101.3 (6)
C10 - O2	1.45 (4)	Cu1 - N1 - C1	175 (2)
O2 - C11	1.40 (4)	N1 - C1 - C2	177 (3)
C11 - C12	1.47 (4)	Cu2 - N2 - C3	176 (2)
		N2 - C3 - C4	177 (3)
		Cu3 - N3 - C5	118 (2)
		Cu3 - N3 - C8	118 (1)
		C5 - N3 - C8	104 (2)
		N3 - C5 - C6	111 (2)
		C5 - C6 - O1	110 (2)
		C6 - O1 - C7	106 (2)
		O1 - C7 - C8	105 (2)
		C7 - C8 - N3	112 (2)
		Cu4 - N4 - C9	112 (1)
		C9 - N4 - C12	108 (2)
		N4 - C9 - C10	111 (2)
		C9 - C10 - O2	111 (2)
		C10 - O2 - C11	111 (2)
		O2 - C11 - C12	109 (2)
		C11 - C12 - N4	112 (2)

TABLE XXXII

CRYSTAL DATA FOR COPPER IODIDE 1,2,3,6 - TETRAHYDROPYRIDINE

Formula	$(CuIC_5NH_9)_4$
MWT	1094.33
a	7.499(2) Å
b	12.058(6)
c	18.887(9)
α	87.78(4) °
β	101.26(3)
γ	71.75(3)
V	1581(1) Å^3
F (000)	1024
μMoK_α	65.43 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.297 g cm^{-3}
Z	2
Meas. Refl.	5607
Obs. Refl.	1597
R	6.5 %
Space Group	P1bar
Octants Meas.	±h, k, ±l

TABLE XXXIII

POSITIONAL PARAMETERS FOR COPPER IODIDE 1,2,3,6 - TETRAMETHYLPYRIDINE

ATOM	X (SIG (X))	Y (SIG (Y))	Z(SIG (Z))
I1	-0.2875 (5)	0.4435 (3)	-0.2790 (2)
I2	-0.0650 (5)	0.0564 (3)	-0.2209 (2)
I3	0.2965 (5)	0.2858 (3)	-0.1321 (2)
I4	0.2148 (5)	0.2140 (3)	-0.3676 (2)
Cu1	-0.0578 (5)	0.2664 (6)	-0.1800 (4)
Cu2	-0.1118 (9)	0.2339 (6)	-0.3202 (4)
Cu3	0.2322 (9)	0.1380 (6)	-0.2313 (4)
Cu4	0.102 (1)	0.362 (1)	-0.2690 (4)
N1	-0.184 (5)	0.293 (3)	-0.090 (2)
N2	-0.298(4)	0.212 (3)	-0.410 (2)
N3	0.475 (4)	-0.010 (3)	-0.202 (2)
N4	0.166 (6)	0.509 (3)	-0.298 (2)
C1	-0.078 (14)	0.197 (10)	-0.034 (4)
C2	-0.215 (10)	0.199 (7)	0.025 (4)
C3	-0.228 (1)	0.298 (9)	0.057 (3)
C4	-0.252 (9)	0.392 (8)	0.020 (5)
C5	-0.159 (11)	0.403 (6)	-0.057 (4)
C6	-0.347 (12)	0.299 (7)	-0.466 (4)
C7	-0.539 (10)	0.294 (7)	-0.525 (4)
C8	-0.493 (13)	0.207 (14)	-0.559 (6)
C9	-0.383 (12)	0.112 (9)	-0.523 (4)
C10	-0.207 (12)	0.099 (7)	-0.442 (4)
C11	0.496 (9)	-0.096 (4)	-0.254 (3)
C12	0.659 (9)	-0.200 (6)	-0.227 (3)
C13	0.699 (7)	-0.240 (4)	-0.155 (4)
C14	0.649 (8)	-0.174 (6)	-0.108 (3)
C15	0.483 (9)	-0.055 (6)	-0.127 (3)
C16	0.145 (7)	0.592 (4)	-0.248 (3)

TABLE XXXIII (Continued)

C17	0.174 (11)	0.702 (5)	-0.275 (3)
C18	0.113 (8)	0.739 (5)	-0.348 (4)
C19	0.092 (11)	0.673 (6)	-0.396 (4)
C20	0.058 (9)	0.557 (6)	-0.373 (3)

TABLE XXXIV

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE 1,2,3,6 - TETRAMETHYLPYRIDINE

ATOM	X	Y	Z
H1	-0.3196	0.2954	-0.1056
H2	-0.4180	0.2092	-0.3973
H3	0.5888	0.0159	-0.1968
H4	0.3009	0.4842	-0.3037
H11	-0.0539	0.1264	-0.0583
H12	0.0385	0.2078	-0.0124
H21	-0.3330	0.1738	0.0092
H22	-0.1596	0.1688	0.0738
H31	-0.2012	0.2965	-0.0483
H41	-0.3076	0.4486	0.0514
H51	-0.2157	0.4726	-0.0904
H52	-0.0152	0.3908	-0.0432
H61	-0.3667	0.3764	-0.4438
H62	-0.2410	0.2904	-0.4901
H71	-0.6419	0.2900	-0.4963
H72	-0.6076	0.3744	-0.5547
H81	-0.5224	0.2242	-0.6113
H91	-0.3961	0.0388	-0.5431
H101	-0.1836	0.0354	-0.4078
H102	-0.0855	0.1059	-0.4513
H111	0.3762	-0.1178	-0.2606
H112	0.4938	-0.0564	-0.3003
H121	0.6506	-0.2590	-0.2594
H122	0.7737	-0.1754	-0.2371
H131	0.7634	-0.3252	-0.1429
H141	0.7242	-0.2002	-0.0568
H151	0.3582	-0.3582	-0.1219
H152	0.5024	-0.0021	-0.0908

TABLE XXXIV (Continued)

H161	0.0185	-0.6134	-0.2387
H162	0.2369	0.5560	-0.2015
H171	0.1257	0.7615	-0.2446
H172	0.3229	0.6828	-0.2611
H181	0.0825	0.8229	-0.3606
H191	0.0907	0.6985	-0.4467
H201	-0.0792	0.5664	-0.3784
H202	0.1031	0.4960	-0.4070

TABLE XXXV

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 1,2,3,6 - TETRAMETHYLPYRIDINE

ATOM	U11	U22	U33	U12	U13	U23
I1	40 (2)	47 (2)	73 (2)	-7 (1)	13 (1)	-6 (2)
I2	51 (2)	48 (2)	75 (2)	-23 (1)	19 (1)	-6 (2)
I3	42 (2)	65 (2)	56 (2)	-25 (1)	9 (1)	-21 (2)
I4	45 (2)	66 (2)	57 (2)	-22 (1)	24 (1)	-20 (2)
Cu1	60 (4)	72 (5)	67 (5)	-25 (3)	24 (3)	-13 (4)
Cu2	55 (4)	66 (4)	69 (5)	-22 (3)	4 (3)	-14 (4)
Cu3	53 (4)	54 (4)	75 (5)	-4 (3)	13 (3)	-6 (3)
Cu4	72 (4)	56 (4)	72 (5)	-30 (3)	17 (3)	-5 (4)
N1	4 (2)	3 (2)	4 (2)	-2 (2)	2 (2)	-2 (2)
N2	2 (2)	3 (2)	4 (3)	-3 (2)	0 (2)	-2 (2)
N3	1 (2)	4 (3)	7 (3)	1 (2)	1 (2)	1 (2)
N4	7 (3)	4 (3)	7 (3)	-4 (2)	2 (2)	1 (2)
C1	24 (1)	31 (4)	2 (6)	3 (9)	6 (6)	-4 (7)
C2	12 (5)	16 (8)	4 (5)	3 (5)	7 (4)	0 (5)
C3	19 (8)	15 (9)	1 (4)	-7 (7)	4 (4)	-9 (4)
C4	9 (5)	14 (8)	12 (7)	-4 (5)	7 (5)	1 (6)
C5	18 (7)	7 (5)	11 (6)	1 (5)	-5 (5)	-6 (4)
C6	2 (1)	12 (8)	4 (5)	-2 (6)	-8 (5)	2 (5)
C7	14 (6)	17 (8)	5 (5)	-1 (1)	- 3 (4)	-4 (5)
C8	15 (9)	4 (1)	1 (1)	118 (4)	11 (7)	19 (2)
C9	14 (6)	253 (5)	9 (6)	17 (8)	8 (5)	13 (7)
C10	28 (9)	14 (7)	9 (5)	11 (6)	8 (5)	-7 (5)
C11	15 (6)	3 (3)	5 (4)	-5 (4)	4 (4)	-3 (3)
C12	12 (5)	9 (5)	4 (4)	10 (4)	0 (3)	-2 (3)
C13	5 (3)	2 (3)	13 (6)	-1 (2)	-2 (3)	-2 (3)
C14	7 (4)	9 (5)	6 (4)	-1 (3)	0 (3)	-3 (4)
C15	10 (5)	8 (5)	9 (6)	1 (4)	7 (4)	0 (4)
C16	13 (5)	3 (3)	4 (4)	2 (3)	0 (3)	-3 (3)

TABLE XXXV (Continued)

C17	21 (8)	7 (4)	7 (5)	11 (5)	2 (5)	-3 (4)
C18	8 (4)	4 (4)	13 (6)	-1 (3)	5 (4)	4 (4)
C19	19 (4)	7 (5)	6 (5)	-8 (5)	2 (5)	-1 (4)
C20	10 (5)	11 (6)	1 (4)	-6 (4)	-4 (3)	2 (3)

Anisotropic thermal parameters in the form:

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

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

TABLE XXXVI

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR COPPER IODIDE 1,2,3,6 - TETRAMETHYLPYRIDINE

I1 - Cu1	2.672 (6)	Cu1 - I1 - Cu2	59.6 (2)
I1 - Cu2	2.682 (7)	Cu1 - I1 - Cu4	58.6 (2)
I1 - Cu4	2.739 (7)	Cu2 - I1 - Cu4	58.1 (2)
I2 - Cu1	2.689 (8)	Cu1 - I2 - Cu2	59.4 (2)
I2 - Cu2	2.678 (8)	Cu1 - I2 - Cu3	57.8 (2)
I2 - Cu3	2.738 (8)	Cu2 - I2 - Cu3	58.8 (2)
I3 - Cu1	2.718 (8)	Cu1 - I3 - Cu3	57.8 (2)
I3 - Cu3	2.711 (8)	Cu1 - I3 - Cu4	59.1 (2)
I3 - Cu4	2.673 (7)	Cu3 - I3 - Cu4	57.3 (2)
I4 - Cu2	2.712 (8)	Cu2 - I4 - Cu3	59.4 (2)
I4 - Cu3	2.662 (8)	Cu2 - I4 - Cu4	58.2 (2)
I4 - Cu4	2.700 (8)	Cu3 - I4 - Cu4	57.6 (2)
Cu1 - Cu2	2.66 (1)	I1 - Cu1 - I2	112.0 (2)
Cu1 - Cu3	2.62 (1)	I1 - Cu1 - I3	112.4 (3)
Cu1 - Cu4	2.66 (2)	I2 - Cu1 - I3	116.2 (2)
Cu1 - N1	2.08 (3)	I1 - Cu1 - N1	103.7 (8)
Cu2 - Cu3	2.66 (1)	I2 - Cu1 - N1	106 (1)
Cu2 - Cu4	2.63 (1)	I3 - Cu1 - N1	104 (1)
Cu2 - N2	2.05 (3)	I1 - Cu2 - I2	112.0 (3)
Cu3 - Cu4	2.58 (1)	I1 - Cu2 - I4	116.0 (3)
Cu3 - N3	2.07 (2)	I2 - Cu2 - I4	112.2 (2)
Cu4 - N4	2.06 (4)	I1 - Cu2 - N2	106.2 (8)
N1 - C1	1.44 (9)	I2 - Cu2 - N2	105 (1)
N1 - C5	1.54 (8)	I4 - Cu2 - N2	103 (1)
N2 - C6	1.36 (8)	I2 - Cu3 - I3	114.8 (3)
N2 - C10	1.52 (8)	I2 - Cu3 - I4	111.9 (2)
N3 - C11	1.45 (6)	I3 - Cu3 - I4	114.5 (3)
N3 - C15	1.47 (8)	I2 - Cu3 - N3	103 (1)
N4 - C16	1.40 (7)	I3 - Cu3 - N3	103 (1)
N4 - C20	1.47 (6)	I4 - Cu3 - N3	106 (1)

TABLE XXXVI (Continued)

C1 - C2	1.6 (1)	I1 - Cu4 - I3	111.8 (3)
C2 - C3	1.3 (1)	I1 - Cu4 - I4	114.5 (2)
C3 - C4	1.2 (1)	I3 - Cu4 - I4	114.5 (2)
C4 - C5	1.7 (1)	I1 - Cu4 - N4	103 (1)
C6 - C7	1.6 (1)	I3 - Cu4 - N4	106 (1)
C7 - C8	1.2 (1)	I4 - Cu4 - N4	104 (1)
C8 - C9	1.2 (1)	Cu1 - N1 - C1	108 (4)
C9 - C10	1.7 (1)	Cu1 - N1 - C5	109 (3)
C11 - C12	1.43 (7)	C1 - N1 - C5	105 (5)
C12 - C13	1.38 (8)	Cu2 - N2 - C6	113 (4)
C13 - C14	1.25 (9)	Cu2 - N2 - C10	111 (3)
C14 - C15	1.54 (7)	C6 - N2 - C10	105 (4)
C16 - C17	1.48 (9)	Cu3 - N3 - C11	115 (2)
C17 - C18	1.37 (9)	Cu3 - N3 - C15	107 (3)
C18 - C19	1.2 (1)	C11- N3 - C15	115 (4)
C19 - C20	1.5 (1)	Cu4 - N4 - C16	114 (3)
		Cu4 - N4 - C20	108 (3)
		C16 - N4 - C20	114 (3)
		N1 - C1 - C2	107 (6)
		C1 - C2 - C3	106 (8)
		C2 - C3 - C4	119 (7)
		C3 - C4 - C5	125 (7)
		C4 - C5 - N1	98 (5)
		N2 - C6 - C7	109 (7)
		C6 - C7 - C8	109 (6)
		C7 - C8 - C9	116 (9)
		C8 - C9 - C10	125 (10)
		C9 - C10 - N2	101 (4)
		N3 - C11 - C12	112 (4)
		C11 - C12 - C13	117 (5)
		C12 - C13 - C14	122 (5)
		C13 - C14 - C15	122 (5)

TABLE XXXVI (Continued)

	C14 - C15 - N3	107 (4)
	N4 - C16 - C17	111 (5)
	C16 - C17 - C18	118 (6)
	C17 - C18 - C19	123 (6)
	C18 - C19 - C20	117 (6)
	C19 - C20 - N4	110 (5)

TABLE XXXVII
CRYSTAL DATA FOR COPPER IODIDE MORPHOLINE

Formula	$CuI(C_4ONH_9)_2$
MWT	364.69
a	8.878(6) Å
b	6.726(3)
c	11.248(9)
α	90.0 °
β	113.22(5)
γ	90.0
V	617.3(7) $Å^3$
F (000)	356
μMoK_α	42.29 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.961 g cm^{-3}
Z	2
Meas. Refl.	1114
Obs. Refl.	835
R	6.9 %
Space Group	$Pna2_1$
Octants Meas.	±h, k, l

TABLE XXXVIII

POSITIONAL PARAMETERS FOR COPPER IODIDE MORPHOLINE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.2528 (3)	0.4359 (2)	0.3156 (7)
Cu1	0.1337 (6)	0.1409 (4)	0.3150 (0)
O1	0.234 (6)	-0.104 (6)	0.112 (2)
O2	0.253 (7)	-0.075 (5)	0.532 (2)
N1	0.240 (6)	0.060 (6)	0.228 (2)
N2	0.267 (6)	0.077 (6)	0.404 (3)
C1	0.167 (8)	0.134 (7)	0.174 (3)
C2	0.257 (7)	0.067 (7)	0.105 (2)
C3	0.329 (8)	-0.157 (6)	0.160 (3)
C4	0.262 (9)	-0.101 (7)	0.226 (2)
C5	0.137 (11)	0.119 (7)	0.465 (4)
C6	0.212 (11)	0.076 (9)	0.519 (5)
C7	0.384 (8)	-0.133 (6)	0.478 (3)
C8	0.282 (11)	-0.093 (9)	0.418 (4)

TABLE XXXIX

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE MORPHOLINE

ATOM	X	Y	Z
H1	0.4089	0.0839	0.2243
H2	0.3999	0.0994	0.4030
H11	0.0282	0.1136	0.1712
H12	0.2041	0.2324	0.1764
H21	0.1943	0.1096	0.0714
H22	0.4025	0.0858	0.1061
H31	0.3238	-0.2704	0.1630
H32	0.4717	-0.1310	0.1604
H41	0.3327	-0.1391	0.2611
H42	0.1159	-0.1439	0.2309
H51	0.1367	0.2372	0.4689
H52	0.0026	0.0824	0.4567
H61	0.3182	0.1444	0.5371
H62	0.0986	0.0993	0.5575
H71	0.5208	-0.0842	0.4827
H72	0.4036	-0.2396	0.4815
H81	0.1459	-0.1292	0.4179
H82	0.3496	-0.1388	0.3794

TABLE XL

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE MORPHOLINE

ATOM	U11	U22	U33	U12	U13	U23
I1	20 (0)	26 (1)	60 (1)	0 (0)	0 (2)	-1 (3)
Cu1	34 (2)	38 (2)	44 (2)	4 (1)	4 (1)	-17 (4)
O1	64 (2)	2 (2)	1 (2)	0 (1)	0 (1)	1 (1)
O2	7 (3)	2 (2)	2 (2)	0 (2)	1 (2)	-1 (1)
N1	3 (3)	2 (2)	0 (1)	-1 (2)	0 (1)	0 (1)
N2	0 (2)	2 (2)	6 (3)	0 (1)	1 (2)	1 (2)
C1	2 (2)	4 (3)	1 (2)	0 (2)	0 (2)	-1 (2)
C2	3 (2)	3 (3)	0 (1)	0 (2)	0 (2)	0 (2)
C3	2 (2)	3 (2)	3 (3)	-1 (2)	1 (2)	0 (2)
C4	6 (4)	1 (2)	0 (1)	-1 (2)	0 (2)	0 (1)
C5	4 (4)	1 (2)	6 (4)	0 (2)	3 (3)	-1 (2)
C6	6 (4)	3 (4)	10 (6)	0 (3)	-3 (4)	1 (3)
C7	2 (3)	4 (3)	5 (3)	0 (2)	0 (2)	2 (2)
C8	3 (3)	2 (4)	6 (6)	1 (3)	3 (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 10^4 for I, Cu; x 10^3 for C, N and O.

TABLE XLI

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

I1 - Cu1	2.727 (4)	I1 - Cu1 - N1	103 (1)
Cu1 - N1	2.05 (4)	I1 - Cu1 - N2	97 (1)
Cu1 - N2	2.11 (6)	N1 - Cu1 - N2	121 (1)
N1 - C1	1.37 (7)	Cu1 - N1 - C1	114 (3)
N1 - C4	1.43 (8)	Cu1 - N1 - C4	113 (3)
C1 - C2	1.37 (7)	C1 - N1 - C4	119 (4)
C2 - O1	1.52 (8)	N1 - C1 - C2	112 (4)
O1 - C3	1.27 (7)	C1 - C2 - O1	104 (3)
C3 - C4	1.51 (8)	C2 - O1 - C3	112 (4)
N2 - C5	1.57 (9)	O1 - C3 - C4	116 (4)
N2 - C8	1.51 (7)	C3 - C4 - N1	111 (4)
C5 - C6	1.27 (8)	Cu1 - N2 - C5	113 (3)
C6 - O2	1.39 (9)	Cu1 - N2 - C8	116 (4)
O2 - C7	1.50 (7)	C5 - N2 - C8	96 (5)
C7 - C8	1.41 (7)	N2 - C5 - C6	113 (6)
		C5 - C6 - O2	122 (7)
		C6 - O2 - C7	107 (5)
		O2 - C7 - C8	105 (4)
		C7 - C8 - N2	115 (6)

TABLE XLII

CRYSTAL DATA FOR COPPER IODIDE 3 - AZASPIRO (5.5) UNDECANE

Formula	$(CuI(C_{10}NH_{19})_2)_2$
MWT	989.93
a	19.522(8) Å
b	6.705(1)
c	16.39(1)
α	101.8445(7) °
β	100.1334(3)
γ	90.0581(6)
V	1114(1) Å^3
F (000)	504
μMoK_α	23.57 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.475 g cm^{-1}
Z	1
Meas. Refl.	3952
Obs. Refl.	1157
R	8.6 %
Space Group	P1
Octants Meas.	±h, k, ±l

TABLE XLIII

POSITIONAL PARAMETERS FOR COPPER IODIDE 3 - AZASPIRO (5.5) UNDECANE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.027 (1)	0.317 (2)	0.008 (1)
Cu1	0.101 (1)	-0.372 (2)	0.034 (1)
Cu2	0.101 (1)	-0.095 (2)	0.033 (1)
N1	0.1019	-0.1744	0.1522
N2	0.2111	-0.2761	-0.0500
C1	0.2337	-0.1460	0.2089
C2	0.2411	0.0304	0.3016
C3	0.1341	-0.0784	0.3404
C4	0.0038	-0.1214	0.2818
C5	-0.0009	-0.0721	0.2056
C6	0.1407	-0.2595	0.3882
C7	0.2674	-0.1937	0.4740
C8	0.2649	0.0208	0.5226
C9	0.2669	0.1764	0.4663
C10	0.1320	0.1573	0.4031
C11	0.1743	-0.2374	-0.1403
C12	0.2513	-0.3474	-0.1986
C13	0.3996	-0.3363	-0.1729
C14	0.4460	-0.2302	-0.0773
C15	0.3595	-0.2532	-0.0221
C16	0.4482	-0.1935	-0.2224
C17	0.4454	-0.2948	-0.3246
C18	0.5157	-0.4992	-0.3239
C19	0.4325	-0.6498	-0.2843
C20	0.4532	-0.5178	-0.1880

TABLE XLIV

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE 3 - AZASPIRO (5.5) UNDECANE

ATOM	X	Y	Z
H11	0.2578	-0.2762	0.2229
H12	0.2952	-0.1030	0.1776
H21	0.3260	0.0417	0.3371
H22	0.2160	0.1640	0.2919
H41	-0.0177	-0.2660	0.2725
H42	-0.0601	-0.0441	0.3097
H51	-0.0862	-0.1121	0.1724
H52	0.0121	0.0746	0.2149
H61	0.0602	-0.2755	0.4077
H62	0.1577	-0.3855	0.3512
H71	0.2629	-0.2853	0.5122
H72	0.3482	-0.2102	0.4530
H81	0.1869	0.0359	0.5469
H82	0.3399	0.0474	0.5677
H91	0.2797	0.3130	0.5011
H92	0.3364	0.1485	0.4343
H101	0.0606	0.1664	0.4337
H102	0.1259	0.2623	0.3699
H111	0.0842	-0.2792	-0.1616
H112	0.1858	-0.0926	-0.1379
H121	0.2241	-0.4901	-0.2097
H122	0.2308	-0.2967	-0.2505
H141	0.5274	-0.2873	-0.0573
H142	0.4593	-0.0855	-0.0744
H151	0.3853	-0.3740	-0.0004
H152	0.3754	-0.1341	0.0238
H161	0.3947	-0.1002	0.0311
H162	0.7156	0.4416	-0.1018
H163	0.5122	-0.2465	0.0396

TABLE XLIV (Continued)

H171	0.3596	-0.3104	-0.3590
H172	0.4949	-0.1905	-0.3399
H181	0.5231	-0.5644	-0.3814
H182	0.6013	-0.4718	-0.2895
H191	0.3423	-0.6640	-0.3113
H192	0.4684	-0.7838	-0.2874
H201	0.4192	-0.6010	-0.1543
H202	0.5456	-0.4946	-0.1686

TABLE XLV

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 3 - AZASPIRO (5.5) UNDECANE

ATOM	U11	U22	U33	U12	U13	U23
I1	27 (2)	39 (2)	39 (2)	0 (1)	7 (1)	10 (2)
Cu1	5 (0)	4 (1)	4 (1)	3 (1)	-6 (7)	10 (7)
Cu2	5 (0)	4 (1)	4 (1)	3 (1)	3 (7)	9 (8)
N1	1 (3)	3 (3)	2 (3)	0 (2)	0 (2)	0 (2)
N2	5 9 3)	6 (4)	3 (3)	0 (3)	2 (3)	1 (3)
C1	1 (3)	5 (4)	4 (4)	1 (3)	-1 (3)	1 (3)
C2	10 (8)	96 (5)	12 (1)	12 (5)	6 (8)	16 (9)
C3	4 (4)	12 (6)	4 (4)	-1 (4)	2 (4)	2 (4)
C4	9 (6)	8 (5)	0 (3)	0 (4)	1 (3)	0 (3)
C5	1 (5)	67 (1)	9 (8)	1 (9)	-3 (5)	9 (3)
C6	20 (1)	4 (5)	9 (7)	3 (6)	-7 (7)	1 (5)
C7	20 (1)	15 (1)	8 (6)	0 (8)	0 (8)	4 (6)
C8	12 (7)	6 (5)	3 (4)	0 (5)	0 (4)	0 (4)
C9	25 (3)	9 (8)	7 (6)	-2 (7)	-6 (7)	3 (5)
C10	20 (2)	6 (5)	7 (6)	-5 (6)	-4 (6)	4 (5)
C11	1 (5)	45 (2)	13 (9)	1 (8)	-3 (5)	1 (2)
C12	5 (4)	6 (5)	2 (3)	0 (3)	1 (3)	0 (3)
C13	4 (4)	6 (5)	2 (3)	1 (3)	1 (3)	0 (3)
C14	10 (8)	43 (7)	10 (8)	6 (9)	6 (7)	-1 (9)
C15	2 (4)	7 (5)	9 (6)	0 (3)	-4 (4)	0 (5)
C16	4 (4)	3 (4)	26 (2)	0 (3)	5 (6)	2 (6)
C17	9 (6)	31 (4)	9 (6)	-4 (7)	-4 (7)	15 (8)
C18	49 (8)	15 (2)	4 (7)	6 (4)	2 (1)	3 (7)
C19	7 (7)	22 (2)	18 (9)	4 (7)	0 (7)	-2 (8)
C20	7 (6)	2 (4)	21 (0)	1 (3)	3 (6)	2 (5)

Anisotropic thermal parameters in the form:

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

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

TABLE XLVI

BOND DISTANCES (Å) AND BOND ANCLES (°) FOR COPPER IODIDE 3 - AZASPIRO (5.5) UNDECANE

I1 - Cu1	2.86 (1)	I1 - Cu1 - N1	96 (1)
I1 - Cu2	2.86 (1)	I1 - Cu1 - N2	111 (1)
Cu1 - N1	2.12 (3)	N1 - Cu1 - N2	117 (1)
Cu1 - N2	2.13 (3)	I1 - Cu2 - N1	96 (1)
Cu2 - N1	2.12 (3)	I1 - Cu2 - N2	111 (1)
Cu2 - N2	2.13 (3)	N1 - Cu2 - N2	117 (1)
N1 - C1	1.51 (4)	Cu1 - N1 - C1	113 (1)
N1 - C5	1.57 (10)	Cu1 - N1 - C5	117 (1)
N2 - C11	1.53 (7)	C1 - N1 - C5	108 (6)
N2 - C15	1.54 (4)	Cu1 - N2 - C11	110 (2)
C1 - C2	1.70 (8)	Cu1 - N2 - C15	117 (1)
C2 - C3	1.64 (7)	C11 - N2 - C15	109 (3)
C3 - C4	1.51 (7)	N1 - C1 - C2	114 (8)
C3 - C6	1.56 (8)	C1 - C2 - C3	97 (1)
C3 - C7	1.70 (8)	C2 - C3 - C4	113 (8)
C4 - C5	1.34 (2)	C2 - C3 - C6	132 (9)
C6 - C7	1.74 (8)	C2 - C3 - C10	83 (8)
C7 - C8	1.49 (8)	C4 - C3 - C6	101 (4)
C8 - C9	1.53 (10)	C4 - C3 - C10	107 (4)
C9 - C10	1.59 (12)	C6 - C3 - C10	114 (4)
C11- C12	1.44 (7)	C3 - C4 - C5	114 (9)
C12 - C13	1.54 (4)	C4 - C5 - N1	115 (10)
C13 - C14	1.57 (4)	C3 - C6 - C7	105 (4)
C13 - C16	1.51 (6)	C6 - C7 - C8	113 (5)
C13 - C20	1.33 (7)	C7 - C8 - C9	112 (5)
C14 - C15	1.42 (9)	C8 - C9 - C10	108 (7)
C16 - C17	1.66 (9)	C9 - C10 - C3	103 (6)
C17 - C18	1.55 (10)	N2 - C11 - C12	113 (4)
C18 - C19	1.63 (9)	C11 - C12 - C13	119 (3)
C19 - C20	1.62 (8)	C12 - C13 - C14	112 (3)
		C12 - C13 - C16	105 (3)

TABLE XLVI (Continued)

C12 - C13 - C20	113 (3)
C14 - C13 - C16	104 (3)
C14 - C13 - C20	109 (4)
C16 - C13 - C20	110 (4)
C13 - C14 - C15	115 (4)
C14 - C15 - N2	123 (3)
C13 - C16 - C17	114 (4)
C16 - C17 - C18	104 (5)
C17 - C18 - C19	109 (5)
C18 - C19 - C20	97 (4)
C19 - C20 - C13	119 (5)

TABLE XLVII

CRYSTAL DATA FOR COPPER IODIDE 3,5 - DIMETHYLPIPERIDINE

Formula	$(CuIC_7NH_{15})_4$
MWT	1206.55
a	7.859(3) Å
b	16.428(8)
c	16.491(7)
α	90.0 °
β	90.0
γ	90.0
V	2129.(1) $Å^3$
F (000)	1152
μMoK_α	48.69 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.882 g cm^{-1}
Z	2
Meas. Refl.	595
Obs. Refl.	189
R	8.8 %
Space Group	$P4_2/nmc$
Octants Meas.	h, k, l

TABLE XLVIII

POSITIONAL PARAMETERS FOR COPPER IODIDE 3,5 - DIMETYLPIPERIDINE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.7500	0.112 (1)	0.447 (1)
Cu1	0.7500	0.168 (1)	0.128 (1)
N1	0.7500	0.083 (5)	-0.040 (12)
C1	0.688 (6)	0.026 (6)	-0.020 (10)
C2	0.658 (9)	-0.029 (8)	-0.141 (16)
C3	0.750	-0.867 (6)	-0.133 (10)
C4	0.599 (10)	-0.087 (6)	-0.115 (13)

TABLE XLIX

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE 3,5 - DIMETHYLPIPERIDINE

ATOM	X	Y	Z
H1	0.7500	0.1037	-0.1686
H11	0.6973	-0.0121	0.0860
H12	0.6327	0.0521	0.0208
H21	0.6569	-0.0064	-0.2683
H31	0.7500	-0.1083	-0.0136
H32	0.7500	-0.1334	-0.2081
H41	0.6075	-0.1284	-0.0168
H42	0.5420	-0.0647	-0.0806
H43	0.5771	-0.1304	-0.2075

TABLE XLX

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 3,5 - DIMETHYLPIPERIDINE

ATOM	U11	U22	U33	U12	U13	U23
I1	119 (7)	86 (6)	102 (5)	0 (0)	0 (0)	16 (6)
Cu1	10 (1)	9 (1)	11 (1)	0 (0)	0 (0)	-3 (9)
N1	4 (7)	8 (8)	15 (7)	0 (0)	0 (0)	-4 (7)
C1	15 (1)	25 (4)	8 (6)	3 (8)	-9 (6)	-7 (7)
C2	26 (7)	33 (7)	28 4)	-10 (5)	6 (3)	13 (3)
C3	16 (2)	3 (9)	1 (4)	0 (0)	0 (0)	-2 (5)
C4	65 (8)	21 (1)	1 (1)	28 (3)	15 (4)	-3 (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 10^3 for I, Cu, C, and N.

TABLE L

BOND DISTANCES (Å) AND BOND ANCLES (°) FOR COPPER IODIDE 3,5 - DIMETHYLPIPERIDINE

I1 - Cu1	2.68 (1)	I1 - Cu1 - N1	112 (2)
Cu1 - N1	1.92 (9)	Cu1 - N1 - C1	114 (5)
N1 - C1	1.4 (1)	C1 - N1 - C1'	92 (8)
C1 - C2	1.4 (1)	N1 - C1 - C2	128 (9)
C2 - C3	1.7 (1)	C1 - C2 - C3	89 (9)
C2 - C4	1.4 (1)	C1 - C2 - C4	126 (9)
		C3 - C2 - C4	105 (10)
		C2 - C3 - C2'	119 (8)

TABLE LI

CRYSTAL DATA FOR COPPER IODIDE 4 (-2- AMINOETHYL) MORPHOLINE

Formula	$CuI(ON_2C_6H_{14})_2$
MWT	446.80
a	12.036(6) Å
b	8.532(4)
c	17.487(6)
α	90.0 °
β	102.36(3)
γ	90.0
V	1754.(1) $Å^3$
F (000)	888
μMoK_α	71.15 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.692 g cm^{-1}
Z	4
Meas. Refl.	2481
Obs. Refl.	1394
R	5.2 %
Space Group	P21/n
Octants Meas.	±h, k, l

TABLE LII

POSITIONAL PARAMETERS FOR COPPER IODIDE 4 (-2- AMINOETHYL) MORPHOLINE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.5204 (1)	0.3257 (1)	0.5943 (1)
Cu1	0.6823 (2)	0.5394 (2)	0.6253 (1)
O1	0.520 (1)	0.727 (1)	0.861 (1)
O2	0.756 (1)	0.426 (1)	1.015 (1)
N1	0.697 (1)	0.689 (1)	0.534 (1)
N2	0.562 (1)	0.749 (1)	0.693 (1)
N3	0.770 (1)	0.421 (1)	0.690 (1)
N4	0.776 (1)	0.343 (1)	0.853 (1)
C1	0.654 (2)	0.846 (2)	0.561 (1)
C2	0.548 (2)	0.831 (2)	0.620 (1)
C3	0.452 (1)	0.707 (2)	0.739 (1)
C4	0.464 (1)	0.626 (2)	0.816 (1)
C5	0.627 (2)	0.768 (2)	0.816 (1)
C6	0.620 (2)	0.847 (2)	0.741 (1)
C7	0.723 (2)	0.276 (2)	0.728 (1)
C8	0.782 (1)	0.225 (2)	0.793 (1)
C9	0.870 (2)	0.321 (2)	0.894 (1)
C10	0.860 (2)	0.439 (2)	0.961 (1)
C11	0.666 (2)	0.452 (2)	0.975 (1)
C12	0.671 (2)	0.336 (2)	0.910 (1)

TABLE LIII

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE 4 (-2- AMINOETHYL) MOEPHOLINE

ATOM	X	Y	Z
H11	0.7189	0.9021	0.5929
H12	0.6226	0.9090	0.5156
H21	0.5245	0.9369	0.6318
H22	0.4803	0.7794	0.5877
H31	0.4167	0.8088	0.7484
H32	0.3955	0.6480	0.7022
H41	0.3893	0.6030	0.8283
H42	0.5030	0.5253	0.8145
H51	0.6852	0.8245	0.8526
H52	0.6627	0.6645	0.8059
H61	0.5837	0.9504	0.7405
H62	0.6966	0.8681	0.7282
H71	0.6501	0.3121	0.7422
H72	0.7043	0.1927	0.6910
H81	0.7576	0.1210	0.8054
H82	0.8626	0.2116	0.7852
H91	0.8821	0.2129	0.9128
H92	0.9322	0.3467	0.8670
H101	0.9328	0.4364	0.9975
H102	0.8520	0.5425	0.9351
H111	0.6015	0.4314	1.0014
H112	0.6536	0.5595	0.9536
H121	0.6786	0.2296	0.9364
H122	0.5963	0.3329	0.8735
H131	0.7767	0.6985	0.5283
H132	0.6515	0.6557	0.4843
H141	0.8269	0.3767	0.6610
H142	0.8128	0.4866	0.7315

TABLE LIV

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 4 (-2- AMINOETHYL) MORPHOLINE

ATOM	U11	U22	U33	U12	U13	U23
I1	56 (0)	49 (0)	51 (0)	-13 (0)	-27 (0)	6 (0)
Cu1	73 (1)	41 (1)	51 (1)	1(1)	-34 (1)	10 (1)
O1	7 (1)	72 (8)	39 (6)	-16 (7)	-29 (6)	-2 (6)
O2	8 (1)	86 (9)	36 (6)	3 (8)	-37 (7)	-1 (6)
N1	5 (1)	47 (7)	40 (6)	-6 (8)	-27 (6)	-4 (6)
N2	4 (1)	30 (6)	46 (7)	-5 (7)	-28 (7)	6 (6)
N3	6 (1)	40 (8)	33 (6)	7 (7)	-27 (6)	2 (5)
N4	5 (1)	35 (7)	39 (6)	6 (7)	-31 (7)	0 (6)
C1	7 (1)	4 (1)	42 (8)	1 (1)	-29 (9)	9 (7)
C2	6 (1)	6 (1)	44 (9)	2 (1)	-34 (9)	6 (9)
C3	4 (1)	4 (1)	54 (9)	-5 (9)	-34 (8)	6 (7)
C4	3 (1)	6 (1)	8 (1)	-5 (9)	-22 (9)	0 (1)
C5	6 (1)	6 (1)	5 (1)	-3 (1)	-3 (1)	-2 (9)
C6	7 (1)	6 (1)	7 (1)	-1 (1)	-2 (1)	-1 (1)
C7	8 (1)	2 (9)	6 (1)	4 (8)	-6 (1)	0 (7)
C8	6 (1)	4 (1)	6 (1)	16 (9)	-4 (1)	3 (8)
C9	4 (1)	8 (1)	7 (1)	0 (1)	-4 (1)	0 (1)
C10	7 (1)	10 (2)	5 (1)	0 (1)	-5 (1)	-1 (1)
C11	8 (2)	11 (2)	4 (1)	3 (1)	-1 (1)	1 (1)
C12	6 (1)	7 (1)	4 (1)	0 (1)	-3 (1)	1 (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, Cu; x 10^3 for O, C, and N.

TABLE LV

BOND DISTANCES (Å) AND BOND ANCLES (°) FOR COPPER IODIDE 4 (-2- AMINOETHYL) MORPHOLINE

I1 - Cu1	2.638 (2)	I1 - Cu1 - N1	116.3 (3)
Cu1 - N1	2.08 (1)	I1 - Cu1 - N3	93.2 (4)
Cu1 - N3	1.80 (1 0	N1 - Cu1 - N3	136.8 (6)
N1 - C1	1.54 (2)	Cu1 - N1 - C1	101 (1)
C1 - C2	1.80 (2)	Cu1 - N3 - C7	121 (1)
C2 - N2	1.42 (2)	N1 - C1 - C2	116 (1)
N2 - C3	1.73 (2)	C1 - C2 - N2	124 (1)
N2 - C6	1.28 (2)	C2 - N2 - C3	123 (1)
C3 - C4	1.47 (2)	C2 - N2 - C6	102 (1)
C4 - O1	1.26 (2)	C3 - N2 - C6	101 (1)
O1 - C5	1.68 (2)	N2 - C3 - C4	125 (1)
C5 - C6	1.46 (2)	C3 - C4 - O1	100 (1)
N3 - C7	1.69 (1)	C4 - O1 - C5	102 (1)
C7 - C8	1.28 (2)	O1 - C5 - C6	127 (1)
C8 - N4	1.45 (2)	C5 - C6 - N2	101 (1)
N4 - C9	1.21 (1)	N3 - C7 - C8	117 (1)
N4 - C12	1.76 (2)	C7 - C8 - N4	107 (1)
C9 - C10	1.56 (2)	C8 - N4 - C9	98 (1)
C10 - O2	1.71 (2)	C8 - N4 - C12	121 (1)
O2 - C11	1.18 (2)	C9 - N4 - C12	110 (1)
C11 - C12	1.51 (2)	N4 - C9 - C10	121 (1)
		C9 - C10 - O2	123 (1)
		C10 - O2 - C11	110 (1)
		O2 - C11 - C12	98 (1)
		C11 C12 - N4	122 (1)

TABLE LVI

CRYSTAL DATA FOR COPPER IODIDE PYRROLIDINE

Formula	$(CuC_{12}N_4H_{24})^+I^-$
MWT	410.81
a	7.2045(5) Å
b	13.2501(9)
c	16.1482(1)
α	75.848(5) °
β	90.090(6)
γ	35.417(3)
V	809.03(9) Å^3
F (000)	408
μMoK_α	32.29 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.686 g cm^{-1}
Z	2
Meas. Refl.	1354
Obs. Refl.	717
R	5.4 %
Space Group	P1bar
Octants Meas.	±h, k, ±l

TABLE LVII

POSITIONAL PARAMETERS FOR COPPER IODIDE PYRROLIDINE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.2500	1.0749 (2)	0.0000
Cu1	0.5000	0.2500	0.2500
N1	0.443 (1)	0.374 (2)	0.133 (1)
N2	0.525 (1)	0.642 (2)	0.138 (1)
C1	0.452 (1)	0.533 (2)	0.097 (1)
C2	0.538 (1)	0.822 (2)	0.100 (1)
C3	0.621 (2)	0.898 (3)	0.180 (2)
C4	0.674 (1)	0.736 (3)	0.233 (1)
C5	0.602 (1)	0.596 (2)	0.228 (1)
C6	0.380 (1)	0.595 (2)	0.002 (1)

TABLE LIII

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE PYRROLIDINE

ATOM	X	Y	Z
H1	0.3876	0.2914	0.1144
H21	0.5473	0.8024	0.0414
H22	0.4854	0.9011	0.0846
H31	0.6540	0.9733	0.1514
H32	0.6032	0.9734	0.2198
H41	0.7165	0.6908	0.2035
H42	0.7184	0.7752	0.2996
H51	0.6211	0.4687	0.2286
H52	0.5852	0.6136	0.2822
H61	0.6236	0.6265	-0.0401
H62	0.3469	0.7282	0.0145
H63	0.3352	0.4600	-0.0191

TABLE LVIII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE PYRROLIDINE

ATOM	U11	U22	U33	U12	U13	U23
I1	55 (1)	47 (0)	64 (1)	0 (0)	16 (1)	0 (0)
Cu1	64 (2)	41 (1)	52 (2)	0 (0)	23 (2)	0 (0)
N1	6 (1)	34 (7)	50 (8)	-12 (8)	20 (9)	0 (5)
N2	5 (1)	40 (7)	43 (9)	1 (7)	9 (9)	8 (6)
C1	6 (1)	3 (1)	4 (1)	1 (1)	3 (3)	7 (7)
C2	8 (2)	3 (1)	8 (1)	1 (1)	4 (1)	-9 (8)
C3	11 (2)	6 (1)	10 (2)	-3 (1)	6 (2)	0 (1)
C4	7 (2)	9 (2)	6 (1)	-2 (1)	3 (1)	-1 (1)
C5	8 (1)	6 (1)	6 (1)	0 (1)	4 (1)	0 (1)
C6	6 (1)	8 (1)	5 (1)	1 (1)	4 (1)	2 (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, Cu; x 10^3 for C, N.

TABLE LIX
BOND DISTANCES (Å) AND BOND ANCLES (°) FOR COPPER IODIDE PYRROLIDINE

Cu1 - N1	1.85 (1)	N1 - Cu1 - N1'	180 (1)
N1 - C1	1.31 (2)	Cu1 - N1 - C1	137 (1)
C1 - N2	1.32 (2)	N1 - C1 - N2	123 (1)
C1 - C6	1.49 (2)	N1 - C1 - C6	120 (1)
N2 - C2	1.47 (2)	N2 - C2 - C6	117 (1)
N2 - C5	1.45 (1)	C1 - N2 - C2	125 (1)
C2 -C3	1.48 (2)	C1 - N2 - C5	123 (1)
C3 - C4	1.47 (2)	N2 - C2 - C3	103 (1)
C4 - C5	1.51 (3)	C2 - C3 - C4	106 (1)
		C3 - C4 - C5	105 (1)
		C4 - C5 - N2	103 (1)

TABLE LX

CRYSTAL DATA FOR COPPER IODIDE 2 - (2 - AMINOETHYL) PYRIDINE

Formula	$CuIN_2C_7H_{10}$
MWT	312.62
a	8.766(6) Å
b	14.581(5)
c	7.554 (2)
α	90.0 °
β	103.35(4)
γ	90.0
V	939.4(8) $Å^3$
F (000)	592
μMoK_α	55.26 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.210 g cm^{-1}
Z	4
Meas. Refl.	1793
Obs. Refl.	1307
R	7.6 %
Space Group	$P2_1/c$
Octants Meas.	±h, k, l

TABLE LXI

POSITIONAL PARAMETERS FOR COPPER IODIDE 2 - (2 - AMINOETHYL) PYRIDINE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.9284 (1)	0.1117 (1)	0.7836 (2)
Cu1	1.0953 (3)	0.0622 (2)	1.1009 (3)
N1	1.326 (2)	0.091(1)	1.115 (2)
N2	1.077 (2)	0.137 (1)	1.332 (2)
C1	1.386 (2)	0.097 (1)	0.965 (3)
C2	1.534 (2)	0.125 (1)	0.962 (3)
C3	1.630 (3)	0.148 (2)	1.129 (4)
C4	1.575 (2)	0.141 (2)	1.284 (3)
C5	1.425 (2)	0.115 (1)	1.273 (2)
C6	1.361 (2)	0.107 (2)	1.445 (3)
C7	1.226 (2)	0.174 (1)	1.442 (3)

TABLE LXII

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE 2 - (2 - AMINOETHYL) PYRIDINE

ATOM	X	Y	Z
H1	1.3430	0.0696	0.8663
H2	1.5802	0..0800	0.9010
H3	1.7300	0.1798	1.1087
H4	1.6373	0.1800	1.3987
H61	1.4549	0.1030	1.5696
H62	1.3318	0.0553	1.5119
H71	1.2191	0.2200	1.3384
H72	1.2111	0.1695	1.5926
H81	1.0133	0.1800	1.2492
H82	1.0261	0.1040	1.4064

TABLE LXIII

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 2 - (2 - AMINOETHYL) PYRIDINE

ATOM	U11	U22	U33	U12	U13	U23
I1	44 (0)	30 (0)	47 (0)	-6 (0)	3 (0)	8 (0)
Cu1	44 (1)	40 (1)	46 (1)	-10 (1)	7 (1)	-5 (1)
N1	35 (7)	24 (7)	30 (7)	5 (6)	4 (6)	2 (6)
N2	47 (9)	40 (9)	40 (8)	7 (7)	18 (7)	0 (7)
C1	3 (1)	4 (1)	5 (1)	1 (1)	0 (1)	0 (1)
C2	5 (1)	4 (1)	5 (1)	0 (1)	1 (1)	0 (1)
C3	4 (1)	6 (1)	11 (2)	0 (1)	3 (1)	0 (1)
C4	4 (1)	6 (1)	6 (1)	-1 (1)	1 (1)	-1 (1)
C5	5 (1)	3 (1)	4 (1)	1 (1)	0 (1)	1 (1)
C6	5 (1)	7 (1)	3 (1)	0 (1)	0 (1)	2 (1)
C7	6 (1)	5 (1)	4 (1)	0 (1)	1 (1)	-1 (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, Cu; x 10^3 for C, N.

TABLE LXIV

BOND DISTANCES (Å) AND BOND ANCLES (°) FOR COPPER IODIDE 2 - (2 - AMINOETHYL) PYRIDINE

I1 - Cu1	2.604 (2)	I1 - Cu1 - N1	109.3 (3)
Cu1 - N1	2.04 (1)	I1 - Cu1 - N2	119.2 (3)
Cu1 - N2	2.09 (1)	N1 - Cu1 - N2	96.6 (5)
N1 - C1	1.35 (2)	C1 - N1 - C5	115 (1)
N1 - C5	1.34 (2)	C1 - N1 - Cu1	122 (1)
C1 - C2	1.36 (2)	C5 - N1 - Cu1	121 (1)
C2 - C3	1.38 (3)	N1 - C1 - C2	126 (1)
C3 - C4	1.37 (3)	C1 - C2 - C3	115 (2)
C4 - C5	1.35 (2)	C2 - C3 - C4	119 (2)
C5 - C6	1.52 (3)	C 3 - C4 - C5	119 (1)
C6 - C7	1.53 (3)	N1 - C5 - C4	122 (1)
C7 - N2	1.47 (2)	N1 - C5 - C6	116 (1)
		C4 - C5 - C6	120 (1)
		C5 - C6 - C7	111 (1)
		C6 - C7 - N2	110 (1)
		C7 - N2 - Cu1	115 (1)

TABLE LXV

CRYSTAL DATA FOR COPPER IODIDE 2-(2-PIPERIDINOETHYL) PYRIDINE

Formula	$CuIN_2C_{12}H_{19}$
MWT	380.74
a	11.1303(9) Å
b	13.3848(6)
c	9.8887(6)
α	90.0 °
β	110.186(5)
γ	90.0
V	1382.7(1) $Å^3$
F (000)	744
μMoK_α	37.71 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.828 g cm^{-1}
Z	4
Meas. Refl.	1809
Obs. Refl.	1135
R	4.8 %
Space Group	$P2_1/n$
Octants Meas.	±h, k, l

TABLE LXVI

POSITIONAL PARAMETERS FOR COPPER IODIDE 2 - (2 - PIPERIDINOETHYL) PYRIDINE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
I1	0.0321 (1)	0.1441 (1)	0.9053 (1)
Cu1	0.0740 (1)	0.0340 (1)	1.1388 (2)
N1	-0.018 (1)	0.114 (1)	1.256 (1)
N2	0.033 (2)	0.040 (1)	1.289 (1)
C1	0.033 (2)	0.120 (1)	1.400 (2)
C2	-0.036 (2)	0.170 (1)	1.745 (2)
C3	-0.152 (2)	0.207 (1)	1.407 (2)
C4	-0.207 (2)	0.202 (1)	1.261 (2)
C5	-0.134 (2)	0.155 (1)	1.194 (2)
C6	0.160 (2)	0.077 (1)	1.470 (1)
C7	0.259 (1)	0.106 (1)	1.407 (2)
C8	0.323 (1)	-0.057 (1)	1.347 (1)
C9	0.353 (2)	-0.122 (1)	1.241 (2)
C10	0.438 (2)	-0.072 (2)	1.171 (2)
C11	0.378 (2)	0.030 (2)	1.116 (2)
C12	0.354 (1)	0.091 (1)	1.230 (2)

TABLE LXV

HYDROGEN POSITIONAL PARAMETERS FOR COPPER IODIDE 2 - (2 - PIPERIDINOETHYL) PYRIDINE

ATOM	X	Y	Z
H2	0.0049	0.1778	1.5829
H3	-0.1981	0.2389	1.4671
H4	-0.2929	0.2305	1.2104
H5	-0.1689	0.1517	1.0861
H61	0.1903	0.0909	1.5732
H62	0.1501	0.0020	1.4607
H71	0.2378	0.1744	1.3694
H72	0.3425	0.1083	1.4837
H81	0.4015	-0.0470	1.4295
H82	0.2620	-0.0931	1.3832
H91	0.3936	-0.1846	1.2862
H92	0.2724	-0.1409	1.1632
H101	0.5235	-0.0618	1.2438
H102	0.4482	-0.1131	1.0941
H111	0.4340	0.0653	1.0724
H112	0.2963	0.0173	1.0354
H121	0.4363	0.1039	1.3060
H122	0.3181	0.1561	1.1888

TABLE LXVI

ANISOTROPIC THERMAL PARAMETERS FOR COPPER IODIDE 2 - (2 - PIPERIDINOETHYL) PYRIDINE

ATOM	U11	U22	U33	U12	U13	U23
I1	57 (0)	41 (0)	40 (0)	-3 (0)	6 (0)	9 (0)
Cu1	46 (1)	45 (1)	34 (1)	3 (1)	5 (0)	-3 (0)
N1	53 (9)	56 (9)	42 (8)	9 (7)	17 (6)	-8 (6)
N2	27 (6)	37 (7)	43 (7)	1 (5)	0 (5)	1 (5)
C1	7 (1)	3 (1)	5 (1)	1 (1)	2 (1)	1 (1)
C2	7 (1)	7 (1)	4 (1)	0 (1)	2 (1)	0 (1)
C3	9 (2)	5 (1)	8 (1)	0 (1)	6 (1)	-1 (1)
C4	6 (1)	6 (1)	9 (1)	2 (1)	3 (1)	-1 (1)
C5	5 (1)	11 (2)	4 (1)	2 (1)	0 (1)	1 (1)
C6	8 (1)	6 (1)	2 (1)	2 (1)	0 (1)	-1 (1)
C7	5 (1)	5 (1)	4 (1)	-1 (1)	-1 (1)	-1 (1)
C8	4 (1)	4 (1)	4 (1)	0 (1)	0 (1)	0 (1)
C9	7 (1)	5 (1)	5 (1)	3 (1)	-1 (1)	-1 (1)
C10	6 (1)	10 (2)	7 (1)	4 (1)	2 (1)	-1 (1)
C11	6 (1)	9 (2)	7 (1)	0 (1)	2 (1)	2 (1)
C12	4 (1)	4 (1)	7 (1)	1 (1)	0 (1)	-1 (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, Cu, and N; x 10^3 for C, .

TABLE LXVII

BOND DISTANCES (Å) AND BOND ANCLES (°) FOR COPPER IODIDE 2 - (2 - PIPERIDINOETHYL) PYRIDINE

I1 - Cu1	2.642 (2)	I1 - Cu1 - N1	103.2 (3)
Cu1 - N1	2.08 (1)	I1 - Cu1 - N2	114.4 (3)
Cu1 - N2	2.15 (1)	N1 - Cu1 - N2	99.1 (4)
N1 - C1	1.35 (2)	C1 - N1 - C5	116 (1)
N1 - C5	1.34 (2)	C1 - N1 - Cu1	121 (1)
N2 - C7	1.49 (2)	C5 - N1 - Cu1	116 (1)
N2 - C8	1.47 (1)	C7 - N2 - C8	110 (1)
N2 - C12	1.45 (2)	C7 - N2 - C12	105 (1)
C1 - C2	1.39 (2)	C8 - N2 - C12	107 (1)
C1 - C6	1.46 (2)	N1 - C1 - C2	118 (1)
C2 - C3	1.33 (2)	N1 - C1 - C6	118 (1)
C3 - C4	1.36 (3)	C2 - C1 - C6	123 (1)
C4 - C5	1.36 (3)	C1 - C2 - C3	121 (1)
C6 - C7	1.48 (2)	C2 - C3 - C4	121 (2)
C8 - C9	1.47 (2)	C3 - C4 - C5	114 (1)
C9 - C10	1.50 (3)	C4 - C5 - N1	127 (1)
C10 - C11	1.52 (2)	C1 - C6 - C7	114 (1)
C11 - C12	1.49 (2)	C6 - C7 - N2	116 (1)
		N2 - C8 - C9	114 (1)
		C8 - C9 - C10	112 (1)
		C9 - C10 - C11	107 (1)
		C10 - C11 - C12	112 (1)
		C11 - C12 - N2	111 (1)

TABLE LXVIII
CRYSTAL DATA FOR COPPER CHLORIDE NORBORNENE

Formula	$Cu_5CL_5(C_7H_{10})_4$
MWT	871.6
a	12.138(6) Å
b	22.849(6)
c	5.953 (1)
α	90.012(3) °
β	75.792(3)
γ	87.776(4)
V	1599.4(7) $Å^3$
F (000)	876
μMoK_α	37.232 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.809 g cm^{-1}
Z	2
Meas. Refl.	????
Obs. Refl.	1365
R	10.8 %
Space Group	P1 bar
Octants Meas.	±h, k, ±l

TABLE LXIX

POSITIONAL PARAMETERS FOR COPPER CHLORIDE NORBORNENE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
Cu1	0.5856 (6)	0.3434 (3)	0.3759 (11)
Cu2	0.6803 (6)	0.1996 (3)	0.3340 (10)
Cu3	0.4176 (6)	0.1565 (3)	0.4600 (11)
Cu4	0.3223 (6)	0.3004 (3)	0.5132 (11)
Cu5	0.5039 (8)	0.2489 (5)	0.8089 (12)
Cl1	0.683 (1)	0.279 (1)	0.567 (2)
Cl2	0.578 (1)	0.136 (1)	0.601 (2)
Cl3	0.316 (1)	0.220 (1)	0.752 (2)
Cl4	0.430 (1)	0.363 (1)	0.674 (2)
Cl5	0.503 (1)	0.249 (1)	0.191 (2)
C1	0.693 (4)	0.376 (2)	0.080 (6)
C2	0.593 (4)	0.412 (2)	0.134 (7)
C3	0.617 (4)	0.464 (2)	0.215 (8)
C4	0.679 (7)	0.492 (3)	-0.007 (12)
C5	0.798 (4)	0.463 (2)	-0.069 (7)
C6	0.778 (4)	0.414 (3)	0.124 (8)
C7	0.711 (6)	0.447 (2)	0.324 (9)
C8	0.799 (5)	0.200 (2)	0.043 (8)
C9	0.764 (5)	0.149 (3)	0.055 (10)
C10	0.843 (4)	0.111 (2)	0.099 (8)
C11	0.944 (5)	0.097 (2)	-0.101 (9)
C12	0.996 (4)	0.158 (2)	-0.123 (8)
C13	0.924 (5)	0.188 (2)	0.094 (9)
C14	0.898 (4)	0.148 (2)	0.263 (9)
C15	0.313 (4)	0.119 (2)	0.266 (8)
C16	0.413 (5)	0.097 (4)	0.216 (11)
C17	0.390 (5)	0.037 (2)	0.314 (12)
C18	0.296 (7)	0.008 (3)	0.191 (14)

TABLE LXIX (Continued)

C19	0.205 (6)	0.044 (3)	0.221 (13)
C20	0.230 (5)	0.083 (3)	0.400 (9)
C21	0.284 (7)	0.050 (3)	0.541 (10)
C22	0.183 (4)	0.299 (2)	0.359 (8)
C23	0.229 (4)	0.350 (3)	0.314 (7)
C24	0.149 (4)	0.390 (2)	0.469 (9)
C25	0.049 (4)	0.400 (2)	0.348 (7)
C26	-0.010 (5)	0.344 (2)	0.383 (10)
C27	0.069 (4)	0.311 (3)	0.540 (10)
C28	0.094 (6)	0.364 (3)	0.680 (9)

TABLE LXX

HYDROGEN POSITIONAL PARAMETERS FOR COPPER CHLORIDE NORBORNENE

ATOM	X	Y	Z
H1	0.7018	0.3359	0.0185
H2	0.5158	0.4002	0.1169
H3	0.5555	0.4871	0.3160
H6	0.8497	0.3937	0.1427
H8	0.7655	0.2387	0.0105
H9	0.6911	0.1319	0.0186
H10	0.8087	0.1319	0.0186
H13	0.9540	0.2255	0.1452
H15	0.2945	0.1581	0.2027
H16	0.4898	0.1117	0.1185
H17	0.4272	0.0110	0.2785
H20	0.1589	0.1074	0.4551
H22	0.2111	0.2589	0.2869
H23	0.3030	0.3532	0.1943
H24	0.1883	0.4283	0.4878
H27	0.0383	0.2768	0.4248
H41	0.6379	0.4849	-0.1388
H42	0.6785	0.5359	-0.0017
H51	0.8207	0.4471	-0.2245
H52	0.8446	0.4912	-0.0499
H71	0.7471	0.4792	0.3787
H72	0.6833	0.4211	0.4650
H111	0.9966	0.0636	-0.0776
H112	0.9219	0.0851	-0.2481
H121	1.0808	0.1555	-0.1134
H122	0.9985	0.1787	-0.2658
H141	0.8507	0.1600	0.4122
H142	0.9694	0.1284	0.2950

TABLE XX (Continued)

H181	0.3314	0.0000	0.0230
H182	0.2766	-0.0318	0.2579
H191	0.1948	0.0632	0.0758
H192	0.1292	0.0219	0.2739
H211	0.2430	0.0132	0.6076
H212	0.3018	0.0691	0.6743
H251	-0.0015	0.4341	0.4169
H252	0.0777	0.4097	0.1806
H261	-0.0914	0.3477	0.4674
H262	-0.0090	0.3224	0.2362
H281	0.1450	0.3539	0.7821
H282	0.0271	0.3846	0.7720

TABLE LXXI

ANISOTROPIC THERMAL PARAMETERS FOR COPPER CHLORIDE NORBORNENE

ATOM	U11	U22	U33	U12	U13	U23
Cu1	83 (5)	56 (5)	56 (4)	-12 (4)	-13 (4)	11 (3)
Cu2	59 (4)	62 (5)	44 4)	3 (3)	-4 (3)	-11 (3)
Cu3	70 (5)	65 (5)	60 (4)	-15 (4)	-23 (3)	-3 (3)
Cu4	65 (5)	79 (5)	64 (4)	-11 (4)	-30 (4)	13 (4)
Cu5	124 (7)	194 (10)	40 (4)	-46 (7)	-28 (4)	10 (5)
Cl1	78 (10)	41 (9)	29 (7)	-4 (7)	-17 (6)	0 (6)
Cl2	88 (12)	64 (11)	53 (9)	1 (9)	-42 (8)	20 (7)
Cl3	55 (9)	63 (10)	34 (7)	22 (7)	-5 (6)	-4 (6)
Cl4	60 (10)	69 (10)	36 (8)	-12 (8)	-7 (6)	-18 (7)
Cl5	51 (8)	34 (7)	28 (6)	9 (6)	-14 (5)	4 (5)
C1	5 (3)	2 (3)	3 (3)	0 (2)	1 (2)	-2 (2)
C2	1 (3)	11 (4)	4 (3)	2 (3)	-1 (2)	3 (3)
C3	2 (3)	0 (3)	7 (3)	0 (2)	2 (2)	0 (2)
C4	13 (7)	2 (5)	15 (6)	0 (4)	3 (5)	-5 (4)
C5	2 (3)	7 (4)	5 (3)	-4 (3)	1 (2)	1 (3)
C6	3 (4)	16 (6)	3 (3)	0 (4)	1 (3)	5 (3)
C7	20 (8)	6 (4)	6 (4)	-5 (5)	10 (5)	4 (3)
C8	13 (6)	2 (3)	5 (3)	0 (3)	-2 (4)	3 (2)
C9	2 (4)	12 (6)	12 (5)	-4 (4)	0 (3)	-6 (4)
C10	3 (3)	5 (4)	5 (3)	-1 (3)	3 (3)	-3 (3)
C11	8 (4)	2 (3)	7 (4)	2 (3)	-5 (3)	0 (3)
C12	3 (3)	7 (4)	8 (4)	-4 (3)	0 (3)	2 (3)
C13	9 (5)	8 (4)	3 (4)	-6 (4)	3 (3)	-2 (3)
C14	4 (3)	8 (4)	1 (2)	3 (3)	0 (2)	-2 (3)
C15	9 (4)	5 (4)	5 (4)	2 (3)	-6 (3)	-3 (3)
C16	8 (5)	18 (8)	8 (6)	3 (5)	-3 (4)	-8 (6)
C17	6 (5)	3 (4)	12 (6)	4 (3)	-4 (4)	-5 (4)
C18	9 (6)	9 (6)	19 (8)	2 (5)	-3 (5)	2 (5)

TABLE LXXI (Continued)

C19	16 (7)	3 (4)	21 (7)	-2 (4)	16 (6)	0 (4)
C20	8 (5)	7 (5)	6 (4)	0 (4)	-1 (3)	-2 (3)
C21	22 (8)	6 (4)	5 (5)	-7 (5)	-5 (5)	3 (4)
C22	2 (4)	5 (4)	5 (3)	2 (3)	-3 (3)	0 (3)
C23	3 (4)	12 (6)	4 (3)	-1 (4)	1 (2)	4 (3)
C24	5 (4)	0 (3)	9 (4)	0 (2)	-3(3)	0 (3)
C25	5 (3)	7 (4)	2 (3)	3 (3)	-1 (2)	2 (2)
C26	9 (5)	1 (3)	14 (6)	-1 (3)	-6 (4)	3 (3)
C27	2 (4)	9 (5)	15 (6)	-4 (3)	-4 (4)	6 (4)
C28	13 (6)	16 (6)	3 (4)	6 (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 10^4 for Cl, Cu; x 10^3 for C, .

TABLE LXXII

BOND DISTANCES (Å) AND BOND ANCLES (°) FOR COPPER CHLORIDE NORBORNENE

Cu1 - Cl1	2.31 (1)	Cl1 - Cu1 - Cl4	98.4 (4)
Cu1 - Cl4	2.28 (1)	C1 - Cu1 - C2	38 (1)
Cu1 - Cl5	2.74 (1)	Cl1 - Cu2 - Cl2	100.8 (4)
Cu1 - C1	2.07 (3)	C8 - Cu2 - C9	37 (2)
Cu1 - Cl2	2.31 (1)	Cl2 - Cu3 - Cl3	99.5 (5)
Cu2 - Cl1	2.28 (1)	Cl3 - Cu4 - Cl4	101.1 (1)
Cu2 - Cl5	2.72 (1)	C22 - Cu4 - C23	36 (2)
Cu2 - C8	1.97 (4)	Cu1 - C11 - Cu2	96.1 (5)
Cu2 - C9	2.06 (5)	Cu2 - Cl2 - Cu3	89.5 (5)
Cu3 - Cl2	2.33 (1)	Cu3 - Cl3 - Cu4	95.0 (4)
Cu3 - Cl3	2.33 (1)	Cu3 - Cl3 - Cu5	87.4 (4)
Cu3 - C15	2.09 (5)	Cu4 - Cl3 - Cu5	87.2 (5)
Cu3 - C16	1.95 (8)	Cu1 - Cl4 - Cu4	90.3 (4)
Cu3 - Cl5	2.73 (1)	Cu2 - C11 - Cu5	88.0 (5)
Cu4 - Cl3	2.32 (1)	Cu1 - Cl1 - Cu5	90.0 (5)
Cu4 - Cl4	2.34 (1)	Cl1 - Cu5 - Cl3	136.7 (5)
Cu4 - Cl5	2.74 (1)	Cl1 - Cu5 - Cl5	112.3 (6)
Cu4 - C22	2.12 (5)	Cl3 - Cu5 - Cl5	110.8 (5)
Cu4 - C23	2.12 (5)	C2 - C1 - C6	104 (4)
Cu5 - Cl1	2.41 (1)	C1 - C2 - C3	107 (3)
Cu5 - Cl3	2.48 (1)	C2 - C3 - C4	101 (3)
Cu5 - Cl5	2.26 (1)	C2 - C3 - C7	100 (3)
C1 - C2	1.37 (6)	C4 - C3 - C7	103 (4)
C1 - C6	1.46 (7)	C3 - C4 - C5	105 (4)
C2 - C3	1.40 (6)	C4 - C5 - C6	98 (3)
C3 - C4	1.50 (7)	C5 - C6 - C1	106 (4)
C3 - C7	1.45 (8)	C5 - C6 - C7	103 (4)
C4 - C5	1.52 (8)	C7 - C6 - C1	98 (4)
C5 - C6	1.56 (7)	C3 - C7 - C6	95 (3)
C6 - C7	1.46 (7)	C9 - C8 - C13	100 (4)

TABLE LXXII (Continued)

C8 - C9	1.29 (8)	C8 - C9 - C10	109 (5)
C8 - C13	1.63 (9)	C9 - C10 - C11	115 (4)
C9 - C10	1.33 (8)	C9 - C10 - C14	104 (4)
C10 - C11	1.47 (6)	C11 - C10 - C14	101 (4)
C10 - C14	1.54 (7)	C10 - C11 - C12	99 (3)
C11 - C12	1.54 (7)	C11 - C12 - C13	99 (3)
C12 - C13	1.51 (6)	C12 - C13 - C8	103 (4)
C13 - C14	1.36 (7)	C12 - C13 - C14	107 (4)
C15 0 C16	1.22 (8)	C14 - C13 - C8	100 (2)
C15 - C20	1.46 (7)	C10 - C14 - C13	89 (4)
C16 - C17	1.53 (10)	C16 - C15 - C20	115 (5)
C17 - C18	1.65 (10)	C15 - C16 - C17	99 (5)
C17 - C21	1.60 (8)	C16 - C17 - C18	108 (5)
C18 - C19	1.30 (8)	C16 - C17 - C21	101 (4)
C19 - C20	1.48 (9)	C18 - C17 - C21	86 (4)
C20 - C21	1.43 (10)	C17 - C18 - C19	112 (6)
C22 - C23	1.31 (8)	C18 - C19 - C20	96 (6)
C22 - C27	1.53 (6)	C19 - C20 - C21	109 (5)
C23 - C24	1.48 (6)	C19 - C20 - C15	102 (4)
C24 - C25	1.54 (7)	C21 - C20 - C15	103 (5)
C24 - C28	1.40 (7)	C17 - C21 - C20	89 (4)
C25 - C26	1.48 (7)	C23 - C22 - C27	106 (4)
C26 - C27	1.66 (8)	C22 - C23 - C24	103 (3)
C27 - C28	1.54 (9)	C23 - C24 - C25	103 (4)
		C23 - C24 - C28	111 (4)
		C25 - C24 - C28	103 (4)
		C24 - C25 - C26	104 (4)
		C25 - C26 - C27	97 (4)
		C26 - C27 - C28	100 (4)
		C26 - C27 - C22	100 (4)
		C28 - C27 - C22	102 (4)
		C24 - C28 - C27	90 (4)

TABLE LXIII
CRYSTAL DATA FOR COPPER BROMIDE NORBORNENE

Formula	$Cu_4Br_4(C_7H_{10})_4$
MWT	759.4.
a	12.743(8) Å
b	12.743(8)
c	9.872 (3)
α	90.0 °
β	90.0
γ	90.0
V	1588(1) Å^3
F (000)	928
μMoK_α	76.522 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.986 g cm^{-1}
Z	2
Meas. Refl.	1145
Obs. Refl.	477
R	7.5 %
Space Group	$P4_1/n$
Octants Meas.	h, k, l

TABLE LXIV

POSITIONAL PARAMETERS FOR COPPER BROMIDE NORBORNENE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
Br1	0.4412 (3)	0.3259 (3)	0.3969 (3)
Cu1	0.5042 (4)	0.3633 (4)	0.6231 (4)
C1	0.485 (4)	0.334 (4)	0.839 (4)
C2	0.401 (3)	0.287 (4)	0.770 (4)
C3	0.420 (6)	0.180 (4)	0.776 (5)
C4	0.338 (5)	0.152 (4)	0.931 (4)
C5	0.474 (5)	0.199 (5)	1.001 (5)
C6	0.550 (3)	0.241 (3)	0.893 (4)
C7	0.524 (5)	0.165 (5)	0.781 (6)

TABLE LXV

HYDROGEN POSITIONAL PARAMETERS FOR COPPER BROMIDE NORBORNENE

ATOM	X	Y	Z
H1	0.4950	0.4106	0.8513
H2	0.3403	0.3205	0.7217
H3	0.3832	0.1345	0.7118
H6	0.6222	0.2570	0.9160
H41	0.3196	0.1886	0.9592
H42	0.3567	0.0784	0.9514
H51	0.4541	0.2533	1.0677
H52	0.5120	0.1435	1.0578
H71	0.5497	0.0948	0.8033
H72	0.5591	0.1856	0.6934

TABLE LXVI

ANISOTROPIC THERMAL PARAMETERS FOR COPPER BROMIDE NORBORNENE

ATOM	U11	U22	U33	U12	U13	U23
Br1	93 (2)	89 (3)	49 (1)	27 (2)	-13 (2)	1 (2)
Cu1	97 (3)	84 (3)	43 (2)	-17 (2)	8 (2)	18 (2)
C1	11 (3)	9 (3)	7 (2)	-6 (2)	3 (2)	0 (2)
C2	1 (2)	14 (4)	7 (2)	0 (2)	-2 (2)	1 (3)
C3	25 (6)	6 (3)	6 (3)	-5 (4)	-1 (3)	-3 (2)
C4	17 (4)	12 (3)	2 (2)	-8 (3)	1 (2)	2 (2)
C5	19 (5)	12 (4)	3 (2)	-1 (3)	0 (3)	5 (2)
C6	6 (2)	15 (4)	5 (2)	1 (2)	-1 (2)	3 (3)
C7	19 (5)	15 (4)	9 (4)	11 (4)	6 (3)	0 (3)

Anisotropic thermal parameters in the form:

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

x 10^4 for Br, Cu; x 10^3 for C.

TABLE LXVII

BOND DISTANCES (Å) AND BOND ANCLES (°) FOR COPPER BROMIDE NORBORNENE

Cu1 - Br1	2.400 (4)	Br1 - Cu1 - Br1'	108.0 (1)
Cu1 - C1	2.16 (3)	C1 - Cu1 - C2	37 (1)
Cu1 - C2	2.17 (3)	Cu1 - Br1 - Cu1'	91.9 (1)
C1 - C2	1.38 (5)	C2 - C1 - C6	105 (3)
C1 - C6	1.52 (5)	C1 - C2 - C3	104 (3)
C2 - C3	1.38 (6)	C2 - C3 - C4	103 (3)
C3 -C4	1.60 (5)	C2 - C3 - C7	105 (4)
C3 C7	1.41 (7)	C4 - C3 - C7	101 (3)
C4 - C5	1.44 (5)	C3 - C4 - C5	99 (3)
C5 - C6	1.48 (5)	C4 - C5 - C6	106 (2)
C6 - C7	1.44 (6)	C5 - C6 - C7	103 (3)
		C5 - C6 - C1	101 (3)
		C7 - C6 - C1	96 (3)
		C3 - C7 - C6	96 (3)

TABLE LXVIII

CRYSTAL DATA FOR COPPER BROMIDE CYCLOOCTADIENE

Formula	$CuBrC_8H_{12}$
MWT	503.3
a	7.406(2) Å
b	10.600(3)
c	10.933(3)
α	90.0 °
β	95.10(2)
γ	90.0
V	854.8(4) $Å^3$
F (000)	496
μMoK_α	71.151 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.955 g cm^{-1}
Z	2
Meas. Refl.	1429
Obs. Refl.	569
R	7.2 %
Space Group	$P2_1/n$
Octants Meas.	±h, k, l

TABLE LXIX

POSITIONAL PARAMETERS FOR COPPER BROMIDE CYCLOOCTADIENE

ATOM	X (SIG (X))	Y (SIG (Y))	Z (SIG (Z))
Br1	0.3328 (4)	0.0144 (2)	0.1218 (2)
Cu1	0.5849 (5)	0.1238 (3)	0.0399 (3)
C1	0.744 (4)	0.196 (3)	0.221 (2)
C2	0.862 (3)	0.174 (4)	0.144 (3)
C3	0.940 (3)	0.268 (3)	0.060 (3)
C4	0.810 (4)	0.136 (3)	0.005 (2)
C5	0.615 (3)	0.323 (2)	-0.040 (2)
C6	0.491 (3)	0.324 (2)	0.032 (2)
C7	0.494 (3)	0.363 (2)	0.160 (2)
C8	0.656 (4)	0.324 (3)	0.246 (2)

TABLE LXX

HYDROGEN POSITIONAL PARAMETERS FOR COPPER BROMIDE CYCLOOCTADIENE

ATOM	X	Y	Z
H1	0.6948	0.1265	0.2680
H2	0.9044	0.0827	0.1383
H31	1.0359	0.3197	0.1076
H32	1.0013	0.2280	-0.0066
H41	0.7988	0.4361	0.0530
H42	0.8578	0.3969	-0.0775
H51	0.5887	0.2903	-0.1243
H61	0.3710	0.2948	-0.0048
H71	0.4774	0.4563	0.1649
H72	0.3843	0.3273	0.1971
H81	0.7580	0.3883	0.2356
H82	0.6355	0.3286	0.3322

TABLE LXXI

ANISOTROPIC THERMAL PARAMETERS FOR COPPER BROMIDE CYLOOCTADIENE

ATOM	U11	U22	U33	U12	U13	U23
Br1	58 (1)	45 (1)	59 (1)	-10 (1)	19 (1)	-13 (1)
Cu1	64 (2)	46 (2)	64 (2)	-13 (1)	15 (1)	-16 (1)
C1	5 (2)	6 (2)	2 (1)	0 (1)	-2 (1)	1 (1)
C2	3 (2)	6 (2)	6 (2)	1 (1)	-4 (1)	-1 (2)
C3	3 (2)	13 (3)	6 (2)	-2 (2)	-2 (1)	0 (2)
C4	8 (2)	5 (2)	5 (2)	0 (2)	0 (2)	2 (1)
C5	4 (1)	4 (1)	4 (1)	-1 (1)	-1 (1)	0 (1)
C6	5 (2)	4 (1)	0 (1)	0 (1)	-1 (1)	0 (1)
C7	4 (2)	5 (2)	7 (2)	2 (1)	-2 (1)	0 (2)
C8	10 (2)	8 (2)	2 (1)	-1 (2)	1 (1)	-3 (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 Br, Cu; x 10^3 for C.

TABLE LXXII

BOND DISTANCES (Å) AND BOND ANCLES (°) FOR COPPER BROMIDE CYCLOOCTENE

Cu1 - Br1	2.435 (4)	Br1 - Cu1 - Br1'	103.4 (1)
Cu1 - C1	2.34 (2)	Cu1 - Br1 - Cu1'	76.5 (1)
Cu1 - C2	2.32 (2)	Br1 - Cu1 - C1	101.1 (7)
Cu1 - C5	2.29 (2)	Br1 - Cu1 - C2	127.2 (7)
Cu1 - C6	2,23 (2)	Br1 - Cu1 - C5	132.9 (7)
C1 - C2	1.29 (4)	Br1 - Cu1 - C6	102.9 (6)
C2 - C3	1.52 (4)	C1 - Cu1 - C2	32 (1)
C3 - C4	1.51 (4)	C5 - Cu1 - C6	32 (1)
C4 - C5	1.50 (4)	C2 - C1 - C8	127 (2)
C5 - C6	1.26 (3)	C1 - C2 - C3	125 (2)
C6 - C7	1.45 (3)	C2 - C3 - C4	116 (2)
C7 - C8	1.53 (3)	C3 - C4 - C5	121 (2)
C8 - C1	1.52 (4)	C4 - C5 - C6	124 (2)
		C5 - C6 - C7	131 (2)
		C6 - C7 - C8	117 (2)
		C7 - C8 - C1	117 (2)

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