I. CORRELATION OF EMISSION AND STRUCTURE IN SOLID STATE ANIONIC COMPLEXES OF COPPER (I) HALIDES

II. POLYMERIC COPPER (II) FLUORIDE COMPLEXES

By

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INTRODUCTION

There are two major areas of investigation in this study. The greater emphasis is placed upon the synthetic, crystallographic, and fluorometric study of "anionic cuprous halide clusters." The second area of interest is the synthesis and X-Ray structural characterization of polymeric cupric fluoride compounds.

Anionic cuprous halide clusters are of interest because they form small discrete centers which emit in the solid state. These can be studied with X-Ray diffractometry to observe the environment of the emitting center. These investigations can give clues leading to correlation of the influences of solid state structure upon emission properties and thus to a knowledge of how to design materials to act as fluorescent/ phosphorescent sensitizers for photoconductors. (1,2)

Luminescence of cuprous halides has been known since 1939 when J. T. Randall discovered this phenomenon and its temperature sensitivity for cuprous chloride. (3) Beginning in 1970, several investigators became actively interested in the luminescence of cuprous halides and their complexes. H. D. Hardt was one of the primary investigators in this area, synthesizing numerous copper (I) complexes and reporting their luminescence at ambient and low temperatures.(4,5,6,7,8) A reversible shift as observed by one's eye in the emission maxima with the reduction of temperatures, was identified by Hardt as "fluorescence thermochromism."

Since the early work of Hardt, many fluorescent cuprous halide complexes have been examined. A common characteristic of many of these complexes is close proximity of unbonded copper atoms in the metal halide cluster.

E. M. Holt, in her review of anionic cuprous halide complexes has demonstrated the great diversity of structures and coordination geometry that these materials exhibit. (9) The simplest structure the dihalocuprate (I) anion consists of a copper bound to two halide atoms in a linear structure. A more complicated structure, the hexahalotetracuprate (I) dianion demonstrates trigonal coordination in its complex three dimensional motif. The last type of coordination found in cuprous halide complexes is tetrahedral in which four halides are bound to each copper in the complex. Several examples of tetrahedral coordination have been found and in many of these, the complex is polymeric in nature. As many of these complexes emit when excited with ultraviolet light, there is a large body of known structures one could examine to relate structure with emission. In these anionic clusters, copper is bound only to halide atoms and is termed "ligandless." Another family of Cu(I)X clusters involves CuX(L) materials where L is an organic ligand. Previous work in this laboratory established metal to ligand charge transfer, metal-metal interactions, and ligand to ligand interactions to be the excitation mechanisms leading to emission in these compounds. (10,11,12,13,14)

Anionic clusters offer an opportunity to study the interactions of copper atoms with each other in different spatial arrangements without competing emission arising from metal to ligand or ligand-ligand interactions. Three classes of ligandless cluster were examined in this study; CuX_2^-, $Cu_2X_4^=$, and $Cu_4X_6^=$ clusters X=I, Br, or Cl. Structural arrangement was determined using single crystal X-Ray diffractometry. Fluorescence measurements were taken at temperatures ranging from 10K to room temperature by scanning the emission spectra while exciting the sample with ultraviolet light of wavelength of 300 nm. Correlations between electronic interactions and structure were explained on the basis of d orbital interactions.

The second area of study, the synthesis and structural determination of copper (II) fluoride clusters, demonstrated a method for preparation of novel polymeric compounds. Most copper (II) fluoride salts exhibit little tendency to form polymeric clusters by fluoride bridging between metal atoms. Many cupric fluoride clusters are of the type MF_6, where the metal has six nonbridging fluorides bound to it with each fluoride atom forming the vertex of an octahedron.

Copper (II) fluoride was reacted with Group I metal fluorides to give mixed salts. These mixed salts were produced by fusion in an atmosphere of anhydrous hydrogen fluoride.

PART I

CORRELATION OF EMISSION AND STRUCTURE IN SOLID STATE ANIONIC COMPLEXES OF COPPER (I) HALIDES

CHAPTER 1

INTRODUCTION AND HISTORICAL

Luminescence in copper (I) halides was first discovered in 1938 by Randall when he examined several materials with an ultraviolet light source and found them to emit visible light. (3,15) Randall examined several of these materials also at liquid nitrogen temperatures. Cuprous chloride exhibited an apparent shift in its emission wavelength as there was a visible change in the color of the emitted light at room temperature compared to that at liquid nitrogen temperature.

The emission properties of cuprous halides were not further examined until Hardt's work in 1973. (16,17) He examined the thermal changes in the emission in a more quantitative manner with a low temperature fluorometer. He proposed two possible explanations for this temperature dependent emission change, which he called fluorescence thermochromism. The visible color change with temperature might be caused by a shift of the actual λ max, or more possibly by the eye's variable sensitivity to intensity change at λ max with temperature. Both effects would cause the color change examined by Randall. However Randall had no way of distinguishing them as the eye was a poor spectrofluorometer.

In Randall's work, where the emission properties of cuprous halide complexes were only examined visually, little information can be determined. The eye sees light as an average of the emitted radiation making it impossible to determine visually the maxima of the spectra and changes with temperature. Correlation of emission with electronic transitions responsible for emission can require the measurement of emission spectra at several temperatures.

Excitation in copper (I) halide complexes can be broken down into three catagories.

1) Metal to Ligand Charge Transfer (MLCT)

2) Ligand - Ligand Interaction (LLI)

3) Metal - Metal Interaction (MMI)

Metal to ligand charge transfer (MLCT) describes a $3d^{10}$ - $3d^{9}$ π^* transition, in which an electron is promoted from a 3d orbital to an antibonding orbital of the ligand. (4,18,19,20) This transition is found in cuprous halide clusters in which copper is ligated to aromatic Lewis bases such as pyridine and quinoline.

Ligand - ligand interactions involve π - π^* transitions caused by close packed parallel π systems. This effect is seen primarily at low temperatures. The emission spectra of solid $(CuI(quinoline))_4$ was shown to exhibit identical emission fine structure to that found in frozen solutions of quinoline in ethanol at 77°K. (21, 22) The separation between aromatic ligands apparently shrinks below the threshold value for interligand π - π^* interaction when the temperature is near 77° K. This emission is not seen at room temperature. The emission from the ligand - ligand interaction shown by Buchner in the spectra of

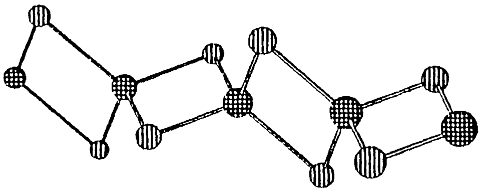
$(Cu(Ph_3P)(phen))^+$ to be less intense, at a shorter wavelength, and shorter lived than the metal to ligand charge transfer interaction. (20)

A wide variety of cuprous halide clusters has been synthesized. This study is primarily interested in the so called ligandless clusters, in which copper halides bond together to form a multitude of anionic species. The copper atoms found in these clusters exhibit three different types of coordination; tetrahedral, trigonal planar, and linear.

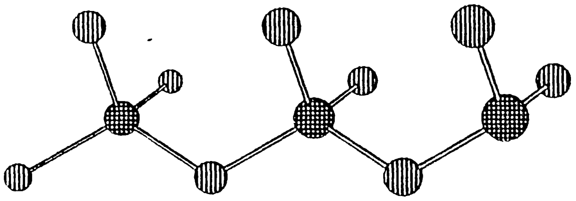
Figure 1 shows examples of tetrahedrally coordinated complexes. The first complex, $(CuX_2)^-{}_x$, is a polymeric structure in which copper atoms are bridged by pairs of halide atoms to form a chain of corner sharing parallelograms. (23,24,25,26,27) The second structure, $(CuX_3)^={}_x$, is a chain of alternating copper and halide atoms in which each copper atom has two terminal halide atoms bound to it. (28) The third structure, $(Cu_2X_3)^-{}_x$, is a polymeric ribbon of edge sharing parallelograms with each copper bound to four bridging halide atoms. (29,30,31,32,33,34,35,36) The fourth structure, $(Cu_2X_3)^-{}_x$, is allotropic with the third structure, however, there is little resemblance between the two. (37,38,39) This last compound is composed of a series of tricyclic clusters, with an alternating up and down pattern, fused to each other by one edge.

Figure 2 shows three examples of copper complexes in which copper shows planar trigonal coordination. The first compound, $(CuX_3)^=$

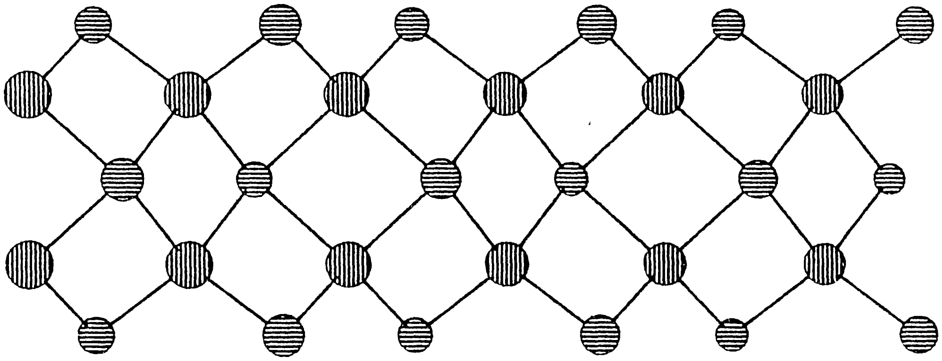
$[CuX_2]_x^-$



$(CuX_3^{=})_x$



$(Cu_2X_3^-)_x$



$(Cu_2X_3^-)_x$

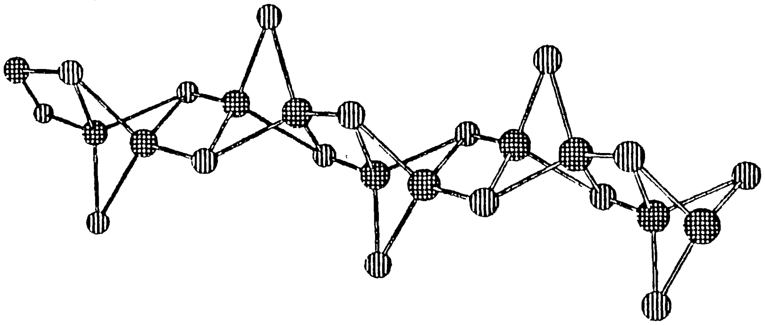


Figure 1. Tetrahedrally Bound Cuprous Halide Anions.

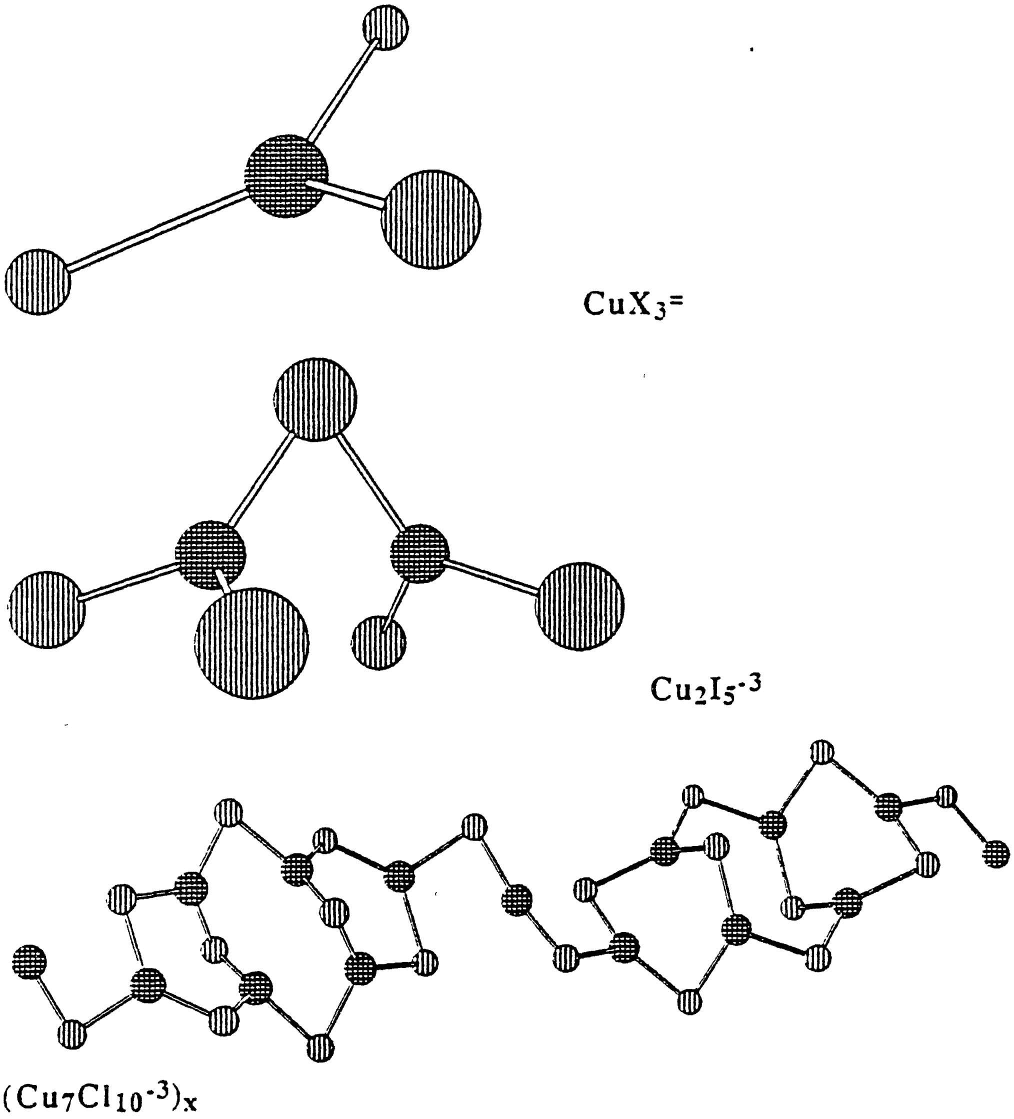


Figure 2. Trigonally Bound Cuprous Halide Anions.

is the simplest one and has a single copper atom bound to three terminal halides. (40,41,42,43) The second cluster, $(Cu_2I_5)^{3-}$, is also relatively simple with two trigonally bound copper atoms bridged by a single halide atom. (44) The third and most complex structure of this type, $(Cu_7Cl_{10})^{3-}$, shows a polymeric cluster of tricyclic ring systems that are bridged by a linear copper dihalide unit which displays the third type of coordination found in cuprous halide clusters, linear dicoordinate. (45)

Two of the anionic clusters of interest in this study exhibit planar trigonal coordination, the hexahalotetracuprate (I) (39,46,47,48) and the tetrahalodicuprate (I) dianions. (49,50,51,52,53,54,55,56,57) The third cluster of interest is the linearly coordinated dihalocuprate (I) anion. (58, 59,60,61,62,63,64,65,66,67,68,69,70,71,72,73,74,75,76,77,78,79,80)

Figure 3 shows an average hexahalotetracuprate (I) dianion. This anion has halide atoms at each of the six apices of an octahedron and four copper atoms oriented inside the halide shell to form the apices of a tetrahedron. This highly symmetrical anion has two-fold axes through each opposing halide, through opposing pairs of copper atoms and three fold axes can be drawn through any of the copper or halide atoms. It might also be bisected by various mirror planes.

Figure 4 shows the two forms of the tetrahalodicuprate (I) dianion. The first form shown is the bent form in which the cluster is bent like a hinge on the line formed by the two bridging halide atoms. The second form, the planar form, has all atoms of the cluster placed in the same plane. The bent form is interesting in that it can place the two

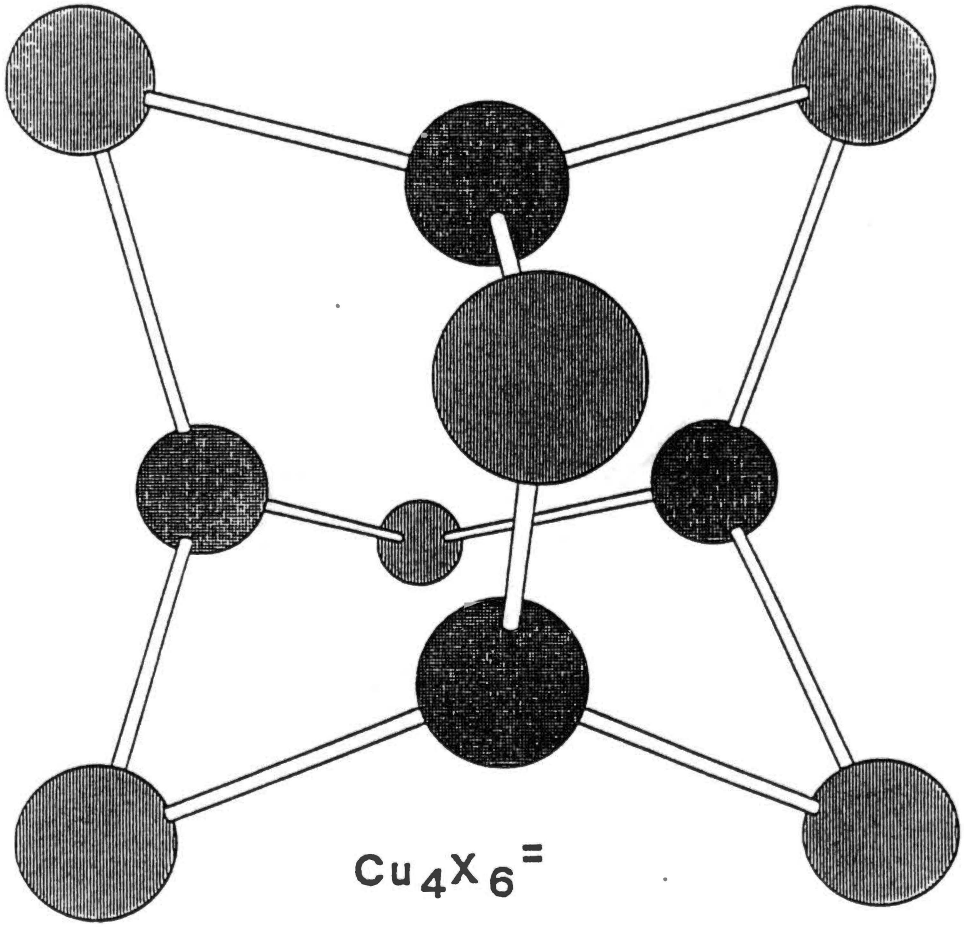


Figure 3. Hexahalotetracuprate Anion.

$Cu_2X_4^{=}$

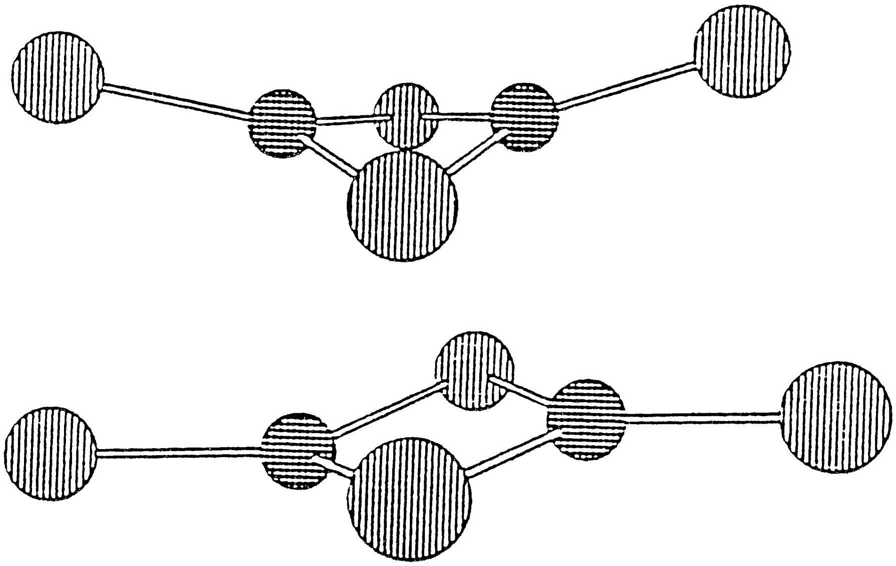


Figure 4. Tetrahalodicuprate Anion.

copper atoms in closer proximity than the planar form if all bond lengths stay constant.

The third and least complex cluster examined is a linear dicoordinate cluster. The dihalocuprate (I) cluster shown in Figure 5 consists of a copper atom bound to two terminal halides. This three atom group can be bent or be absolutely linear but is normally found to deviate one or two degrees from perfect linearity.

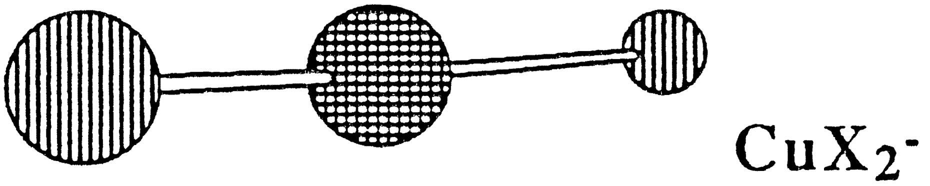


Figure 5. Dihalocuprate Anion.

CHAPTER II

X-RAY CRYSTALLOGRAPHY

X-ray crystallography is the most definitive method of structural determination, as one can derive the composition, interatomic distances, and bonding angles, as well as the areas of electron density occupied by the atoms of the material. One can get a three dimensional picture of the molecule by this powerful method, establishing its conformation and configuration.

Single crystals with a high degree of internal order are required. The atoms and molecules making up the crystal are arranged in an orderly repeating motif. This periodic structure allows the use of X-ray diffraction methods to give the structure of the unit cell which represents the unique three dimensional repeating pattern of the crystal.

The unit cell of a crystal, the smallest unique repeating unit, is defined by its three edges <u>a</u>, <u>b</u>, and <u>c</u>, and the three angles between the edges; α, β, and γ. The length of the edges and the angles formed by these edges place a crystal in one of the seven crystal classes.

1) triclinic $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma$

2) monoclinic $a \neq b \neq c$, $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$

3) orthorhombic $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$

4) tetragonal $a=b\neq c$, $\alpha=\beta=\gamma=90^\circ$

5) cubic $a=b=c$, $\alpha=\beta=\gamma=90^\circ$

6) hexagonal $a=b\neq c$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$

7) rhombohedral $a=b=c$, $\alpha=\beta=\gamma\neq 90^\circ$

The seven crystal systems define only the shape of the volume of space that repeats, but give no idea of its contents or internal arrangement. Each unit cell is like all others in the crystal and is defined by a combination of these three dimensional shapes with internal symmetry elements such as rotation axes, and mirrors.

There are fourteen distinct Bravais space lattices. They define the repetition of the crystal's pattern in space without reference to the details of the repeated motif. There are seven simple lattices that do not exhibit face or body centering. These simple lattices are denoted by P for primitive except in the case of the rhombohedral cell which is a primitive type lattice but is denoted with an R. The seven non-primitive lattices are denoted by the type of centering involved, C, F, or I. C-centering involves centering with respect to one of the faces of the simplest unit of the space lattice. Face centering can also be denoted by A or B for centering on that face. F-centering involves centering with respect to all three faces simultaneously. I-centering, also known as body centering, involves centering with respect to a point at the intersection of the body diagonals of the basic unit space lattice.

There are 32 crystal classes or point groups, which are associated with the arrangement of symmetry elements that can be present in the unit cell. The general nature of the unit cell determines the crystal system, while the internal symmetry determines the crystal class. The internal symmetry allows one to solve structures by finding only the atoms found in one of the symmetrically associated motifs in the crystal.

The coordinate system of the crystal lattice allows us to see the symmetry relationships between the asymmetric units of the unit cell, the smallest symmetry related repeating unit of a crystal. Each asymmetric unit is related to all other asymmetric units in the unit cell by symmetry operations such as rotational axes, mirror planes, and centers of inversion. The symmetry operations displayed by the point group, and the Bravais lattice, define the crystal's space group from the 230 possible space groups.

Determination of the structure of a crystal, since it is made of regularly repeating units, is simplified to the determination of the unit cell and in most cases of one asymmetric unit. What one actually determines is the space and time averaged structure for the crystal as most solid matter has some random disorder imperfections and atoms are constantly vibrating within a small area. This averaging is taking place over a crystal containing 10^{15} to 10^{18} unit cells with atomic vibrations on the order of 10^{13} per seconds. The structure determined, however, can give distances to thousandths of angstroms and angles to hundredths of degrees which is more than adequate for most purposes.

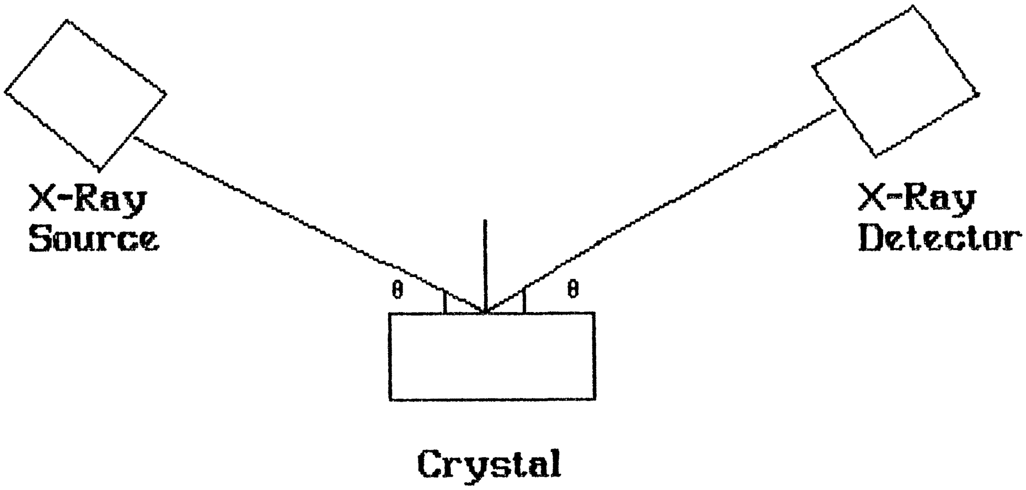
The crystals used must be approximately 0.2 mm on each edge. They should have sharp well-defined faces without cracks and bubbles. They should be transparent, if the color is light enough. If no small crystals are available, pieces can be carefully cleaved from larger crystals for use.

The crystals used in this study were air stable and required no special preservation techniques, such as isolation in a sealed capillary or preservation in a stream of low temperature nitrogen gas, to prevent decomposition. The crystals were attached by a drop of super glue to a glass fiber held in a brass support . The brass support was placed in a goniometer head and optically centered on a four circle Syntex P3 automatic diffractometer. A rotational photograph was taken to ascertain crystal quality and to obtain starting data to precisely height center the crystal. Crystals of adequate quality for study give rotational photographs in which the pattern of spots on the photograph extend to the edge of the photograph and are intense with well defined edges. Poor crystals give spots that are larger and more diffuse in appearance, and halos or rings appear in the photograph.

The spots on the rotational photograph are points where diffraction occurs and the conditions of the Bragg equation are met:

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

n is an integer number, usually one; λ is the wavelength of the X-ray radiation used; for molybdenium radiation λ is 0.71069 Å ; θ is the angle of incidence of the X-ray beam on the set of planes diffracting and giving constructive interference, and d is the distance in angstroms between repeating planes in a crystal. (Figure 6) The planes may be represented as parallel and successive slices of the unit cell with the first slice through the origin. The planes are designated by their Miller indices h, k, and l where h is the number of planes that cut through the unit cell along the a cell edge, k along the b cell edge, and l along the c cell edge. The Miller indices can be related to d from the Bragg equation by use of



$$N\lambda = 2d \sin\theta$$

Figure 6. Bragg Equation.

vector methods to give the following general equation which is the equation for the triclinic crystal class.

$$1/d^2 = U^{-2}(h^2b^2c^2\sin^{-2}\alpha + k^2c^2a^2\sin^2\beta + l^2a^2b^2\sin^2\gamma + 2abc(kla(\cos\beta\cos\gamma - \cos\alpha) + lhb(\cos\gamma\cos\alpha - \cos\beta) + hkc(\cos\alpha\cos\beta - \cos\gamma))) \quad (2)$$

where

$$U = abc(1 + 2\cos\alpha\cos\beta\cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma)^{1/2} \quad (3)$$

The sphere of reflection (Ewald sphere) is a graphical means of representing the amount of the data that can be collected. In the version of the Ewald construction shown in Figure 7 the radius of the Ewald Sphere is $1/\lambda$. The incident beam's direction vector s_0 strikes the crystal center at point O. The point O is the origin of the reciprocal lattice. The vector s is the vector describing the reflected beam and intersects the limiting sphere at point B. Reflection occurs when the vector S intersects the sphere of reflection at the reciprocal lattice point hkl where hkl are the Miller indices for the reciprocal lattice point. The limiting sphere is the sphere with radius $2/\lambda$ which is a geographical representation of all possible reflections accessible to radiation of wavelength l. The limiting sphere is centered on the origin of the reciprocal lattice and is the envelope of all possible positions of the Ewald sphere within the reciprocal lattice. (81)

The reciprocal lattice is described in terms of axes a^*, b^*, and c^* which are vectors that can be related to the vectors represented by the cell axes a, b, and c by the following vector relationships.

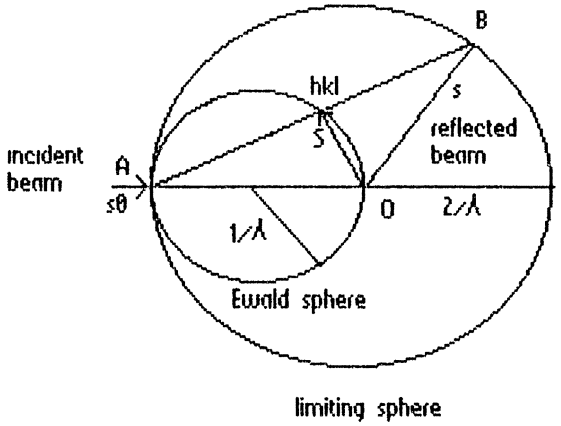


Figure 7. Ewald Sphere.

$a . a^* = 1, \quad a . b^* = 0, \quad a . c^* = 0$

$b . a^* = 0, \quad b . b^* = 1, \quad b . c^* = 0$

$c . a^* = 0, \quad c . b^* = 0, \quad c . c^* = 1$

The reciprocal axes are normal to the plane formed by the normal axes not designated by the same letter as the reciprocal axis of interest. For example a^* is normal to the plane formed by axes b and c. By extension of this argument it can be shown that the normal lattice, L, is reciprocal to the reciprocal lattice, L^*.

The reciprocal lattice has two properties that make it useful for describing diffraction. First, the reciprocal lattice vector is normal to a family of planes (hkl) in the normal space lattice. Second, the length of the reciprocal lattice vector S is the reciprocal of the interplanar spacing d(hkl) for the planes (hkl). These two properties are significant in that the essential features of orientation and spacing for a whole set of parallel planes (hkl) are expressed by the reciprocal lattice vector or the reciprocal lattice point hkl. If these indices, commonly called the Miller indices, represent an X-ray reflection; then the reciprocal lattice is a map of the diffraction pattern for the crystal.

Neither the Bragg equation nor any of the above mentioned methods of describing observed diffraction deals with intensity of diffraction. Lattice planes that coincide or nearly coincide in orientation and position with densely populated planar or nearly planar groups of atoms will show the greatest diffraction intensity. The intensity of reflections is readily measured as total crystal intensity.

The intensity of the measured reflection however gives no idea of the phase of the reflected beam. The phase of the reflection must be known to solve the structure. Phase cannot be measured as intensity can, so it must be calculated. The inability to directly measure phase is known as the phase problem. There are several methods for determining the solution of the phase for a group of reflections. The determination of phase is easier for centrosymmetric structures where all phases are 0 or π and the sign of the structure factor, F, is either + or -. The phases for an asymmetric structure vary from $-\pi$ to π which complicates the phase determination greatly.

The phase of structure factors are then determined indirectly by use of one of the programs for sequentially determining phase such as MULTAN, by the use of triplet relationships and the use of magic integer values. The probability of the phase being positive is calculated at every step along the phase determination to ensure correctness of the solution. As the determination of the phase is a statistical determination several solutions can be given. The solutions are then assigned figures of merit by how well the solutions agree with the phase relationships and the "squared structure." The solution with the best figures of merit is then assumed to be the correct solution, which is not necessarily true. The trial structure from the best solution is then used as the starting point for the refinement of the structure.

There are three distinct steps in the determination of a crystal structure by X-ray diffraction. First, one must experimentally determine the unit cell dimensions and collect the intensity data of the diffracted beam from the crystal. Second, one must derive a trial structure, using some direct methods technique such as MULTAN or SHELX or by the use of Patterson, heavy atom methods, when heavy atoms exist in the unit cell. Third and finally, one must refine the trial structure until the calculated and observed data agree within desired limits.

The experimental starting point for the determination of a structure by X-ray diffraction is optically centering the crystal on the goniometer head. Next, a rotational photograph is taken to obtain starting diffraction data that is used to precisely height center the crystal and begin the process of determining the unit cell parameters. Cell parameters are determined by least squares fit of the refined positions of 15 reflections selected from the rotational photograph. In cases where errors in cell parameters are high, a fast data scan is run to identify intensely diffracting data points with $2\theta > 20^{\circ}$ to improve the cell parameter errors. Once the errors reach an acceptable minimum, then data is collected. The number of octants of data collected is dependent on the diffraction symmetry of the crystal class; for triclinic crystals, four octants must be collected; for monoclinic crystals, two, and for orthorhombic and higher symmetry classes, one octant of data must be observed.

During data collection, the diffractometer records the intensity data, I , associated with each reflection of index, h k l, in the following format: sequence number (negative for standard reflections), h, k, l, 2θ, ω, ϕ, x, 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 corrected for four different experimental artifacts. Correction factors are applied for background, polarization, Lorentz effect, and crystal decomposition.

The correction for the background is calculated using the following equations.

$$I\ int = (I\ meas - Lbg - Rbg) * \text{scan speed.} \qquad (4)$$

$$\sigma I\ int = (I\ meas + Lbg - Rbg)^{1/2} * \text{scan speed.} \qquad (5)$$

I int = Integrated Intensity.

σI int = Standard deviation of I int.

I meas = Measured Intensity.

Lbg = Left Background.

Rbg = Right Background.

The polarization correction is necessary due to unequal reflection of the unpolarized components of the x-ray beam. Each vector of the x-ray beam has a parallel component and a perpendicular component. In the reflected beam, the parallel component (parallel to the reflecting plane) is diffracted with greater efficiency compared to the perpendicular component causing the diffracted beam to be polarized. The polarization correction is calculated by the following expression:

$$p = (1 + \cos^2 2\theta) / 2 \qquad (6)$$

therefore, p is a function of 2θ and does not depend on the geometry of data collection.

The Lorentz effect depends on collection methods and the size of 2θ. When crystals are rotated at constant speed, reflections with low 2θ spend more time in the beam than those with high 2θ. The Lorentz factor is given by:

$$L = 1/\sin 2\theta \qquad (7)$$

The combined Lorentz-polarization correction is given by:

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

In the cases where significant decomposition of the crystal occurs during the course of data collection, one must apply a correction factor which assumes that decomposition is a linear function with respect to time. Therefore standard reflections are remeasured periodically and the correction is applied to each data point between every set of standard reflections. The composition correction is given by the following equation.

$$\text{Cor decomp} = I_{\text{orig}} / I_{\text{ave}} \qquad (9)$$

where

I orig = starting intensity of a standard reflection

I ave = is the average current intensity of the standard reflection in between any two observations.

The above mentioned corrections can be combined into a single expression to give the overall corrected intensity:

$$I_{\text{cor}} = I_{\text{int}} * (Lp)^{-1} * (I_{\text{orig}} / I_{\text{ave}}) \qquad (10)$$

One then determines the structure factor F as the absolute value of the square root of the corrected integrated intensity, I_{cor}:

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

The associated error in | F hkl |, $F\sigma$ is calculated by the following:

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

$$(N_t - N_{Lbg} - N_{Rbg})^{1/2} \qquad (12)$$

where

N_t = # of counts

N_{Lbg} = # of left background counts

N_{Rbg} = # of right background counts

$$N_{pK} = N_t - N_{Rbg} - N_{Lbg} \qquad (13)$$

Although the structure factor $|F|$ is derived from the collected intensity data, the measured data contains no information about phase α, as phases cannot be measured The phase is the difference in period, expressed as an angle, between the wave resulting from reflection of a specific set of planes and a wave resulting from reflection at the origin.

$$\rho\ (xyz) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |Fhkl| \cos (2\pi\ (hx+ky+lz) - \phi\ hkl$$

(14)

To find the solution for the structure one must determine the phase of at least some reflections.

One can then use a Fourier transform of the phased structure factors to synthesize an interpretable electron density map of the structure, showing the positions of at least some of the atoms. There are two mathematical approaches to determining phase; Patterson mapping, also called the Heavy Atom Method, and Direct Methods. The Patterson map is used for structures containing a few heavy atoms, when F is squared, the phase angle's sign is eliminated. The Patterson map is the Fourier transform of $|F|^2$. Peaks on the map are interpreted as the positions of the ends of vectors between heavy atoms translated to the origin. The vectors between heavy atoms are the most intense. Depending upon space group symmetry, groups of vectors may appear on specific planes or lines. These are called Harker lines and planes, and from these positions heavy atoms may be calculated.

In this study, Direct Methods were most often used to determine heavy atom positional parameters for the trial structure . Through the use of Sayre's rule, triplet relationships, and magic integer methods, one can determine the phases of a limited number of reflections. Enough phased structure factors are generated to permit the Fourier transform map to display the trial structure . MULTAN, the program used for this study, begins with a starting set of reflections, the phases of which are "permuted". Each permutation is a starting point for phase extension and refinement using the tangent formula. The tangent formula as given by Karle and Hauptman in 1956 is: (83)

$$\tan f(h) = \frac{\sum_{h'} |E(h')\, E(h-h')| \sin(\phi(h') + \phi(h-h'))}{\sum_{h} |E(h')\, E(h-h')| \cos(\phi(h') + \phi(h-h'))} \qquad (15)$$

The steps in MULTAN are as follows: (82)

(i) Calculate the $|E|$s, normalized structure factors, from $|F|_{obs}$ values using a Wilson plot method

(ii) Set up $\Sigma 2$ relationships to determine a limited number of reflections of type 2h 2k 2l that have a fixed positive phase

(iii) Use of the triplet relationships to extend the set of phases.

$$\phi(h) - \phi(h') - \phi(h-h') = 0 \qquad (16)$$

(iv) During solution determination, values are assigned to unknown phases by magic integer phase permutation. A number of starting assignments are made and from these, several solutions are calculated.

(v) Calculate Figures of Merit for each solution.

(a) ABSFOM which is a measurement of the extent to which phase relationships are satisfied. Theoretically ABSFOM can vary from zero for totally incorrect random phases and 1.0 for theoretically correct phase relationships, however, in practice ABSFOM for correct phase relationships are in the range of 1 1 to 1.4. (82)

(b) PSIZERO as defined by

$$\psi_0 = \frac{\sum_{h} \left| \sum_{h} E(h')\ E(h-h') \right|}{\sum_{h} \left(\sum_{h} \left| E(h')\ E(h-h') \right|^2 \right)^{1/2}} \qquad (17)$$

where E (h) is a weak or accidentally absent reflection and the summation includes all the E s in terms of which the structure is to be solved. This test function was derived from a statistical form of Sayre's sign relationship where the sign of the product of the phases of a triplet defined by h, h', and h + h' is probably equal to +1.0. For correct sets of phases PSIZERO should have a value between 1.0 and 2 0 (82)

(c) R, the residual which is a measure how well the "squared structure" resembles the "structure" for the set of phase under consideration

It is defined by the parametric equation:

$$R = \frac{\sum_{h} \big|\, |E(h)|\,\mathrm{obs} - |E(h)|\,\mathrm{calc} \,\big|}{\sum_{h} |E(h)|\,\mathrm{obs}} \qquad (18)$$

$$\text{where } E\,(h)\,\mathrm{calc} = K \sum_{h} E\,(h')\,E\,(h\text{-}h') \qquad (19)$$

and K is a constant such that

$$\sum_{h} |\,E\,(h)\,|^{2}\,\mathrm{obs} = \sum_{h} |\,E\,(h)\,|^{2}\,\mathrm{calc} \qquad (20)$$

(d) The three previous Figures of Merit are usually combined to give a combined Figure of Merit CFOM.

$$\mathrm{CFOM} = W1 \left\{ \frac{z - z\ \mathrm{min}}{Z\ \mathrm{max} - z\ \mathrm{min}} \right\} + W2 \left\{ \frac{(\Psi\ \theta)\ \mathrm{max} - \ \theta}{(\Psi\ \theta)\ \mathrm{max} - (\psi\ \theta)\ \mathrm{min}} \right\} + W3 \left\{ \frac{R\ \mathrm{max} - R}{R\ \mathrm{max} - R\ \mathrm{min}} \right\}$$

(21)

The weights W1 + W2 + W3 = 3 and Z and R are ABSFOM and the residual. The best theoretical CFOM is 3.0.

(vi) The E values are used with the phase angles of the solution with the best CFOM to calculate a preliminary trial structure.

The preliminary atomic coordinates are input into the binary data file used by the X-RAY SYSTEM for least squares refinement of the data to give an improved structure. (85) Each least squares refinement is followed by a difference Fourier synthesis and creation of a bond distance and angles comparison with refined atoms and peaks of electron density from the difference Fourier to find remaining atoms. The new unrefined atoms are input into the binary data file, then refined using least squares refinement. This cyclic process is continued until all atoms are found as shown by the low intensity of the electron density peaks from the difference Fourier map until the structure is complete and chemically reasonable.

In the first stages of the structural solution, the thermal elipsoid that describes the area in space in which the electron density of an atom is most likely to be found is estimated as a spherical area in which displacements along the x, y, and z axes are equal. This is related to the atomic scattering factor by the parametric equation shown below.

$$f=f_\theta \exp(-B(\sin \Theta)^2 / \lambda^2) \qquad (22)$$

where

$$B=8\pi^2u^2 \qquad (23)$$

f= atomic scattering factor

f_θ= scattering factor for a stationary atom

λ= wavelength of X-ray used

B= isotropic thermal parameter or Debye-Waller temperature factor

u^2= mean squared amplitude of thermal motion

After all of the nonhydrogen atoms are found, an anisotropic least squares refinement is performed to allow the thermal parameters to vary in six specific dimensions as described by its six different root mean squared displacements The isotropic and anisotropic thermal parameters are related by:

$$S^T \beta S = \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\,\beta_{12}hk + 2\,\beta_{23}kl + 2\,\beta_{31}lh \qquad (24)$$

where

S^T= (h k l) vector

S= the column symbol for the vector S in the reciprocal axes basis

β = the isotropic thermal parameter

β_{xx}= the anisotropic thermal parameters

After atoms are refined to completion, the structure is viewed using ORTEP. (84) The ORTEP drawing gives an accurate three dimensional representation of the atomic arrangement of the molecules in the crystal including the atomic thermal parameters.

CHAPTER III

LUMINESCENCE

Luminescence is defined as the process in which radiation is emitted by a molecule or an atom after it has absorbed energy to go to an excited state. (86) There are four laws which govern the process of luminescence. (87) They are outlined below.

The De Ment Absorption Law, the first law of Luminescence, states that "before emission can occur from a luminescent system, absorption must take place." (88) This law requires that a quantum of light be absorbed for a quantum of light to be emitted but says nothing of how this emission occurs. However it is easily seen that if no light is absorbed then none can be emitted.

The second and best known law of luminescence, the Stokes Emission Law, deals with the emission quantum. It states that " the energy released from a luminescent body is always less than the energy absorbed for initial excitation." (87) In other words, in accordance with the second law of thermodynamics some energy is lost between absorption and emission. The loss of energy is most noticeable in the shift to longer wavelength from the absorbed light to the emitted light. This shift to longer wavelength is known as the Stokes shift. There are some violations of the Stokes Law where more energy is emitted than absorbed, as shown by a shift to shorter wavelengths. This shift is called an Anti-Stokes shift. Anti-Stokes Shifts arise from surplus energy being available to the system while it is in a thermally excited state. Anti-Stokes Shifts are seen more frequently as one increases the temperature at which the experiment is being performed. Anti-Stokes Shifts are virtually nonexistent at low temperature.

Temperature also effects the shape and intensity of emission peaks in measured spectra. These effects arise by the changes in populations of the available rotational and vibrational levels with increase in temperature. At low temperature, peaks are sharper and more intense as there are fewer absorbing centers that are at thermally excited levels. The transitions that occur are primarily electronic and not vibrational or rotational in nature. Electronic transitions require much larger amounts of energy in discrete quantum than rotational or vibrational transitions. They show up as a single wavelength emission or absorption, and not as a near continuous spectrum as for rotational and vibrational transitions.

In systems that obey the first two laws, the third law is generally obeyed. The third law of luminescence, the Law of Quantum Yield, states that " the absorption of radiation by a luminescent system is a quantum process involving one quantum per absorbing center; the yield of luminescence in the ideal case being near unity." (87) Put more simply, for each quantum absorbed, one is emitted. In reality, efficiencies near unity are seen only in dilute solutions at low temperatures.

The final law of luminescence, the Law of the Optimum, states that "the intensity of emission increases to an optimum value in both solid and liquid solutions with an increase in concentration of luminescent centers, followed by a decreasing emission at higher concentrations." (87) This implies that the optimum is a point at which increasing concentration causes a loss of efficiency by shielding and other effects.

There are several processes encompassed by the general umbrella of luminescence. There are several types of luminescence, cathodoluminescence, light emission caused by electron bombardment; triboluminescence caused by mechanical interaction; chemoluminescence through chemical reactions such as the luminol reaction; and photoluminescence, reemission of absorbed light. Photoluminescence is the major area of interest and will be simply called luminescence.There are several events that occur during luminescence. The first process, absorption, is self explanatory. After absorption, radiative and nonradiative operations can occur. The nonradiative operations are vibrational relaxation; the loss of energy by conversion to thermal energy, and internal conversion, such as the conversion of an excited singlet state to an excited triplet state or decay from singlet to singlet state. The radiative operations are fluorescence, which is the immediate reemission of absorbed light, and phosphorescence, the delayed reemission of absorbed light. Of the luminescence processes, fluorescence and phosphorescence, fluorescence is the process of primary interest.

The process of fluorescence consists of a photon being absorbed by the fluorescing species, moving it to a vibrationally and electronically excited singlet state, with nonradiative relaxation to the lowest vibrational level of the electronically excited singlet state, followed by photon emission to drop to a vibrationally excited level of the ground singlet state with nonradiative relaxation to the lowest occupied vibrational level of the ground singlet state. (Figure 8) An excited singlet state has a lifetime of 10^{-9} to 10^{-7} seconds, thus the decay time for fluorescence is equally short. In other words when one turns off the excitation source, commonly an ultraviolet light source, the material stops fluorescing immediately. The radiation emitted by the fluorescing material is generally of a longer wavelength, lower energy than the excitation wavelength. This shift to longer wavelength is called the Stokes shift.

In the singlet state, electrons are spin coupled, the spin orientation of the two electrons in each orbital is opposite. The triplet state is the electronically excited state in which one electron is promoted to an orbital of higher energy and spin orientation as the electron remaining in the orbital from which it was promoted. The singlet state has both electrons in the same energy state while the triplet state has three degenerate energy states due to the three possible spin orientations for the two electrons.

Fluorescence is measured using a fluorometer which records the light emitted at right angles to the path of the incident beam. A typical fluorometer consists of the following parts: the radiation source, a monochromator between the source and the sample, a sample chamber with the incident beam inlet window oriented 90° from the window exiting the sample chamber to the emission measurement pathway, a monochromator between the sample chamber and the detector, the

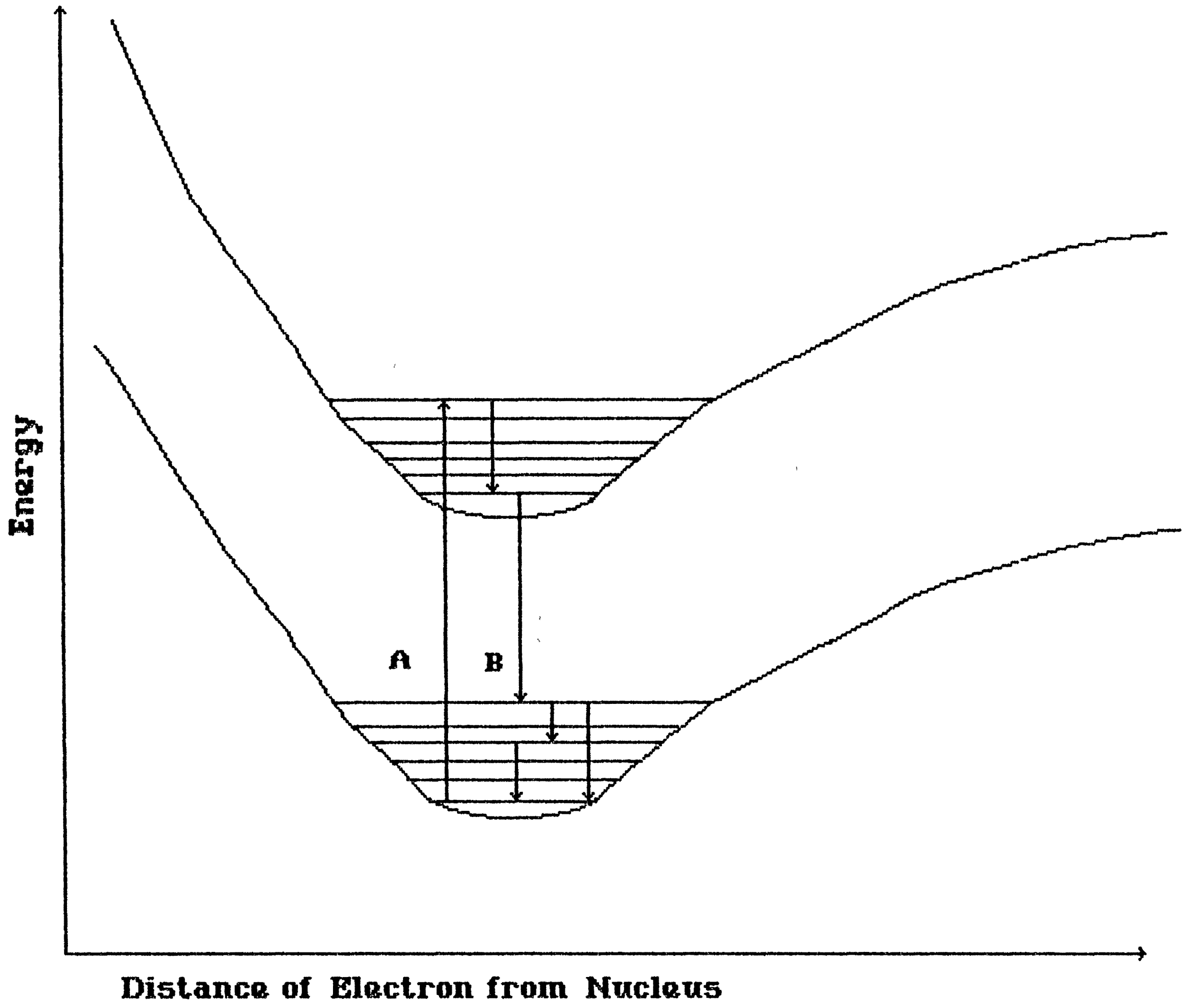


Figure 8. Fluorescence.

detector which is attached to a signal amplifier and some sort of output device. (Figure 9) (89)

The source is commonly a mercury or xenon arc lamp. The mercury arc has the advantages 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 suffers from a lower intensity and produces a small number of lines in the 4000 Å and 6600-8000 Å regions. This can cause errors in high resolution work but has little effect in low resolution studies. These sources need water or forced air cooling. They decrease in emitted intensity with aging, which can be corrected by use of a reference photodetector.

Monochromators are used to select the excitation and emission wavelengths. Light is separated into a small band of wavelengths by the monochromator by use of gratings or prisms. Many instruments incorporate bandpass filters, which use gratings to remove light from higher order spectra. Grating instruments have a lower loss of intensity than prism instruments due to absorbance. One must select materials used for fluorometer prisms to minimize the absorbance and fluorescence of the prism in the area of interest. Quartz is used when measurements are made in the ultraviolet region of the spectrum. Monochromators require calibration to known standards such as wavelengths of mercury. Resolution is improved at the expense of sensitivity and controlled by the monochromator slit width. Maximum resolution is obtained with a minimum slit width, however sensitivity is lost with the decrease in intensity caused by the narrowed band of light

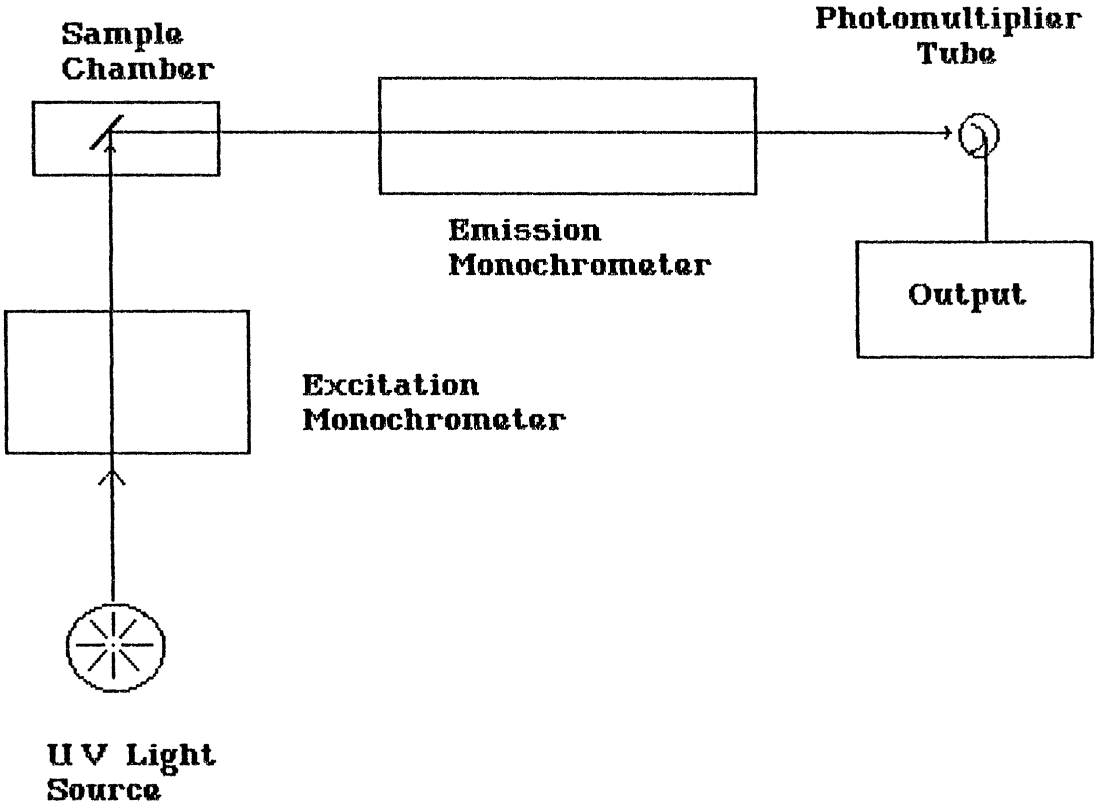


Figure 9. Diagram of a Typical Fluorometer.

allowed to pass through the monochromator. One other area that must be corrected is the variable transmission of the spectra with changing wavelengths by the dispersing media. Some prisms and gratings have discontinuities or dips in the spectral intensity with a change in wavelength forcing all spectra to be corrected.

The sample cell must be transparent to wavelengths of interest. Quartz is the material of choice for sample chamber windows. One must be particular about the quartz used, as some optical fused quartz can vary by 100,000 times in self fluorescence from others. (90) Some glasses have even higher inherent fluorescence. The sample cell must be designed to minimize the amount of stray and scattered light in order to maximize sensitivity.

Detection systems normally involve high gain photomultiplier tubes with high voltage power supplies. The use of photomultiplier tubes requires correction for wavelength sensitive response. It is best to use a photomultiplier tube with maximal response in the spectral region of interest. The signal-to-noise ratio can be improved by up to 100 fold by cooling the photomultiplier tube.

The output can be displayed by meter, strip recorder, or more commonly recorded on magnetic media, floppy disk or tape. Use of magnetic media allows one to manipulate data efficiently, correct for background effects from the sample chamber, plot the data using various scales, and overlay multiple plots for ease of comparison.

CHAPTER IV

EXPERIMENTAL

Crystallographic

A crystal of the desired material was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions were determined by least squares refinement of the best angular positions for fifteen independent reflections ($2\theta > 15^\circ$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.71069$ Å). 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. Backgrounds were measured at each side of the scan for a combined time equal to the scan time. The intensities of three standard reflections were remeasured after every 97 reflections. When necessary the intensities of the reflections were corrected for decomposition. Data was corrected for Lorentz , polarization and background effects. Redundant and space group forbidden data were removed. Points where the intensity was more than three times background were considered observed. The trial structure was determined using MULTAN to locate heavy atom positions. Least squares refinement was used to refine the positions and thermal parameters of the trial structure. Difference Fourier synthesis was used to compare the refined trial structure with the observed electron density map. The most intense peaks from the difference Fourier were input into a program that calculates bonding distances and bonding angles between known atoms and the peaks found in the difference Fourier. The data from this program identifies positions of probable atoms. The probable atomic positions are loaded into the binary data file, then refined using least squares refinement. This process continued until all nonhydrogen atoms were found.

Scale factors, positional, and anisotropic thermal parameters for nonhydrogen atoms were refined to convergence. Hydrogen positions were calculated then included in fixed positional and isotropic thermal parameters in the final least squares refinement of the structure.

Fluorometric

Materials used in fluorometric analysis were isolated by Pasture separation. Crystals were checked for uniform optical emission prior to sample preparation. All spectra were determined using an Oriel modular spectrofluorometer with an evacuated liquid helium cooled sample chamber. The optical path consisted of a xenon lamp as an excitation source, with an excitation beam monochromator, the sample chamber, with inlet and outlet windows at 90° angles from each other, an emission monochromator, and the photomultiplier tube detector. The signal from the photomultiplier was amplified, then recorded by an Apple II computer. Spectra were measured from 350 nm - 700 nm in 0.2 nm intervals with a scan speed of 1 nm per second with an excitation wavelength of 300 nm. The intensity of emission was measured as a ratio of the emitted light and the intensity of the incident light from the xenon lamp. Spectra were measured at 10, 25, 50, 75, 125, 175, 225, and 275° Kelvin.

The collected spectra were then corrected for background and photomultiplier tube spectral response. The correction was performed using a program written by Dr. Dorothy Hamiliton, Mr. Jeff Armstrong, and Miss Linda Mansker.

Synthesis

Cuprous halide salts were purchased from Aldrich Chemical Company and used without further purification. Triphenylphosphine, triphenylarsine, and tris 2-(2-methoxyethoxy)ethyl)amine were also purchased from Aldrich Chemical Company.

The phosphonium and arsonium salts used were synthesized by addition of equimolar amounts of the alkyl halide to a solution of triphenylphosphine or triphenylarsine in refluxing benzene. The reaction was considered complete when no further precipitation of salts occurred. The products were recrystallized from water or ethanol prior to use.

[Potassium (Tris(2-(2-methoxyethoxy)ethyl)amine)] Hexaiodotetracuprate.

To 5.0 ml of saturated aqueous potassium iodide was added 0.38 g (2.0 mmol) cuprous iodide. After the copper salt dissolved, a solution of 1.0 ml (3.2 mmol) tris (2-(2-methoxyethoxy)ethyl)amine) and 5.0 ml acetone was then added. The mixture was covered with a watch glass then allowed to stand. Yellow crystals formed after one week. The crystals fluoresced an intense yellow-green color which showed no change in color of emission on cooling with liquid nitrogen.

[Barium Iodo (Tris(2-(2-methoxyethoxy)ethyl)-amine)] Hexaiodotetracuprate.

Use the same method as above procedure. Yellow crystals formed after one week; they fluoresced an intense yellow-green. These crystals were also visually nonthermochromic.

[Sodium (Tris(2-(2-methoxyethoxy)ethyl)amine)] Hexaiodotetracuprate.

These crystals were prepared by the same procedures as those used for the potassium salt. The crystals initially formed were not large enough for X-ray crystallographic purposes. The crystals were redissolved in acetone and the solution placed in a container saturated with diethylether vapor. Large yellow prisms were formed after two weeks. These crystals fluoresced yellow-green which was unchanged on cooling with liquid nitrogen.

[Rubidium (Tris(2-(2-methoxyethoxy)ethyl)amine)] Hexaiodotetracuprate

Preparation was by the same procedure as the potassium salt. Yellow crystals that fluoresced under U.V. light source formed after one week. Cooling with liquid nitrogen produced no change in emission.

[Strontium Iodo (Tris(2-(2-methoxyethoxy)ethyl)-amine)] Hexaiodotetracuprate

This compound was prepared using the same procedure as the potassium salt. Despite repeated attempts at recrystallization, no sufficiently ordered crystals were obtained for structural work.

Bis(Triphenylphosphoranylidine)ammonium) Dichlorocuprate.

To 30.0 ml of 95% ethanol, 1.0 g (1.9mmol) bis(triphenylphosphoranylidine) ammonium chloride, 0.4 g (4.0 mmol) cuprous chloride, and 1.0 g (5.7 mmol) ascorbic acid was added. The mixture was heated to boiling then allowed to set. Colorless crystals that fluoresced yellow formed after a few hours.

Bis(methyltriphenylarsonium) Hexaiodotetracuprate

A mixture of 1.5 g (3.3 mmol) methyltriphenylarsonium iodide, 0.3 g (1.6 mmol) cuprous iodide, and 8.0 ml nitromethane was heated to boiling to dissolve all components. To the hot solution was added 15.0 ml anhydrous ethanol. The solution was allowed to cool. Bright yellow crystals formed after 2 hours. The crystals fluoresced yellow under U.V. light with no change when cooled with liquid nitrogen.

Parabromophenacyltriphenylphosphonium Dibromocuprate.

A mixture of 0.82 g (1.6 mmol) of p-bromophenacyltriphenylphosphonium bromide, 0.30 g (2.1 mmol) cuprous bromide, 0.5 g (2.8 mmol) ascorbic acid, and 40.0 ml nitromethane were heated to boiling. The solution was allowed to cool slowly. Colorless needle shaped crystals formed after two hours. The crystals fluoresced bright blue when excited by a U.V. light source.

Bis(Parabromophenacyltriphenylarsonium) Hexabromotetracuprate.

A mixture of 2.0 g (3.6 mmol) of p-bromophenacyltriphenylarsonium bromide, 0.5 g (3.5 mmol) cuprous bromide, and 20.0 ml of anhydrous ethanol was heated to boiling and then allowed to slowly cool. Colorless crystals formed overnight. These crystals fluoresced blue when examined under a U.V. light source.

Bis(Paranitrobenzyltriphenylphosphonium) Tetraiododicuprate.

A mixture of 2.0 g (4.0 mmol) of p-nitrobenzyltriphenylphosphonium iodide, 60.0 ml of 95% ethanol, 40.0 ml nitromethane and 0.5 g (2.6 mmol) cuprous iodide was heated to boiling then allowed to cool. Colorless crystals formed overnight. The crystals fluoresced blue under a U. V. light source.

Phenacyltriphenylphosphonium Dichlorocuprate.

A mixture of 3.0 g (7.2 mmol) of phenacyltriphenylphosphonium chloride, 0.5 g (5.1 mmol) cuprous chloride, 1.0 g (5.7 mmol) ascorbic acid, and 50.0 ml of 95% ethanol was heated to boiling then allowed to cool. After 2 hours colorless crystals formed that fluoresced light green under U.V. light source.

Bis(biphenacyltriphenylphosphonium) Tetrabromodicuprate.

A mixture of 0.5 (3.5 mmol) cuprous bromide, 2.0 g (1.9 mmol) biphenacyltriphenylphosphonium bromide, 1.0 g (5.7 mmol) ascorbic acid, and 30.0 ml ethanol was warmed to boiling. The mixture was allowed to slowly cool. Large colorless prismlike crystals formed in two days. The crystals fluoresced orange under U.V. light source. There was no emission change when cooled with liquid nitrogen.

Bis(paranitrobenzyltriphenylphosphonium) Tetrabromodicuprate.

A mixture of 1.5 g (3.1 mmol) p-nitrobenzyltriphenylphosphonium bromide, 0.4 g (2.8 mmol) cuprous bromide, 1.0 g (5.7 mmol) ascorbic acid, and 30.0 ml of 95% ethanol was warmed to boiling. The solution was allowed to cool slowly. Colorless crystals that fluoresced blue formed overnight.

Benzyltriphenylphosphonium Dichlorocuprate.

A mixture of 0.4 g (4.0 mmol) cuprous chloride, 1.57 g (4.0 mmol) benzyltriphenylphosphonium, 0.50g (2.8 mmol) ascorbic acid, and 50.0 ml of 95% ethanol was warmed to boiling. Nonfluorescent colorless crystals formed in 6 hours. The crystals gave a positive test for copper.

Bis(trimethylphenylammonium) Tetrachlorocuprate

A mixture of 0.40 g (4.0 mmol) cuprous chloride, 2.0g (11.7 mmol) phenyltrimethylammonium chloride, 1.0 g (5.7 mmol) ascorbic acid, and 30.0 ml of 95% ethanol was warmed to boiling. The solution was allowed to cool slowly. Yellow brown nonfluorescent crystals formed overnight.

CHAPTER V

RESULTS AND DISCUSSION

In this study a series of 14 previously unknown anionic cuprous halide complexes were prepared. These were grouped into three families: CuX_2^-, $Cu_2X_4^=$, and $Cu_4X_6^=$. The $Cu_2X_4^=$ and $Cu_4X_6^=$ complexes exhibit trigonal coordination of the copper atoms to three halide atoms, while the CuX_2^- complexes exhibit the less common linear coordination with two halide atoms bound to copper (I) in the anionic complex.

The solid state structures of the compounds were determined using single crystal X-ray diffraction. Complete results can be found in the tables and figures following this chapter. After the compound's structure was determined, emission data were measured on a powdered sample over a range of temperatures between 10 and 275°K. Emission data were corrected for spectral response of the photomultiplier. These spectra are shown with the ORTEP drawings (84) of the compounds in the section following this chapter.

Certain overall conclusions can be drawn from the structural and emission data of this study from work done by Hamilton and Holt (91) and from work done earlier in this laboratory. (10) The multiplicity of copper coordination, identity of the halide, copper-copper distances, and placement of copper atoms on crystallographic symmetry elements appear to have an effect on the λ max of the emission spectrum.

The $Cu_4X_6^=$ and $Cu_2X_4^=$ clusters prepared in this study both display three coordinate copper complexed to three halide atoms . Yet the copper coordination is not identical. In $Cu_4X_6^=$ clusters, all three halide atoms are bridging ones, linking copper atoms in pairs. In $Cu_2X_4^=$ two of the three halide atoms bound to each copper atom are bridging. The third halide is a terminal one. Moreover, the copper atoms in this structure are doubly bridged where in $Cu_4X_6^=$ any two coppers are bridged by only one halide atom. Thus the copper environments are not identical in the two clusters.

Conclusions from the data measured in this study are based on the expectation that copper atoms in identical environments should emit in an identical way if emission arises from a copper based mechanism. This expectation is borne out by observation of a 520 nm emission maximum for the [Na(tris(2-(2-methoxyethoxy)ethyl)amine]$_2$, [Ba(tris(2-(2-methoxyethoxy)ethyl)amine]$_2$, [K(tris(2-(2-methoxyethoxy) ethyl)amine]$_2$, [Rb(tris(2-(2-methoxyethoxy)ethyl)amine]$_2$, and [K(12-crown-4)]$_7$ (Cu_8I_{13}) Cu_4I_6 complexes. It is also substantiated by the observance of 445-465 nm emission in the Cu_2I_4 complexes with bis(tetraethylammonium) and bis(tetrabutylammonium) measured here. The λ max of the emission spectrum shifts to longer wavelength as iodide is replaced by bromine in any particular complex. Thus the $Cu_4Br_6^=$ complexes with bis (parabromophenacyltriphenylarsonium) and bis-(tetrapropylammonium) emission in the 600-610nm region and bis-

(paranitrobenzyltriphenylphosphonium) Cu_2Br_4 emits at 580 nm. Attempts to prepare chloride analogs of these materials were unsuccessful. The measurement of an emission spectrum does not offer detailed information about the excitation mechanism in situations where the emission wavelength is highly Stokes shifted from the excitation wavelength. Absorption spectra for complexes of anionic Cu(I) halides are typically broad and featureless. Emission spectra are independent of the excitation wavelength (within ± 50 nm). Thus the shift of emission maxima to longer wavelengths (lower energies) with change in halide from I to Br suggests that the change to a more electronegative halide may lower the energy level of the emitting state.

Copper halide complexes may be seen to be built up of simple rhombohedra composed of alternate copper (I) and halide atoms sharing edges to form more complicated structures. Within these rhombohedra, angles at halides may compress or expand to bring copper atoms into close proximity or increase their separation. Thus copper-copper separations have been observed to range from 2.5 - 3.2 Å .

Hoffman determined that copper (I) atoms in polynuclear clusters may exhibit a metal - metal interaction. (92) His calculations demonstrated a continuous increase in the metal -metal attraction as the copper -copper distances decreased. The strength of this interaction was explained on the basis of overlap of the empty 4s and 4p orbitals of the copper atoms with filled d orbitals on the neighboring copper atom. Hoffman's calculations showed that the attraction between copper atoms becomes significant when the distance between copper atoms is something less than 2.7Å .

Only one complex in this study was found to have a Cu-Cu separation of less than 2.7Å . (Tables 1 and 2) The short separation distance found in the [Na(tris(2-(2-methoxyethoxy)ethyl)amine]$_2$ is thought to be an artifact of the disorder of the structure. Copper-copper separations in the $Cu_4X_6^=$ clusters averaged 2.77(2)Å . Those in the $Cu_2X_4^=$ clusters averaged 2.865(5)Å . This copper -copper separation was maintained when bromide replaced iodide in these clusters. The rhombohedra distorted to maintain this separation when iodine atoms were replaced by the smaller bromine atom with subsequently shorter Cu-X bonds. The Cu-X-Cu angle widened from approximately 60° in iodide complexes to approximately 70° in bromide complexes. Thus the potential copper to copper excitation mechanism, $d^{10}, d^{10} \rightarrow d^{9}, d^{10}s^{1}$, is believed to be unimportant in determination of the λ max observed in this study. However the intensity of the emission appeared to increase as the copper-copper distance decreased. In compounds where the copper-copper distance was greater than 3.00Å the fluorescent emission was not observable at room temperature to the human eye. However this observation is difficult to quantify as no method was found to insure equivalent preparation of samples for fluorometric observation.

The $Cu_4X_6^=$ clusters exist with a tetrahedron of copper atoms inside an octahedron of halide atoms. Various crystallographic symmetry elements may be imposed upon this idealized cluster. Two fold symmetry axes may pass through any opposite pair of iodine atoms, bisecting

TABLE 1

SUMMARY OF STRUCTURAL AND EMISSION DATA FOR $CU_4X_6^=$

CATION	CU-CU	CU-X	X-CU-X	CU-X-CU	λ MAX
NaTDA-1	2.55(4)	2.52(1)	114.9(2)	60.9(8)	520
	2.855(7)	2.64(3)	126.7(6)	67.8(2)	
BaITDA-1	2.73(2)	2.53(2)	117.51(2)	64.1(2)	520
	2.79(3)	2.60(2)	122.0(2)	66.2(2)	
KTDA-1	2.72(1)	2.52(1)	116.2(3)	63.7(3)	520
	2.88(1)	2.58(1)	126.0(3)	69.2(3)	
RbTDA-1	2.71(2)	2.53(1)	116.8(5)	63.2(4)	520
	2.84(2)	2.62(1)	125.9(5)	68.3(4)	
$MePh_3As$	2.748(3)	2.535(2)	118.66(10)	64.04(4)	535, 630
	2.759(2)	2.633(3)	121.22(6)	65.33(5)	
PBPTAs*	2.75(1)	2.380(7)	117.4(3)	70.0(3)	610
	2.83(1)	2.4(1)	121.5(3)	72.9(2)	

* parabromophenacyltriphenylarsonium

TABLE 2

SUMMARY OF SYMMETRY AND EMISSION DATA FOR $CU_4X_6^=$

CATION	SYMMETRY	λ MAX
	IODIDES	
NaTDA-1	two fold through iodides, disordered	520
BaITDA-1	Center of symmetry in center, disordered	520
KTDA-1	two fold through two iodides	520
RbTDA-1	two fold through two iodides	520
$[K(12\text{-crown-}4)]_7$ $[Cu_8I_{13}]$	4 bar in center of motif	520
$MePh_3As$	3 fold axis through one copper second copper in general position	535, 630
	BROMIDES	
PBPTAs*	2 fold through bromine	610
bis(Pr_4N)	centrosymetric	600
bis($BuPh_3P$)	3 fold through copper second copper in general position disordered	445, 530

* parabromophenacyltriphenylarsonium

opposite edges of the copper rhombohedron. Mirror planes may contain any pair of copper atoms and the iodine atom bridging them as well as the iodine atom on the opposite side of the iodine octahedron. Three fold axes may pass through any copper atom and emerge through the center of the opposite face defined by the other three copper atoms. A 4 bar symmetry element may exist in the center of the tetrahedron . $Cu_4X_6^{=}$ clusters are not in themselves centrosymmetric.

$Cu_4X_6^{=}$ clusters often disorder in the solid state. The disorder takes the form of eight half occupancy positions to account for the four copper atoms. These disordered positions form the corners of a cube which then shows each of the six iodine atoms centered above one face of the cube. However, at any one time, only alternate copper atoms are present. Thus the tetrahedron of copper atoms exhibits disorder about a two fold axis which passes through two opposite edges. Figure 11 illustrates this disorder and its resolution. Figure 10 illustrates the presence of a three fold axis in this disordered motif and also the presence of a center of symmetry which cannot be present in either of the two ordered motifs.

X-ray diffraction determines the average of the contents of the entire array of unit cells. And thus, while any specific unit cell contains one of the two ordered motifs, the entire array of unit cells shows approximately a 50/50 distribution of the two motifs.

The presence or absence of a symmetry element through a copper atom of the motif appears to influence λ max in the emission spectra of $Cu_4X_6^{=}$ clusters. If one tabulates λ max with crystallographic symmetry

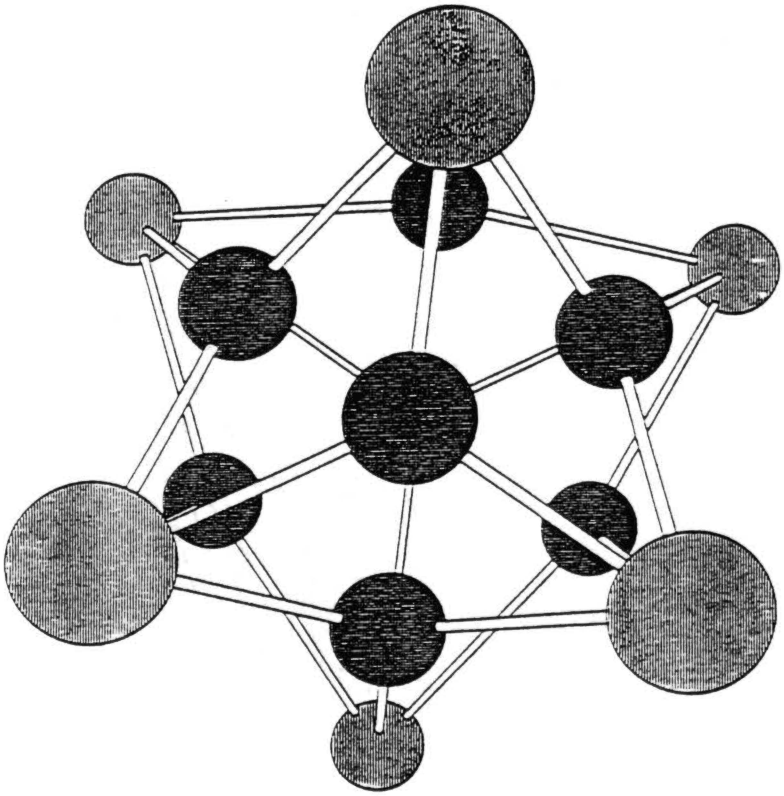
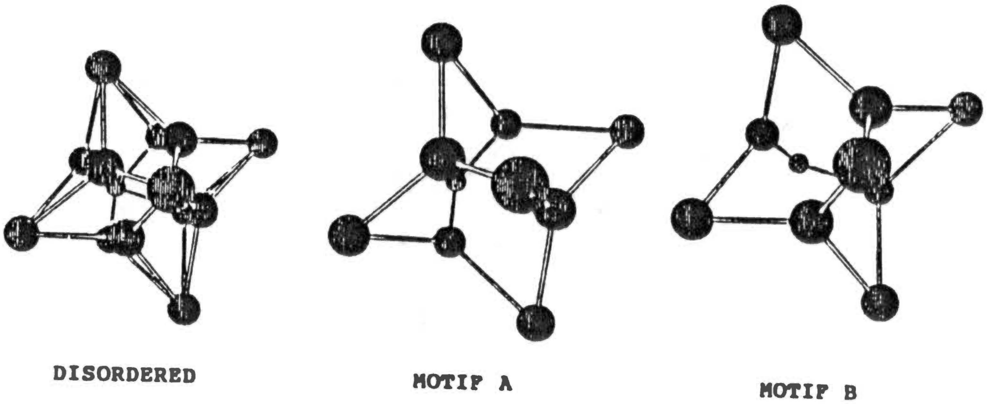


Figure 10. Three Fold Axis through Hexahalotetracuprate.



DISORDERED MOTIF A MOTIF B

Figure 11. Disorder in Hexahalotetracuprate.

elements present in the $Cu_4X_6^=$ complexes examined in the course of this work, one finds an interesting phenomenon. (Table 3) One finds that the $Cu_4X_6^=$ clusters in which X= iodine and in which copper atoms do not lie on a crystallographic symmetry element, are consistent in showing emission at 520 nm. The presence of a symmetry element within the cluster or through iodine atoms does not apparently influence the wavelength of maximum emission. This is also true for $Cu_4X_6^=$ clusters in which X = Br. The clusters in which a symmetry element passes through a copper atom display changed emission. Consistent perhaps with the creation of two crystallographically different copper sites, one on the symmetry element and one in a general position, both complexes show two emission maxima. Bis(methyltriphenylarsonium) Cu_4I_6 shows maxima at 535 and 630 nm as compared with the 520 nm observed when no copper atom exists on a symmetry element. Bis(butyltriphenylphosphonium) Cu_4X_6 shows emission maxima at 445 and 530 nm as compared to the 600 - 610 nm emission when symmetry elements are absent. There has been no previous mention in the literature of the influence of solid state or crystallographic symmetry elements at an atom upon the emission spectra observed. An explanation of this effect may be expected to involve a discussion of the influence of symmetry elements upon the vibrational levels of the atom. At this point, there is insufficient data to support any such discussion.

Three previously unknown $Cu_2X_4^=$ clusters were prepared in this study. Tetrahalodicuprate (I) clusters in the literature display two conformations. (Figure 12) The bent form in which the complex is bent

TABLE 3

SUMMARY OF STRUCTURAL AND EMISSION DATA FOR CU$_2$X$_4^=$

CATION	CU-CU	CU-BR$_t$	CU-BR$_b$
X=Br			
PNBzPh$_3$P*	2.974(4)	2.304(3)	2.38(3)
			2.47(4)
X=I			
PNBzPh$_3$P*	2.755(6)	2.517(5)	2.564(5)
			2.574(5)

CATION	BR$_t$-CU-BR$_b$	BR$_b$-CU-BR$_b$	CU-BR$_b$-CU	λ MAX
X=BR				
PNBzPh$_3$P*	124.0(1)	104.6(1)	75.4(1)	594
	131.4(2)			
X=I				
PNBzPh$_3$P*	121.6(2)	115.1(2)	64.9(1)	
	123.3(2)			

* Paranitrobenzyltriphenylphosphonium

$Cu_2X_4^=$

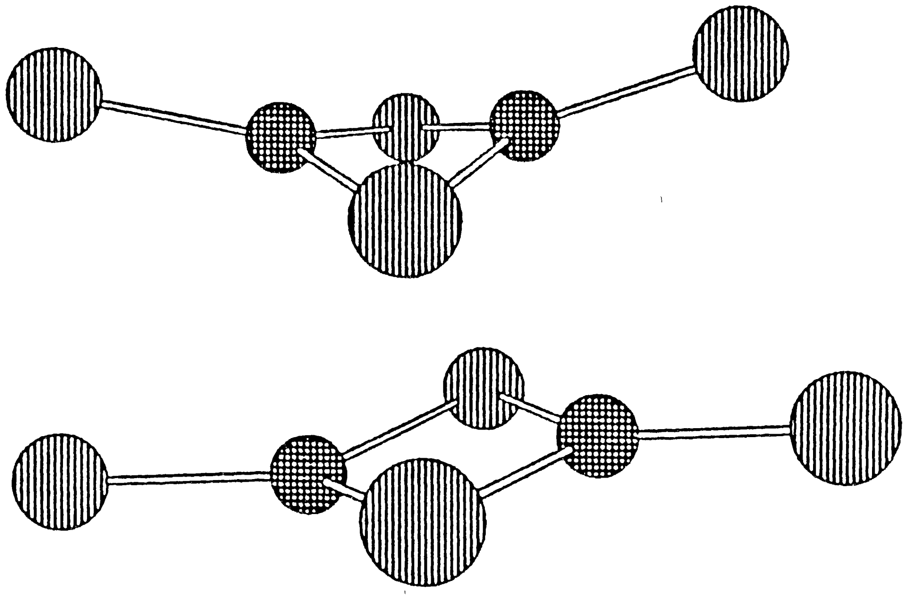


Figure 12. Tetrahalodicuprate Anion.

like a hinge through a line formed by the two bridging halides is shown at the top of figure 12. The other form, the planar form, has all atoms in the anionic complex in the same plane as illustrated by the structure at the bottom of figure 12. The $Cu_2X_4^=$ clusters prepared in this study were all of the planar type. None of these clusters contains a symmetry element through copper, despite the potential presence of crystallographic two fold axes or mirrors in the idealized motif. None of these clusters display copper-copper separations of less than 2.7Å . Thus the emission maxima of the two $Cu_2I_4^=$ emission spectra are consistent and the change of emission maxima are consistent and the change of emission maxima with replacement of iodide by bromide is anticipated although the direction of the change is unexplained.

The synthesis of the complexes prepared in this study afforded new materials of several anionic CuX families. However such a synthesis is not controlled by intention. While stoichiometries of reactants can be controlled, this does not necessarily translate to stoichiometry of product. The formation of a $Cu_2X_4^=$ as opposed to a $Cu_4X_6^=$ cluster is not under the direction of the experimenter. The stoichiometry of the mother liquor changes as the crystallization of product occurs with methyltriphenylphosphonium as the cation one can get three different products to crystallize from the same beaker. Indeed a change of solvent or temperature of crystallization may lead to the production of a different anionic CuX structure. Thus, an interpretation of the $Cu_2X_4^=$, emission must depend upon the preparation of more members of this structural type. Attempts to extend the knowledge of mechanisms leading to emission of the $Cu_2X_4^{=}$ family of complexes is underway.

CuX_2^- complexes appear to be more stable when X = Cl. Thus there are many $CuCl_2^-$ complexes known, some $CuBr_2^-$ structures have been reported, and only two CuI_2^- complexes in the literature. (79) Complexes of this family are characterized by short Cu-X bonds which appear to indicate considerable multiple bond character and by linear or nearly linear bond angles at copper. (Table 4) Bis(triphenylphosphoranyl) ammonium dichlorocuprate (I) [Cu-Cl, 2.086(5), 2.084(6)Å ; Cl-Cu-Cl, 178.9(6)°] and benzyltriphenylphosphonium dichlorocuprate (I) [Cu-Cl, 2.088(3), 2.097(3)Å , Cl-Cu-Cl, 175.4(2)°] show emission maxima at 415-425 nm. Parabromophenacyltriphenyl phosphonium dibromocuprate (I) [Cu-Br, 2.207(8), 2.229(8)Å ; Br-Cu-Br, 178.0(5)°] emits at 440 nm. None of these exists with a crystallographic center of symmetry present at copper.

Two other new materials were prepared: bis(phenyltrimethyl ammonium) $CuCl_4$ and bis(methyltriphenylphosphonium) CuI_3. These were unique within the group of complexes prepared in this study and their emission spectra were not measured.

TABLE 4

SUMMARY OF STRUCTURAL AND EMISSION DATA FOR CUX_2^-

CATION	CU-X	X-CU-X	λ MAX
$X=Cl^-$			
$PnPh_3P$*	2.086(9)	175.0(4)	
	2.095(8)		
$BzPh_3P$	2.088(3)	175.4(2)	425
	2.097(3)		
BTPA**	2.084(6)	178.9(6)	415
	2.086(5)		
$X=Br^-$			
PBPTPP***	2.207(8)	178.0(5)	440
	2.229(8)		

* Phenacyltriphenylphosphonium

** Bis(triphenylphosphoranyl)ammonium

*** Parabromophenacyltriphenylphosphonium

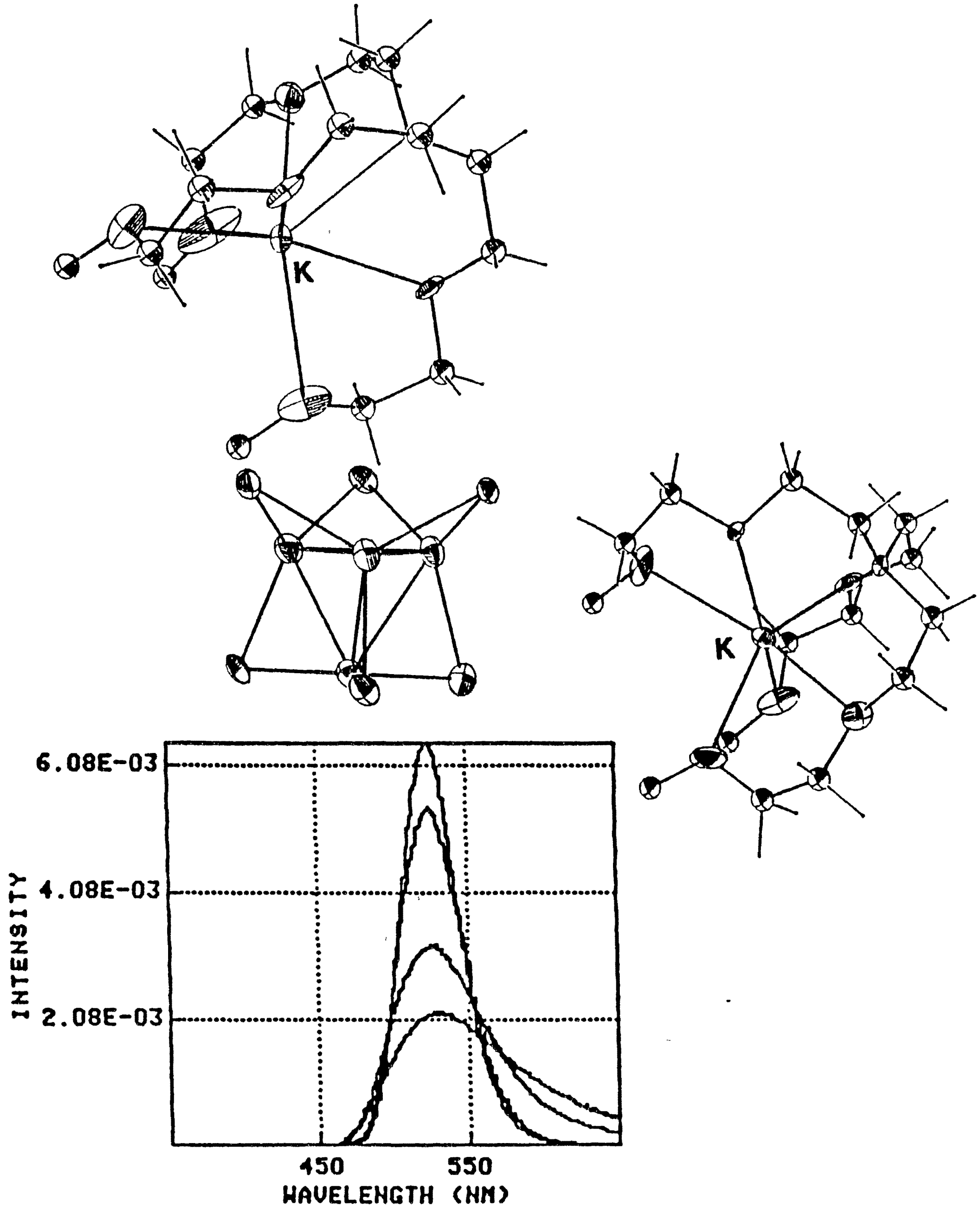


Figure 13. Bis[Potasium(Tris(2-(2-methoxyethoxy)ethyl) amine] Hexaiodotetracuprate.

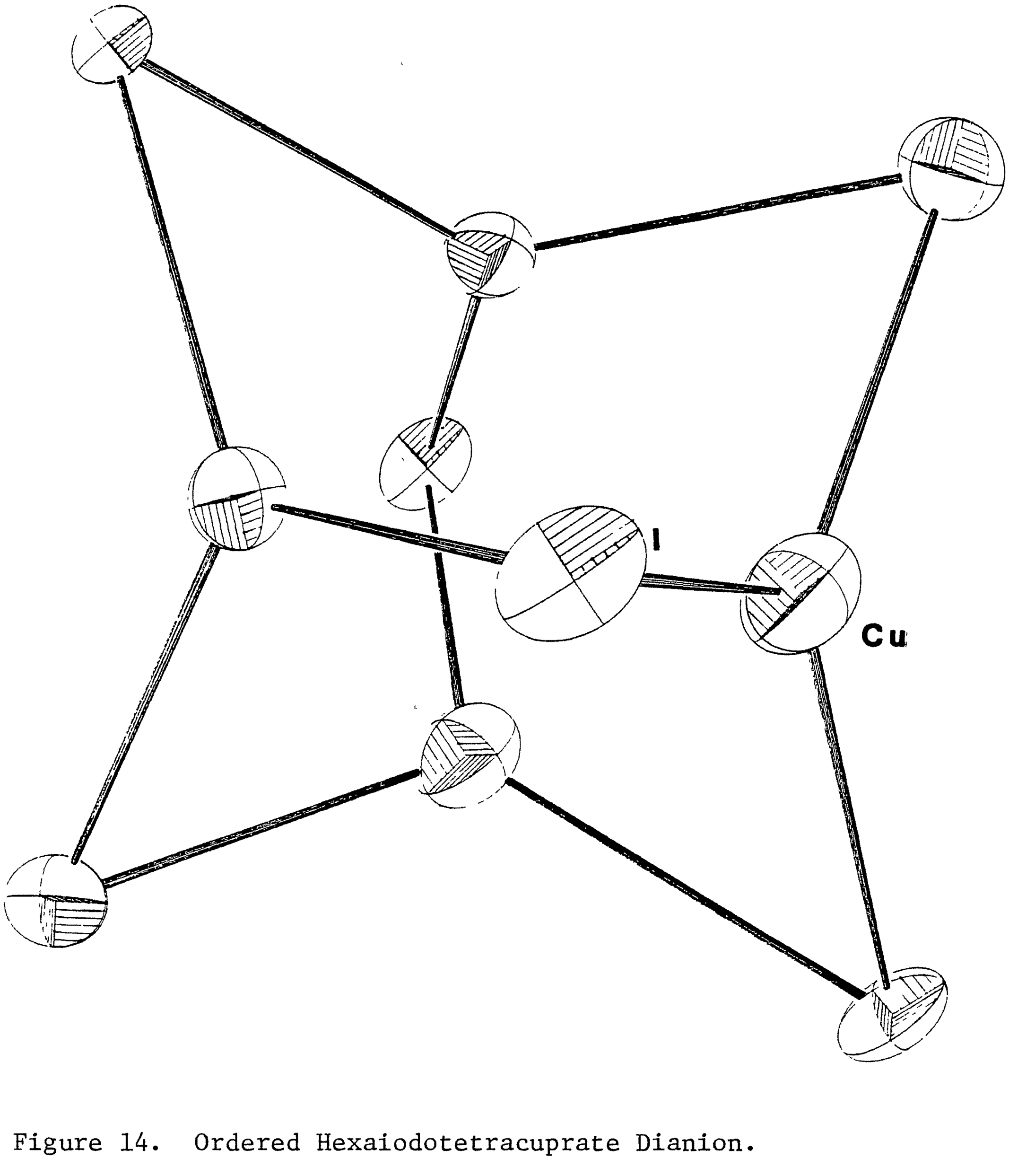


Figure 14. Ordered Hexaiodotetracuprate Dianion.

TABLE 5

CRYSTAL DATA FOR BIS (POTASSIUM (TRIS (2-(2-METHOXYETHOXY) ETHYL) AMINE)) HEXAIODOTETRACUPRATE (I)

Formula	$(K(NC_{15}O_6H_{33}))_2(Cu_4I_6)$
MWT	1740.7 g mole^{-1}
a	21.754 (9) Å
b	21.209 (8)
c	12.100 (6)
α	90.0°
β	90.0
γ	90.0
V	5582. (4) Å^3
F (000)	3180
μMoK_α	51.77 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.031 g cm^{-3}
Z	4
Obs. refl.	1217
R	8.3%
R_w	10.5%
Space group	Pbnb (Orthorhombic)
Octants meas.	+h, +k, +l

TABLE 6

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR BIS (POTASSIUM (TRIS (2-(2-METHOXYETHOXY) ETHYL) AMINE) HEXAIODOTETRACUPRATE (I)

I1-Cu1'	2 52(1)	Cu1'-I1-Cu2"	69.2(3)
I1-Cu2"	2 56(1)	Cu1'-I2-Cu2"	65.1(3)
I2-Cu1'	2.58(1)	Cu2'-I3-Cu2"	63.7(3)
I2-Cu2"	2.56(1)	Cu1'-I4-Cu1'	64.7(3)
I3-Cu2'	2.58(1)	I1'-Cu1'-I2'	116.2(3)
I3-Cu2"	2.58(1)	I1'-Cu'-I4'	117.4(4)
I4-Cu1'	2.57(1)	I2'-Cu1'-I4'	126.0(3)
I4-Cu1"	2.57(1)	I2'-Cu2'-I3'	119.6(3)
K1-011	2.73(4)	I2'-Cu2'-I1"	119.7(3)
K1-012	2 80(5)	I3'-Cu2'-I1"	120.2(3)
K1-021	2.71(4)	011-K1-012	65.(1)
K1-022	2.83(10)	011-K1-021	98.(1)
K1-031	2.67(4)	011-K1-022	65.(2)
K1-032	2 91(4)	011-K1-031	103.(1)
K1-N1	2.87(4)	011-K1-032	100.(1)
N1-C11	1 47(8)	011-K1-N1	63.(1)
N1-C21	1.36(8)	012-K1-021	152.(2)
N1-C31	1.43(8)	012-K1-022	95.(1)
C11-C12	1 53(8)	012-K1-031	106 (1)
C21-C22	1.56(9)	012-K1-032	100.(1)
C31-C32	1.50(9)	012-K1-N1	120.(1)
C12-011	1.45(9)	021-K1-022	68.(1)

TABLE 6 (Continued)

C22-O21	1 38(7)	O21-K1-O31	99.(2)
C32-O31	1.42(8)	O21-K1-O32	102.(1)
O11-C13	1 44(6)	O21-K1-N1	62.(1)
C21-C23	1.53(9)	O22-K1-O31	99.(2)
O31-C33	1 53(6)	O22-K1-O32	89.(2)
C13-C14	1.54(8)	O22-K1-N1	127.(2)
C23-C24	1.50(11)	O31-K1-O32	63.(1)
C33-C34	1.49(7)	O31-K1-N1	62.(1)
C14-O12	1.33(8)	O32-K1-N1	119.(2)
C24-O22	1 14(14)	K1-O11-C12	117.(3)
C34-O32	1.43(7)	K1-O11-C13	116.(3)
C12-C15	1 40(7)	C12-O11-C13	110.(4)
O22-C25	1 27(12)	K1-O21-C22	115.(3)
O32-C35	1 40(8)	K1-O21-C23	107.(3)
Cu1-Cu2	2 76(1)	C22-O21-C23	121.(5)
Cu1-Cu1	2 75(1)	K1-O31-C32	120.(3)
Cu1-Cu2'	2 88(1)	K1-O31-C33	117.(3)
Cu2-Cu1	2 88(1)	C32-O31-C33	112.(4)
Cu2-Cu2	2 72(1)	K1-O12-C14	101.(4)
		K1-O12-C15	116.(3)
		C14-O12-C15	113.(5)
		K1-O22-C24	98.(7)
		K1-O22-C25	113.(7)
		C24-O22-C25	124.(9)

TABLE 6 (Continued)

K1-O32-C34	98.(3)
K1-O32-C35	116.(3)
C34-O32-C35	120. (4)
K1-N1-C11	109.(3)
K1-N1-C21	109.(3)
K1-N1-C31	109.(3)
C11-N1-C21	110.(5)
C11-N1-C31	111.(5)
C21-N1-C31	109.(5)
N1-C11-C12	113.(5)
N1-C21-C22	112.(5)
N1-C31-C32	113.(5)
C11-C12-O11	107.(4)
C21-C22-O21	110.(5)
C31-C32-O31	110.(5)
O11-C13-C14	107.(4)
O21-C23-C24	111.(6)
O31-C33-C34	106.(4)
O13-C14-O12	120.(6)
C23-C24-O22	130.(10)
C33-C34-O32	111.(5)

' = symmetry operation x, y, z
" = symmetry operation 0.5-x, y, 1.5-z

TABLE 7

POSITIONAL PARAMETERS FOR BIS (POTASSIUM (TRIS (2-(2-METHOXYETHOXY) ETHYL) AMINE) HEXAIODOTETRACUPRATE (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.1994 (2)	0.2376 (2)	0.5185 (3)
I2	0.3844 (2)	0.2458 (2)	0.6485 (3)
I3	0.2500	0.3924 (2)	0.7500
I4	0.2500	0.0896 (2)	0.7500
Cu1	0.2782 (4)	0.1920 (3)	0.6483 (8)
Cu2	0.3082 (4)	0.2891 (3)	0.7908 (6)
K1	0.0782 (4)	0.4538 (5)	0.2572 (10)
O11	0.1247 (19)	0.5107 (17)	0.4411 (29)
O12	0.0537 (22)	0.3912 (26)	0.4561 (36)
O21	0.1561 (19)	0.5047 (19)	0.1068 (33)
O22	0.1662 (44)	0.3652 (49)	0.1811 (56)
O31	-0.0225 (17)	0.5209 (21)	0.2127 (25)
O32	-0.0132 (17)	0.3942 (26)	0.1156 (32)
N1	0.0893 (26)	0.5888 (18)	0.2529 (45)
C11	0.1294 (24)	0.6087 (21)	0.3437 (46)
C12	0.1133 (37)	0.5777 (37)	0.4540 (43)
C13	0.1134 (25)	0.4786 (24)	0.5440 (42)
C14	0.1020 (32)	0.4084 (31)	0.5160 (59)
C15	0.0470 (27)	0.3256 (23)	0.4501 (45)
C21	0.1145 (34)	0.6063 (25)	0.1548 (50)
C22	0.1725 (28)	0.5665 (28)	0.1257 (57)

TABLE 7 (Continued)

C23	0.2042 (33)	0.4544 (40)	0.0808 (42)
C24	0.1787 (38)	0.3898 (31)	0.1004 (103)
C25	0.1738 (51)	0.3067 (30)	0.1983 (85)
C31	0.0296 (28)	0.6161 (21)	0.2634 (58)
C32	-0.0178 (28)	0.5864 (31)	0.1895 (56)
C33	-0.0718 (22)	0.4890 (22)	0.1423 (45)
C34	-0.0670 (27)	0.4204 (26)	0.1659 (49)
C35	-0.0076 (33)	0.3287 (27)	0.1033 (51)
H111	0.1718	0.5951	0.3253
H112	0.1304	0.6549	0.3501
H121	0.1342	0.5977	0.5153
H122	0.0672	0.5866	0.4675
H131	0.1455	0.4876	0.5979
H132	0.0739	0.4943	0.5772
H141	0.1457	0.3975	0.4882
H142	0.1042	0.3891	0.5947
H211	0.0832	0.5951	0.0945
H212	0.1218	0.6502	0.1491
H221	0.1939	0.5859	0.0626
H222	0.2010	0.5710	0.1902
H231	0.2250	0.4751	0.0074
H232	0.2382	0.4622	0.1342
H241	0.1439	0.3957	0.0207
H242	0.2112	0.3676	0.0305

TABLE 7 (Continued)

H311	0.0161	0.6066	0.3420
H312	0.0332	0.6610	0.2578
H321	-0.0566	0.6111	0.1941
H322	-0.0031	0.5954	0.1096
H331	-0.1144	0.5048	0.1604
H332	-0.0668	0.4970	0.0622
H341	-0.0649	0.4148	0.2464
H342	-0.1033	0.3977	0.1393

TABLE 8

THERMAL PARAMETERS FOR BIS (POTASSIUM (TRIS (2-(2-METHOXYETHOXY) ETHYL) AMINE) HEXAIODOTETRACUPRATE (I)

ATOM	U11	U22	U33	U12	U13	U23
I1	89.(3)	56.(2)	62.(2)	-20.(2)	-19.(2)	1.(2)
I2	46.(2)	48.(2)	86.(2)	0.(2)	14.(2)	3.(2)
I3	70.(4)	27.(2)	49.(3)	0.	-8.(4)	0.
I4	62.(4)	20.(2)	86.(4)	0.	0.(4)	0.
Cu1	84.(6)	50.(4)	79.(6)	1.(4)	11.(5)	-3.(5)
Cu2	71.(5)	48.(4)	69.(5)	-3.(4)	-26.(5)	0.(4)
O11	93.(34)	49.(25)	16.(25)	30.(23)	-1.(22)	0.(19)
O12	74.(34)	151. (50)	70.(36)	55.(36)	-20.(29)	54.(33)
O21	57.(28)	64.(29)	66.(35)	-17.(24)	11.(25)	-5.(25)
O22	306.(98)	289.(23)	77.(51)	224.(96)	37.(56)	23.(60)
O31	68.(28)	104.(35)	10.(24)	28.(26)	0.(18)	0.(20)
O32	21.(24)	156.(48)	61.(28)	-13.(27)	-1.(24)	-27.(32)
N1	142.(52)	23.(23)	43.(33)	-6.(31)	59.(42)	17.(30)
C11	44.(38)	28.(30)	31.(34)	-9.(25)	-8.(31)	-25.(33)
C12	148.(70)	117.(67)	6.(36)	56.(57)	27.(41)	19.(37)
C13	46.(33)	36.(33)	28.(37)	-22.(28)	-25.(31)	-3.(27)
C14	76.(52)	64.(49)	79.(55)	46.(42)	65.(45)	22.(43)
C15	103.(49)	22.(31)	67.(42)	-15.(31)	1.(40)	35.(29)
C21	98.(53)	43.(38)	45.(40)	6.(37)	-26.(37)	38.(38)

TABLE 8 (Continued)

C22	49.(41)	53.(42)	120.(65)	-36.(35)	19.(44)	39.(42)
C23	101.(59)	150.(73)	7.(33)	-15.(58)	23.(39)	-16.(42)
C24	63.(58)	9.(33)	338.(62)	19.(33)	-99.(86)	-52.(64)
C25	248.(12)	40.(44)	222.(20)	81.(59)	65.(93)	73.(62)
C31	57.(38)	15.(26)	99.(53)	9.(27)	35.(43)	-23.(36)
C32	56.(44)	55.(41)	99.(54)	55.(36)	-4.(43)	-8.(42)
C33	44.(34)	23.(29)	41.(36)	16.(25)	-18.(32)	15.(28)
C34	58.(42)	54.(41)	56.(42)	-44.(34)	-28.(38)	-8.(34)
C35	119.(63)	35.(36)	79.(52)	11.(41)	3.(47)	-51.(36)

Anisotropic parameters are in the form:

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

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

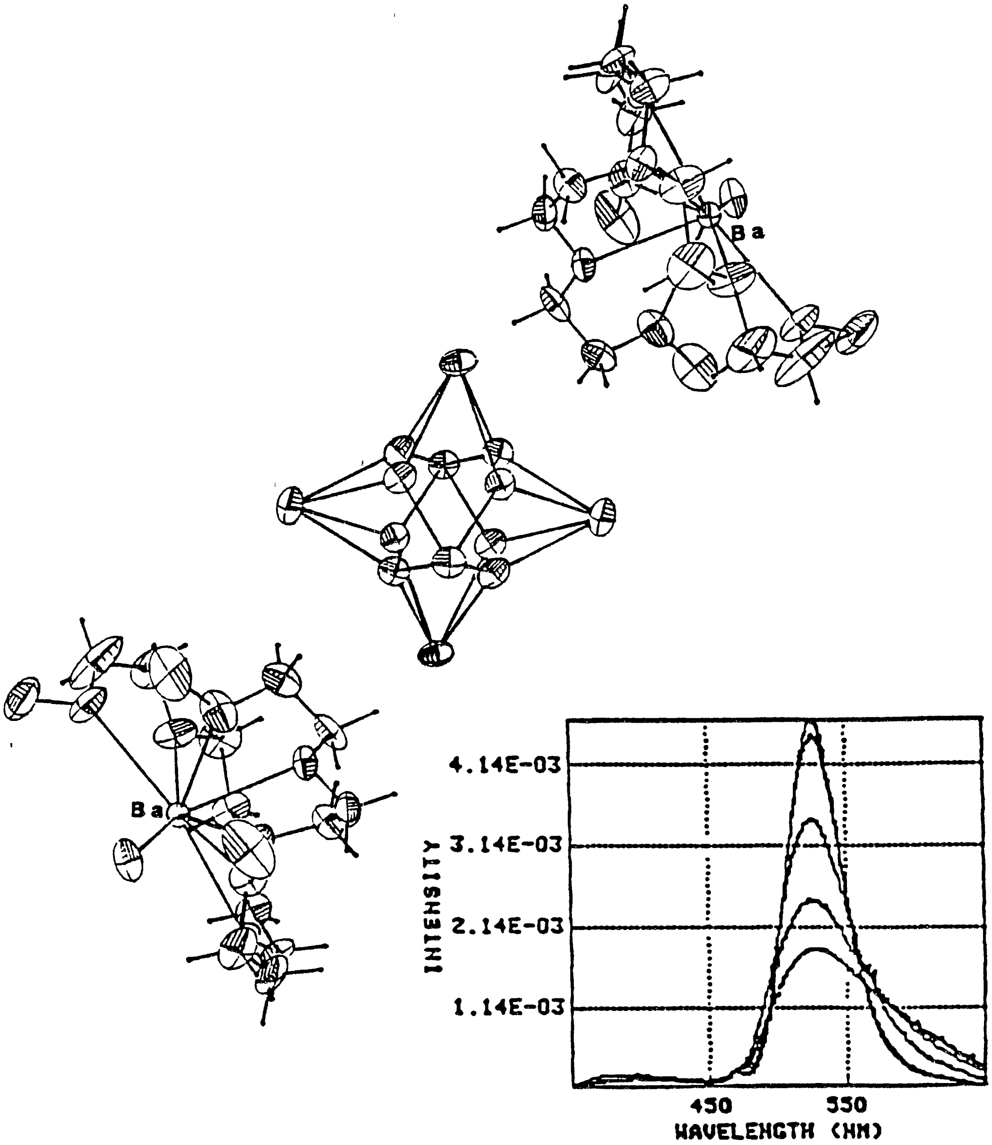


Figure 15. Bis[Barium Iodo(Tris(2-(2-methoxyethoxy)ethyl) amine] Hexaiodotetracuprate.

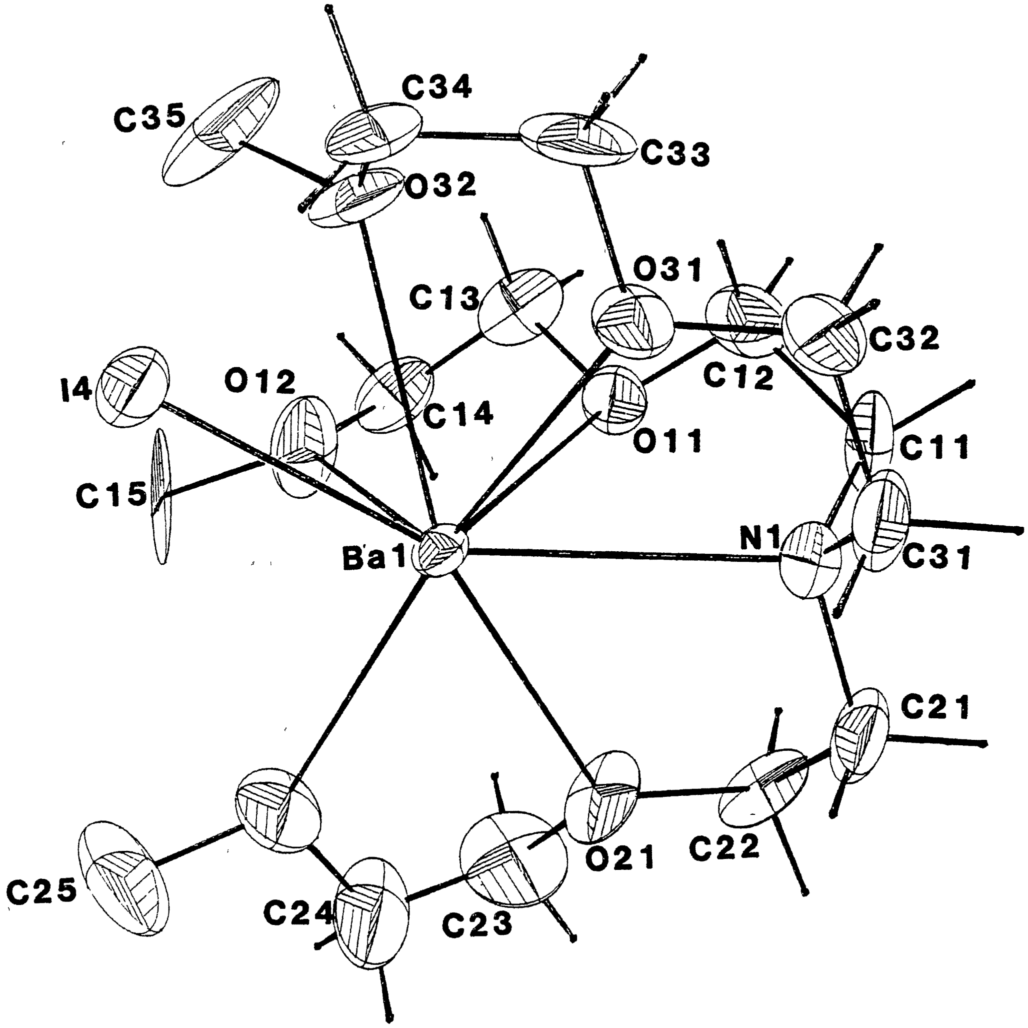


Figure 16. [Barium Iodo(Tris(2-(2-methoxyethoxy)ethyl)amine] Cation.

TABLE 9

CRYSTAL DATA FOR BIS (BARIUM IODO (TRIS(2-(2-METHOXYETHOXY) ETHYL) AMINE)) HEXAIODOTETRACUPRATE (I)

Formula	$[BaI(NC_{15}O_6H_{33})]_2(Cu_4I_6)$
MWT	2190.9 g mole^{-1}
a	10.274 (2) Å
b	10.275 (3)
c	14.398 (4)
α	82.36 (2) °
β	95.36 (2)
γ	87.47 (2)
V	1497.3 (7) Å^3
F(000)	1008
μMoK_α	51.77 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.429 g cm^{-3}
Z	1
Obs. refl	3304
R	5.7%
R_w	8.6%
Space group	P1 (Triclinic)
Octants meas.	±h, +k, ±l

TABLE 10

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR BIS (BARIUM IODO (TRIS(2-(2-METHOXYETHOXY) ETHYL) AMINE)) HEXAIODOTETRACUPRATE (I)

Ba1-I4	3.57(3)	Cu1'-I1-Cu2"	44.5(2)
Ba1-O11	2.80(2)	Cu1'-I1-Cu4"	46.1(1)
Ba1-O12	2.78(2)	Cu1'-I1-Cu3'	66.2(2)
Ba1-O21	2.78(2)	Cu2"-I1-Cu4"	64.8(2)
Ba1-O22	2.91(4)	Cu2"-I1-Cu3'	45.7(2)
Ba1-O31	2.81(3)	Cu4"-I1-Cu3'	43.5(2)
Ba1-O32	2.89(3)	Cu4"-I2-Cu2'	43.1(1)
N1-C11	1.48(3)	Cu4"-I2-Cu3"	65.6(1)
N1-C21	1.45(3)	Cu4"-I2-Cu1'	46.1(2)
N1-C31	1.49(3)	Cu2'-I2-Cu3"	46.0(2)
C11-C12	1.49(3)	Cu2'-I2-Cu1'	66.2(2)
C21-C22	1.55(3)	Cu3"-I2-Cu1'	45.7(1)
C31-C32	1.49(3)	Cu3"-I3-Cu4'	43.6(2)
C12-O11	1.39(3)	Cu3"-I3-Cu2"	64.1(2)
C22-O21	1.38(3)	Cu1'-I3-Cu4'	64.2(2)
C32-O31	1.41(3)	Cu1'-I3-Cu2"	44.4(2)
O11-C13	1.44(3)	Cu4"-I3-Cu2"	43.0(1)
O21-C23	1.45(3)	I1'-Cu1'-I1"	119.9(2)
O31-C33	1.42(3)	I1'-Cu1'-I3'	121.8(2)
C13-C14	1.49(3)	I2'-Cu1'-I3'	117.9(2)
C23-C24	1.40(5)	I1"-Cu2'-I2'	117.5(2)
C33-C34	1.56(4)	I1"-Cu2'-I3"	120.0(2)

TABLE 10 (Continued)

C14-O12	1.40(3)	I2'-Cu2'-I3''	122.0(2)
C24-O22	1.39(3)	I1'-Cu3'-I2''	119.4(2)
C34-O32	1.40(3)	I1'-Cu3'-I3''	120.9(2)
C35-O32	1.45(3)	I2''-Cu3'-I3'	118.8(2)
O12-C15	1.43(4)	I4-Ba1-N1	152.(1)
O22-C24	1.39(3)	I4-Ba1-O11	140.(1)
C24-O22	1.39(3)	I4-Ba1-O12	88.(1)
O22-C25	1.43(3)	I4-Ba1-O21	134.(1)
O32-C35	1.45(3)	I4-Ba1-O22	80.(1)
I1-Cu1	2.57(2)	I4-Ba1-O31	98.(1)
I1-Cu2	2.59(3)	I4-Ba1-O32	71.(1)
I1-Cu3	2.53(2)	Ba1-N1-C11	113.(1)
I1-Cu4	2.58(2)	Ba1-N1-C21	107.(1)
I2-Cu1	2.55(2)	Ba1-N1-C31	104.(1)
I2-Cu2	2.54(2)	C11-N1-C21	114.(2)
I2-Cu3	2.56(2)	C11-N1-C31	111.(1)
I2-Cu4	2.59(2)	C21-N1-C31	107.(2)
I3-Cu1	2.58(3)	N1-C11-C12	115.(2)
I3-Cu2	2.60(2)	N1-C21-C22	111.(2)
I3-Cu3	2.55(2)	N1-C31-C32	113.(2)
I3-Cu4	2.55(2)	C11-C12-O11	109.(2)
Cu1-Cu2	2.78(3)	C21-C22-O21	107.(2)
Cu1-Cu3	2.79(2)	C31-C32-O31	110.(2)
Cu1-Cu4	2.73(2)	C12--O11-C13	113.(2)

TABLE 10 (Continued)

Cu2-Cu3	2.73(2)	C12-O11-Ba1	111.(1)
Cu2-Cu4	2.76(3)	Ba1-O11-C13	113.(1)
Cu3-Cu4	2.79(3)	Ba1-O21-C23	116.(1)
		C22-O21-C23	113.(2)
		C22-O21-Ba1	121.(1)
		C32-O31-C33	110.(1)
		C32-O31-Ba1	123.(1)
		Ba1-O31-C33	123.(1)
		O11-C13-C14	109.(2)
		O21-C23-C24	112.(2)
		O31-C33-C34	107.(2)
		C13-C14-O12	110.(2)
		C23-C24-O22	115.(2)
		C33-C34-O32	109.(2)
		C14-O12-Ba1	120.(1)
		C14-O12-C15	117.(2)
		Ba1-O12-C15	120.(2)
		C24-O22-Ba1	118.(2)
		C24-O22-C25	112.(2)
		Ba1-O22-C25	126.(1)
		C34-O32-Ba1	108.(1)
		C34-O32-C35	114.(2)
		Ba1-O32-C35	123.(2)

' = symmetry operation x, y, z
" = symmetry operation -x, 1-y, 1-z

TABLE 11

POSITIONAL PARAMETERS FOR BIS (BARIUM IODO (TRIS(2-(2-METHOXYETHOXY) ETHYL) AMINE)) HEXAIODOTETRACUPRATE (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
Ba1	0.4222 (1)	0.0938 (1)	-0.8434 (1)
I1	-0.0366 (1)	0.1975 (1)	0.5182 (1)
I2	0.3002 (1)	0.4505 (1)	0.4956 (1)
I3	-0.0326 (1)	0.58231 (1)	0.2767 (1)
I4	0.3584 (1)	-0.1630 (1)	-0.9840 (1)
Cu1	0.0715 (5)	0.3944 (4)	0.4341 (3)
Cu2	0.1166 (5)	0.5688 (4)	0.5641 (3)
Cu3	-0.0919 (5)	0.4134 (4)	0.5761 (3)
Cu4	-0.0915 (5)	0.6133 (4)	0.4248 (3)
O11	0.3684 (12)	0.1663 (13)	0.3306 (8)
O12	0.1748 (13)	0.0649 (16)	0.2179 (11)
O21	0.3892 (14)	0.3666 (11)	0.1242 (11)
O22	0.2255 (15)	0.2306 (15)	0.0144 (11)
O31	0.6510 (12)	-0.0224 (12)	0.2631 (9)
O32	0.4257 (15)	-0.1542 (12)	0.2789 (10)
N1	0.6010 (15)	0.2545 (15)	0.2600 (10)
C11	0.5707 (19)	0.2578 (21)	0.3580 (15)
C12	0.4807 (22)	0.1568 (21)	0.3929 (14)
C13	0.2625 (21)	0.0982 (19)	0.3702 (14)
C14	0.1451 (22)	0.1151 (21)	0.2994 (17)

TABLE 11 (Continued)

C15	0.0678 (27)	0.0368 (40)	0.1547 (22)
C21	0.5973 (21)	0.3836 (19)	0.2043 (16)
C22	0.4548 (26)	0.4442 (17)	0.1825 (18)
C23	0.2582 (32)	0.4198 (23)	0.0882 (20)
C24	0.2120 (32)	0.3673 (27)	0.0073 (27)
C25	0.1766 (29)	0.1852 (29)	-0.0710 (18)
C31	0.7338 (20)	0.1910 (20)	0.2568 (15)
C32	0.7486 (19)	0.0519 (20)	0.3033 (14)
C33	0.6604 (26)	-0.1531 (21)	0.3119 (14)
C34	0.5422 (27)	-0.2258 (19)	0.2714 (16)
C35	0.3118 (29)	-0.2324 (23)	0.2850 (19)
H111	0.6528	0.2465	0.3999
H112	0.5295	0.3439	0.3629
H121	0.5249	0.0677	0.3972
H122	0.4589	0.1673	0.4564
H131	0.2877	0.0040	0.3867
H132	0.2429	0.1322	0.4281
H141	0.0716	0.0704	0.3260
H142	0.1182	0.2093	0.2848
H212	0.6334	0.3748	0.1439
H221	0.4140	0.4444	0.2420
H222	0.4535	0.5361	0.1529
H231	0.1975	0.3952	0.1357
H232	0.2567	0.5153	0.0762

TABLE 11 (Continued)

H241	0.1228	0.3993	-0.0137
H242	0.2665	0.4053	-0.0449
H311	0.7506	0.1920	0.1900
H312	0.8002	0.2434	0.2853
H321	0.8365	0.0132	0.2980
H322	0.7405	0.0504	0.3715
H331	0.7461	-0.1964	0.3036
H332	0.6578	-0.1514	0.3794
H341	0.5534	-0.2341	0.2038
H342	0.5442	-0.3161	0.3040

TABLE 12

THERMAL PARAMETERS FOR BIS (BARIUM IODO (TRIS(2-(2-METHOXYETHOXY) ETHYL) AMINE)) HEXAIODOTETRACUPRATE (I)

ATOM	U11	U22	U33	U12	U13	U23
Ba1	31.4(6)	14.9(5)	24.0(5)	-2.4(4)	3.4(4)	-1.8(4)
I1	42.4(7)	18.8(6)	47.2(8)	-3.5(5)	5.2(6)	-1.8(5)
I2	32.8(7)	27.3(7)	58.1(9)	1.3(5)	2.6(6)	3.8(6)
I3	67.2(9)	44.4(8)	31.7(7)	-6.5(7)	-2.1(7)	0.1(6)
I4	69.4(10)	37.5(7)	36.8(7)	-20.3(7)	17.2(7)	-11.2(6)
Cu1	41.(3)	24.(2)	44.(3)	-2.(2)	7.(2)	-3.(2)
Cu2	40.(3)	25.(3)	45.(3)	-5.(2)	0.(2)	2.(2)
Cu3	44.(3)	25.(2)	39.(3)	3.(2)	6.(2)	1.(2)
Cu4	46.(3)	22.(2)	42.(3)	0.(2)	-3.(2)	4.(2)
O11	41.(7)	50.(8)	27.(6)	-16.(6)	7.(5)	- 7.(6)
O12	41.(8)	70.(11)	63.(10)	-30.(7)	23.(7)	-30(8)
O21	58.(9)	8.(6)	89.(11)	4.(6)	-12.(8)	-8.(6)
O22	59.(10)	52.(10)	66.(10)	7.(8)	-21.(7)	9.(8)
O31	46.(8)	29.(7)	40.(7)	8.(6)	-9.(6)	-2.(6)
O32	74.(10)	15.(6)	54.(9)	-1.(7)	13.(7)	8.(6)
N1	43.(9)	31.(8)	37.(8)	-9.(7)	-9.(7)	-6.(7)
C11	33.(11)	55.(13)	54.(13)	-21.(10)	3.(10)	-31.(11)
C12	58.(14)	53.(14)	28.(11)	1.(11)	3.(10)	-5.(10)
C13	65.(14)	40.(12)	45.(11)	-7.(10)	38.(10)	-15.(9)
C14	48.(14)	40.(12)	59.(17)	-11.(11)	19.(13)	-5.(11)

TABLE 12 (Continued)

C15	54.(18)	25.7(41)	95.(24)	-78.(22)	2.(16)	-83.(26)
C21	49.(13)	31.(11)	77.(14)	-19.(10)	-12.(10)	-11.(10)
C22	90.(20)	6.(9)	84.(15)	-6.(11)	4.(15)	0.(10)
C23	117.(26)	27.(13)	102.(20)	40.(15)	-11.(18)	6.(13)
C24	122.(25)	45.(16)	120.(31)	6.(16)	-84.(23)	12.(18)
C25	109.(22)	88.(21)	59.(17)	18.(17)	-36.(15)	-17.(15)
C31	33.(12)	41.(12)	67.(14)	-14.(10)	-8.(10)	-10.(10)
C32	31.(11)	42.(12)	48.(12)	2.(9)	-8.(9)	5.(10)
C33	103.(20)	32.(12)	37.(11)	26.(13)	-10.(12)	14.(9)
C34	95.(21)	14.(10)	61.(15)	3.(12)	-11.(14)	10.(10)
C35	126.(24)	33.(14)	108.(19)	-33.(15)	66.(18)	-4.(13)

Anisotropic parameters are in the form:

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

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

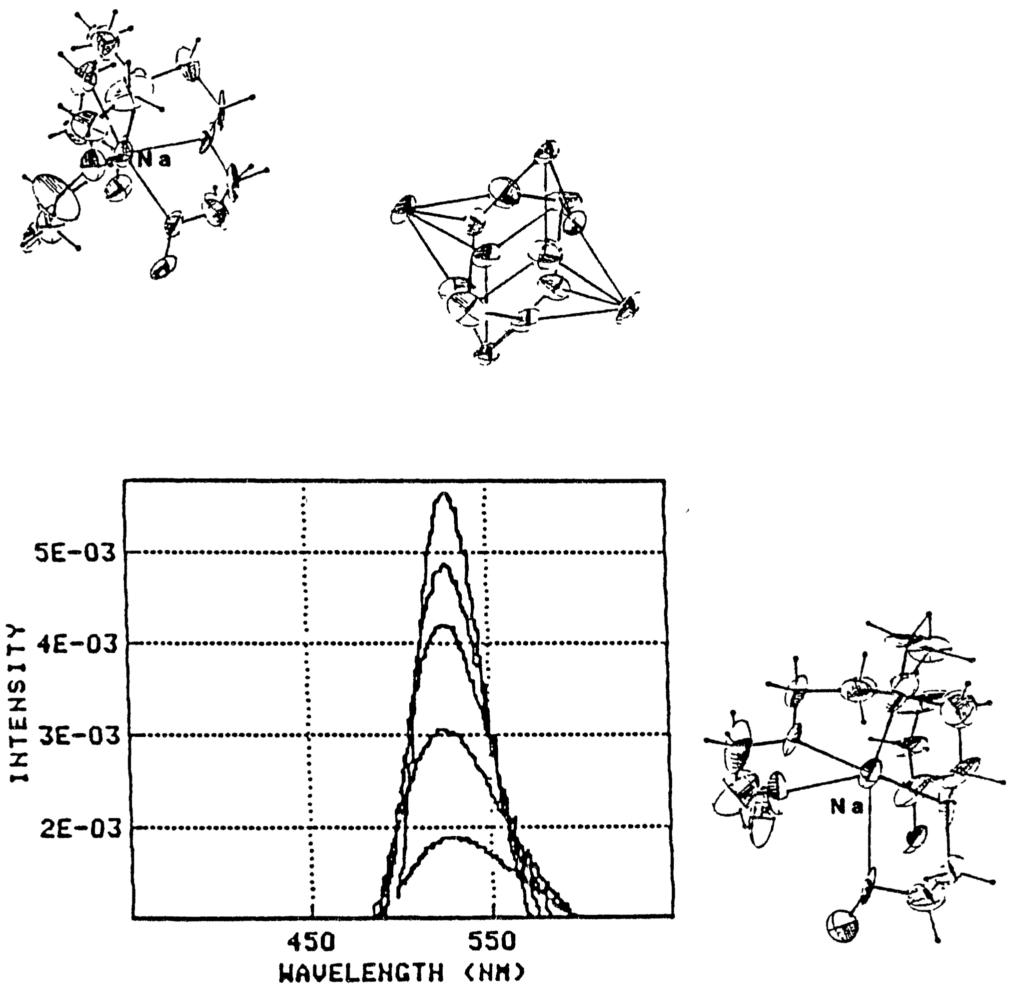


Figure 17. Bis[Sodium(Tris(2-(2-methoxyethoxy)ethoxy)ethyl) amine] Hexaiodotetracuprate.

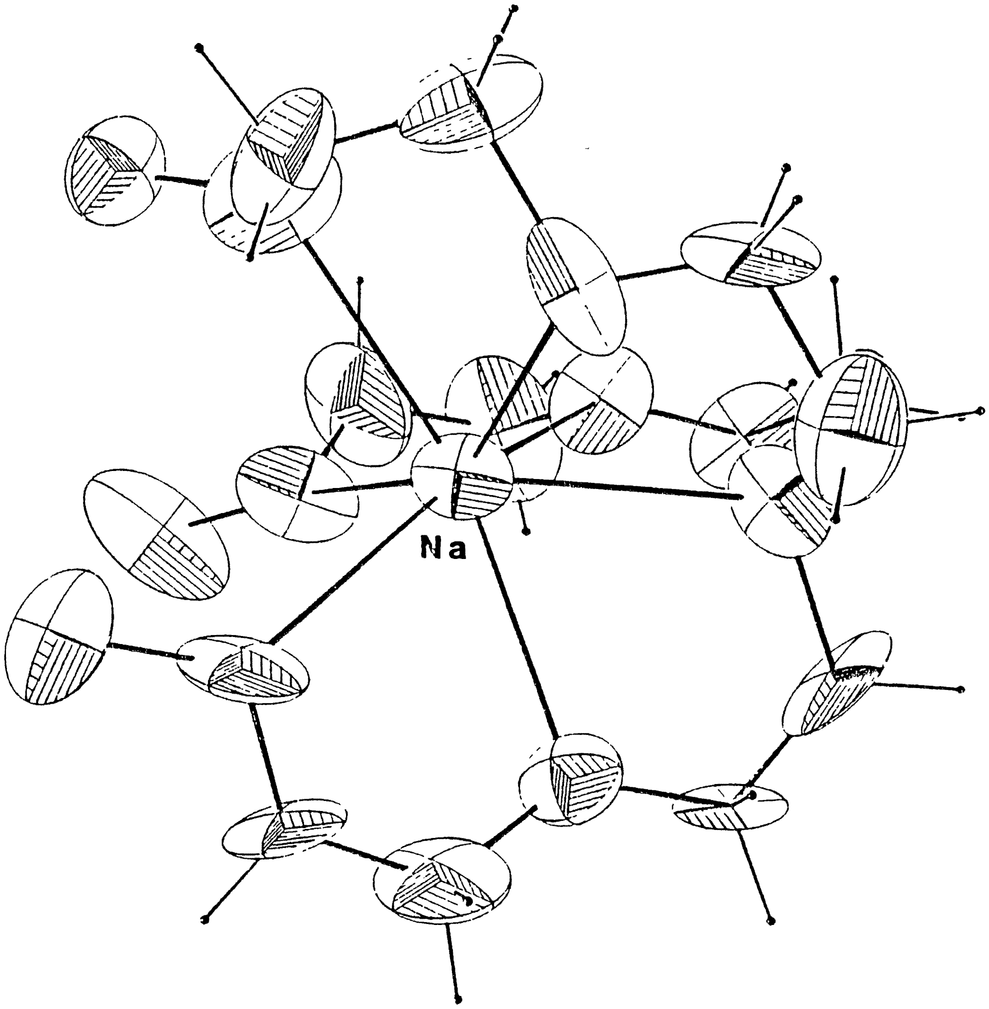


Figure 18. [Sodium(Tris(2-(2-methoxyethoxy)ethyl)amine] Cation.

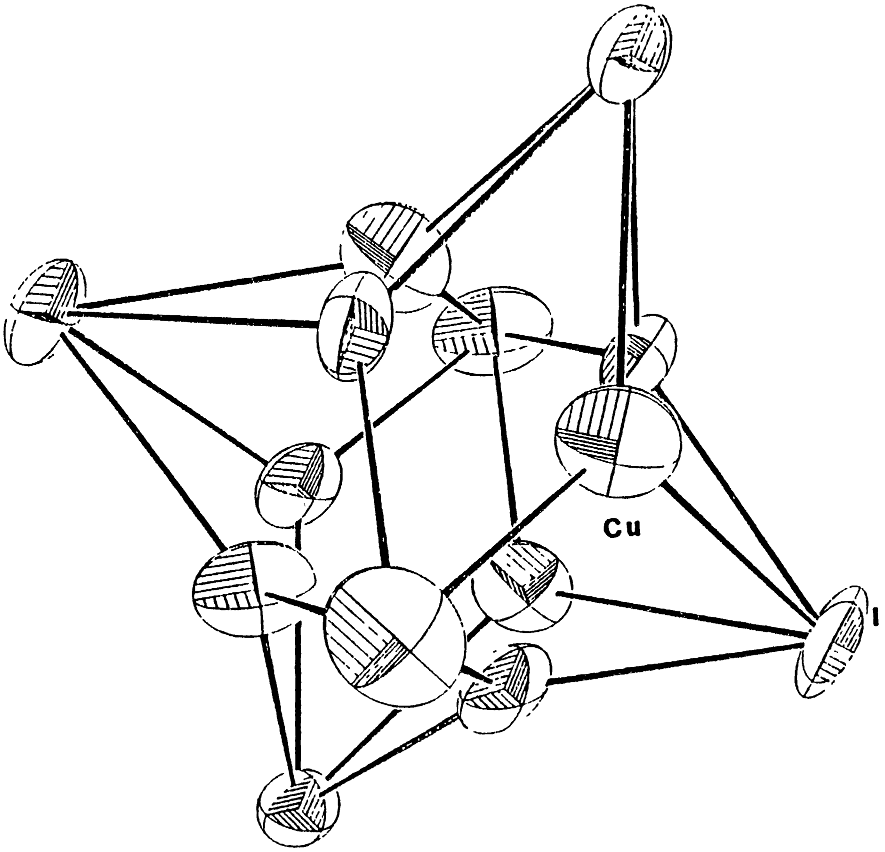


Figure 19. Disordered Hexaiodotetracuprate Dianion.

TABLE 13

CRYSTAL DATA FOR BIS (SODIUM (TRIS (2-(2-METHOXYETHOXY) ETHYL)AMINE)) HEXAIODOTETRA CUPRATE (I)

Formula	$[Na(NC_{15}O_6H_{33})]_2(Cu_4I_6)$
MWT	1708.4 g $mole^{-1}$
a	21.39 (2)Å
b	11.968 (3)
c	21.04 (1)
α	90.0°
β	90.0
γ	90.0
V	5287.(5) $Å^3$
F(000)	3224
μMoK_α	51.77 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.106 g cm^{-3}
Z	4
Obs. refl	1892
R	8.9%
R_w	12.3%
Space group	Pccn (Orthorhombic)
Octants meas.	+h, +k, +l

TABLE 14

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR BIS (SODIUM (TRIS (2-(2-METHOXYETHOXY)ETHYL)AMINE)) HEXAIODOTETRA CUPRATE (I)

I1-Cu1'	2.55(3)	Cu1'-I1-Cu3'	43.6(7)
I1-Cu2'	2.52(3)	Cu1'-I1-Cu1"	63.7(2)
I1-Cu1"	2.55(3)	Cu1'-I1-Cu3"	45.1(6)
I1-Cu2"	2.52(3)	Cu3'-I1-Cu1"	45.1(6)
I2-Cu1'	2.57(1)	Cu3'-I1-Cu3"	65.43(7)
I2-Cu2"	2.55(1)	Cu1"-I1-Cu3"	43.6(9)
I2-Cu3"	2.54(2)	Cu1'-I2-Cu4'	46.7(5)
I2-Cu4'	2.57(2)	Cu1'-I2-Cu2"	67.8(2)
I3-Cu2'	2.54(1)	Cu1'-I2-Cu3"	44.8(5)
I3-Cu4'	2.52(3)	Cu4'-I2-Cu2"	44.9(6)
I3-Cu2"	2.54(1)	Cu4'-I2-Cu3"	62.2(7)
I3-Cu4"	2.52(3)	Cu2"-I2-Cu3"	48.6(5)
I4-Cu1'	2.56(1)	Cu2'-I3-Cu4'	40.5(6)
I4-Cu2'	2.54(1)	Cu2'-I3-Cu2"	64.1(2)
I4-Cu3'	2.53(3)	Cu2'-I3-Cu4"	45.5(6)
I4-Cu4'	2.64(3)	Cu4'-I3-Cu2"	45.5(6)
Na1-O11	2.45(3)	Cu4'-I3-Cu4"	60.9(8)
Na1-O12	2.52(3)	Cu2"-I3-Cu4"	40.5(6)
Na1-O21	2.58(3)	Cu1'-I4-Cu2'	65.0(2)
Na1-O22	2.57(3)	Cu1-I4-Cu3'	43.5(5)
Na1-O31	2.42(3)	Cu1'-I4-Cu4'	46.1(5)

TABLE 14 (Continued)

Na1-O32	2.72(3)	Cu2'-I4-Cu3'	48.8(5)
N1-C11	1.48(5)	Cu2'-I4-Cu4'	39.5(6)
N1-C21	1.52(6)	Cu3'-I4-Cu4'	64.6(7)
N1-C31	1.51(7)	I1'-Cu1'-I2'	120.3(6)
C11-C12	1.58(6)	I1'-Cu1'-I4'	119.0(8)
C21-C22	1.44(6)	I2'-Cu1'-I4'	120.2(2)
C31-C32	1.55(7)	I3'-Cu2'-I4'	126.7(6)
C12-O11	1.33(4)	I3'-Cu2'-I2"	117.8(6)
C22-O21	1.31(4)	I4'-Cu2'-I2"	114.9(2)
C32-O31	1.32(5)	I1'-Cu3'-I4'	121.(2)
O11-C13	1.47(6)	I1'-Cu3'-I2"	123.(2)
O21-C23	1.37(6)	I4'-Cu3'-I2"	115.6(8)
O31-C33	1.57(5)	I2'-Cu4'-I3'	117.9(9)
C13-C14	1.36(7)	I2'-Cu4'-I4'	117.4(9)
C23-C24	1.28(7)	I3'-Cu4'-I4"	123.7(9)
C33-C34	1.48(6)	O11-Na1-O12	68.1(8)
C14-O22	1.31(4)	O11-Na1-O21	103.9(9)
C34-O32	1.37(5)	O11-Na1-O22	152.(1)
O12-C15	1.34(5)	O11-Na1-O31	105.4(9)
O22-C25	1.43(4)	O11-Na1-O32	100.0(9)
O32-C35	1.38(4)	O11-Na1-N1	67.(1)
Cu1-Cu2	2.744(7)	O12-Na1-O21	105.7(9)
Cu1-Cu1'	2.695(8)	O12-Na1-O22	88.8(9)
Cu1-Cu2'	2.855(7)	O12-Na1-O31	146.8(9)

TABLE 14 (Continued)

Cu2-Cu1'	2.855(7)	O12-Na1-O32	82.2(9)
Cu2-Cu2'	2.697(7)	O12-Na1-N1	130.(1)
Cu3-Cu4	2.76(3)	O21-Na1-O22	66.0(8)
Cu3-Cu3'	2.73(3)	O21-Na1-O31	107.4(9)
Cu3-Cu4'	2.83(3)	O21-Na1-O32	156.1(9)
Cu4-Cu3'	2.83(3)	O21-Na1-N1	65.8(9)
Cu4-Cu4'	2.55(4)	O22-Na1-O31	102.7(9)
		O22-Na1-O32	92.1(9)
		O31-Na1-O32	66.6(8)
		Na1-O11-C12	120.(2)
		Na1-O11C13	110.(2)
		C12-O11-C13	116.(3)
		Na1-O21-C22	56.8(7)
		Na1-O21-C23	109.(1)
		C22-O21-C23	119.(3)
		Na1-O31-C32	121.(2)
		Na1-O31-C33	118.(2)
		C32-O31-C33	109.(3)
		Na1-O12-C14	110.(3)
		Na1-O12-C15	135.(2)
		C14-O12-C15	113.(3)
		Na1-O22-24	107.(2)
		Na1-O22-C25	129.(2)
		C24-O22-C25	116.(3)

TABLE 14 (Continued)

Na1-O32-C34	100.(2)
Na1-O32-C35	127.(2)
C34-O32-C35	113.(3)
C11-N1-C21	114.(3)
C11-N1-C31	107.(3)
C21-N1-C31	105.(3)
N1-C11-C12	107.(2)
N1-C21-C22	115.(3)
N1-C31-C32	110.(3)
C11-C12-O11	108.(3)
C12-C22-O21	112.(3)
C31-C32-O31	109.(3)
O11-C13-C14	115.(4)
O21-C23-C24	122.(4)
O31-C33-C43	103.(3)
O13-C14-O12	110.(4)
C23-C24-O22	120.(4)
C33-C34-O32	111.(3)

' = symmetry operation x, y, z
" = symmetry operation 1.5-x, 0.5-y,z

TABLE 15

POSITIONAL PARAMETERS FOR BIS (SODIUM (TRIS (2-(2-METHOXYETHOXY)ETHYL)AMINE)) HEXAIODOTETRA CUPRATE (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.7500	0.2500	0.1039 (1)
I2	0.7996 (1)	0.0124 (2)	0.2582 (1)
I3	0.7500	0.2500	0.4069 (1)
I4	0.8857 (1)	0.3505 (2)	0.2508 (1)
Cu1	0 .8082 (3)	0.2067 (4)	0.2070 (2)
Cu2	0.7791 (3)	0.3499 (4)	0.3045 (2)
Cu3	0.7764 (12)	0.3538 (17)	0.2048 (9)
Cu4	0.8056 (13)	0.2114 (19)	0.3037 (10)
Na1	0.0808 (7)	0.2429 (11)	-0.0338 (6)
O11	0.1466 (12)	0.3987 (20)	0.0094 (11)
O12	0.1579 (12)	0.3207 (18)	-0.1150 (11)
O21	0.1295 (12)	0.0691 (20)	0.0120 (10)
O22	0.0640 (12)	0.0756 (19)	-0.1036 (13)
O31	-0.0204 (12)	0.2733 (17)	0.0162 (10)
O32	-0.0004 (12)	0.3727 (21)	-0.1045 (13)
N1	0.0877 (17)	0.2455 (27)	0.0877 (13)
C11	0.1079 (21)	0.3558 (30)	0.1115 (16)
C12	0.1655 (21)	0.3934 (27)	0.0693 (18)
C13	0.1951 (25)	0.4298 (37)	-0.0373 (24)
C14	0.1768 (25)	0.4264 (39)	-0.0989 (23)

TABLE 15 (Continued)

C15	0.1700 (21)	0.2958 (36)	-0.1758 (22)
C21	0.1272 (22)	0.1479 (44)	0.1111 (18)
C22	0.1228 (20)	0.0480 (30)	0.0728 (18)
C23	0.1217 (27)	-0.0154 (41)	-0.0314 (25)
C24	0.1082 (20)	0.0045 (28)	-0.0894 (19)
C25	0.0399 (18)	0.0696 (33)	-0.1668 (17)
C31	0.0232 (27)	0.2243 (38)	0.1145 (19)
C32	-0.0254 (29)	0.2947 (32)	0.0778 (21)
C33	-0.0704 (19)	0.3439 (34)	-0.0205 (20)
C34	-0.0549 (21)	0.3219 (34)	-0.0882 (18)
C35	0.0032 (19)	0.3947 (31)	-0.1687 (16)
H111	0.0736	0.4122	0.1062
H112	0.1174	0.3549	0.1574
H121	0.1810	0.4631	0.0879
H122	0.1972	0.3353	0.0775
H131	0.2128	0.5061	-0.0193
H132	0.2310	0.3788	-0.0285
H141	0.1349	0.4870	-0.0964
H142	0.2033	0.4670	-0.0121
H211	0.1727	0.1784	0.1092
H212	0.1202	0.1379	0.1571
H221	0.1530	-0.0067	0.0884
H222	0.0804	0.0172	0.0824

TABLE 15 (Continued)

H231	0.1554	-0.0720	-0.0261
H232	0.0823	-0.0628	-0.0152
H242	0.1028	-0.0678	-0.1128
H311	0.0123	0.1442	0.1101
H321	-0.0683	0.2763	0.0953
H322	-0.0187	0.3739	0.0890
H331	-0.1152	0.3234	-0.0056
H332	-0.0682	0.4255	-0.0095
H341	-0.0578	0.2390	-0.0935
H342	-0.0938	0.3487	-0.1142

TABLE 16

THERMAL PARAMETERS FOR BIS (SODIUM (TRIS (2-(2-METHOXYETHOXY)ETHYL)AMINE)) HEXAIODOTETRA CUPRATE (I)

ATOM	U11	U22	U33	U12	U13	U23
I1	37.(3)	55.(1)	42.(1)	5.(1)	0.	0.
I2	71.(2)	64.(1)	76.(1)	34.(1)	-19.(1)	-3.(1)
I3	23.(3)	70.(2)	42.(1)	0.(2)	0.	0.
I4	16.(2)	114.(2)	74.(1)	-15.(1)	-2.(1)	12.(1)
Cu1	21.(5)	70.(3)	57.(3)	17.(3)	1.(2)	2.(2)
Cu2	27.(5)	54.(3)	54.(2)	-7.(3)	6.(2)	-2.(2)
Cu3	55.(24)	51.(12)	61.(12)	26.(13)	-7.(12)	-8.(9)
Cu4	77.(25)	76.(17)	58.(12)	0.(16)	3.(14)	1.(11)
Na1	29.(11)	49.(6)	74.(7)	-9.(8)	-3.(7)	-5.(7)
O11	26.(25)	81.(18)	86.(17)	-34.(15)	-7.(15)	12.(14)
O12	62.(24)	48.(13)	116.(20)	-23.(14)	33.(17)	3.(13)
O21	49.(24)	59.(15)	73.(15)	1.(14)	-17.(14)	2.(12)
O22	35.(22)	63.(16)	128.(21)	32.(15)	-18.(15)	-34.(15)
O31	67.(26)	58.(17)	57.(12)	-49.(14)	32.(13)	-23.(11)
O32	17.(22)	94.(20)	123.(20)	-31.(15)	7.(16)	26.(16)
N1	31.(35)	76.(21)	75.(18)	-23.(22)	-11.(19)	-28.(18)
C11	77.(44)	58.(23)	62.(21)	-7.(24)	-40.(23)	0.(19)
C12	54.(42)	50.(21)	104.(27)	-45.(22)	-40.(27)	8.(20)
C13	111.(57)	99.(35)	126.(40)	-87.(36)	1.(39)	-36.(31)
C14	110.(52)	117.(38)	123.(38)	-18.(35)	-31.(35)	-59.(32)

TABLE 16 (Continued)

C15	72.(45)	110.(37)	165.(43)	-39.(32)	85.(34)	-43.(32)
C21	58.(45)	158.(47)	78.(27)	62.(37)	-12.(26)	60.(30)
C22	51.(41)	59.(23)	87.(26)	55.(23)	-9.(24)	-2.(21)
C23	125.(59)	118.(42)	145.(47)	92.(39)	-93.(43)	-46.(36)
C24	41.(37)	46.(21)	108.(31)	27.(21)	-30.(26)	8.(20)
C25	28.(35)	112.(32)	75.(23)	-26.(26)	-16.(22)	14.(22)
C31	99.(63)	197.(39)	75.(26)	-35.(36)	-14.(30)	5.(25)
C32	13.(37)	71.(26)	120.(34)	25.(25)	-16.(27)	-21.(25)
C33	30.(40)	84.(29)	116.(33)	8.(25)	-5.(27)	29.(25)
C35	60.(37)	88.(29)	62.(20)	-2.(25)	3.(21)	15.(21)

Anisotropic parameters are in the form:

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

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

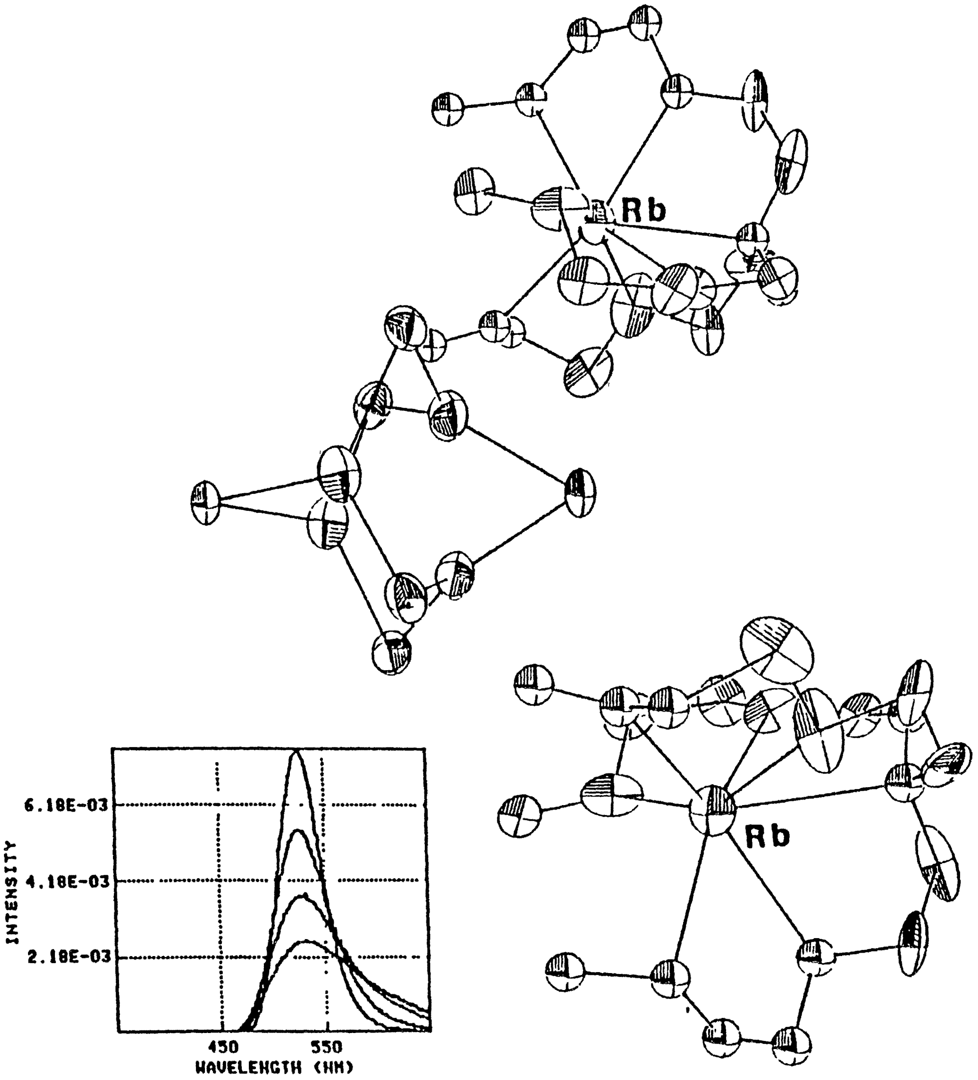


Figure 20. Bis(Rubidium(Tris(2-(2-methoxyethoxy)ethyl)amine Hexaiodotetracuprate.

TABLE 17

CRYSTAL DATA FOR BIS (RUBIDIUM (TRIS(2-(2-METHOXYETHOXY) ETHYL)AMINE)) HEXAIODOTETRACUPRATE (I)

Formula	$[Rb(NC_{15}O_6H_{33})]_2(Cu_4I_6)$
MWT	1833.4 g mole^{-1}
a	12.305 (5) Å
b	21.778 (4)
c	21.204 (9)
α	90.0 °
β	90.0
γ	90.0
V	5682.4 (40) Å^3
F (000)	3456
μMoK$_\alpha$	64.10 cm^{-1}
λMoK$_\alpha$	0.71069 Å
D$_{calc}$	2.143 g cm^{-1}
Z	4
Obs. refl.	1573
R	11.8%
R$_w$	17.92%
Space group	Pccn (Orthorhombic)
Octants meas.	+h, +k, +l

TABLE 18

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR BIS [RUBIDIUM(TRIS(2-(-METHOXYETHOXY)ETHYL) AMINE)] HEXAIIDOTETRACUPRATE (I)

I1-Cu1	2.54(1)	Cu1-I1-Cu2	68.3(4)
I1-Cu2	2.53(1)	Cu1-I2-Cu2	65.1(4)
I2-Cu1	2.55(1)	Cu2-I3-Cu2'	63.2(4)
I2-Cu2	2.62(1)	Cu1-I4-Cu1'	65.4(4)
I3-Cu2	2.59(1)	I1-Cu1-I2	116.8(5)
I4-Cu1	2.58(1)	I1-Cu1-I4	117.0(5)
Rb1-O11	2.88(6)	I2-Cu1-I4	125.9(5)
Rb1-O12	2.89(8)	I1'-Cu2-I2	120.8(5)
Rb1-O21	2.88(6)	I1'-Cu2-I3	121.8(5)
Rb1-O22	2.93(1)	I2-Cu2-I3	117.4(5)
Rb1-O31	2.89(5)	O11-Rb1-O12	61.(2)
Rb1-O32	3.04(5)	O11-Rb1-O21	96.(2)
Rb1-N1	3.02(0)	O11-Rb1-O22	97.(1)
N1-C11	1.35(19)	O11-Rb1-O31	100.(2)
N1-C21	1.54(9)	O11-Rb1-O32	151.(2)
N1-C31	1.44(11)	O12-Rb1-O21	142.(2)
C11-C12	1.57(14)	O12-Rb1-O22	91.(1)
C21-C22	1.40(13)	O12-Rb1-O31	113.(2)
C31-C22	1.53(12)	O12-Rb1-O32	106.(2)
C12-O11	1.51(9)	O21-Rb1-O22	97.(1)
C22-O21	1.56(10)	O21-Rb1-O31	100.(2)
C32-O31	1.44(10)	O21-Rb1-O32	107.(2)

TABLE 18 (Continued)

O11-C13	1.47(6)	O22-Rb1-O31	155.(1)
O21-C23	2.67(20)	O22-Rb1-O32	110.(1)
O31-C33	1.28(9)	O31-Rb1-O32	59.(2)
C13-C14	1.54(0)	N1-Rb1-O11	61.(1)
C23-C24	1.97(18)	N1-Rb1-O12	119.(2)
C33-C34	1.59(13)	N1-Rb1-O21	62.(1)
C14-O12	1.38(6)	N1-Rb1-O22	113.2(3)
C24-O22	1.51(0)	N1-Rb1-O31	60.(1)
C34-O32	1.511(1)	N1-Rb1-O32	115.(1)
O12-C15	1.32(8)	Rb1-O11-C12	120.(4)
O22-C25	1.598(1)	Rb1-O11-C13	120.(4)
O32-C35	1.55(6)	C12-O11-C13	103.(6)
Cu1-Cu2	2.77(2)	Rb1-O12-C14	108.(4)
Cu1-Cu2'	2.84(2)	Rb1-O12-C15	128.(4)
Cu1-Cu1'	2.78(2)	C14-O12-C15	120.(5)
Cu2-Cu2'	2.71(2)	Rb1-O21-C22	118.(5)
		Rb1-O21-C23	123.(5)
		C22-O21-C23	115.(7)
		Rb1-O22-C24	99.5(2)
		Rb1-O22-C25	103.8(2)
		C24-O22-C25	130.52(1)
		Rb1-O31-C32	121.(4)
		Rb1-O31-C33	119.(5)
		C32-O31-C33	111.(6)

TABLE 18 (Continued)

Rb1-O32-C34	96.(4)
Rb1-O32-C35	145.(6)
C34-O32-C35	116.(6)
Rb1-N1-C11	107.(4)
Rb1-N1-C21	107.(3)
Rb1-N1-C31	104.(4)
C11-N1-C21	113.(6)
C11-N1-C31	116.(7)
C21-N1-C31	108.(6)
N1-C11-C12	126.(10)
C11-C12-O11	102.(7)
O11-C13-C14	93.(5)
C13-C14-O12	114.(4)
N1-C21-C22	116.(6)
C21-C22-O21	117.(7)
O21-C23-C24	104.(1)
C23-C24-O22	130.(7)
N1-C31-C32	125.(10)
C31-C32-O31	99.(6)
O31-C33-C34	109.(6)
C33-C34-O32	113.(7)

' = symmetry operation 1.5-x, 0.5-y, z

TABLE 19

POSITIONAL PARAMETERS FOR BIS [RUBIDIUM (TRIS (2-(2-METHOXYETHOXY) ETHYL) AMINE)] HEXAIODOTETRACUPRATE (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.5186(5)	0.2003(3)	0.2346(3)
I2	0.6515(5)	0.3846(3)	0.2424(3)
I3	0.7500	0.2500	0.3893(3)
I4	0.7500	0.2500	0.0869(3)
Rb1	0.2622(7)	0.0748(4)	0.4452(4)
Cu1	0.6491(10)	0.2792(5)	0.1895(5)
Cu2	0.7954(10)	0.3068(6)	0.2854(5)
O11	0.0994(44)	0.1562(35)	0.4979(29)
O12	0.1654	0.1688	0.3644
O21	0.2091(38)	-0.0258(25)	0.5195(24)
O22	0.1105	-0.0190	0.3996
O31	0.4512(38)	0.1186(25)	0.5109(27)
O32	0.4849(38)	0.0514(26)	0.3935(30)
N1	0.2533	0.0926	0.5862
C11	0.1570	0.1202	0.5993
C12	0.1098(55)	0.1786(42)	0.5656(35)
C13	0.0632(61)	0.2166(43)	0.4610(43)
C14	0.0633	0.1800	0.3872
C15	0.1899	0.1800	0.3053
C21	0.2654(66)	0.0307(45)	0.6158(36)

TABLE 19 (Continued)

C22	0.2012(64)	-0.0163(46)	0.5899(37)
C23	0.1482	-0.0800	0.4957
C24	0.1416	-0.0713	0.4428
C25	0.1174	-0.0132	0.3246
C31	0.3491	0.1284	0.6002
C32	0.4612(54)	0.1117(37)	0.5821(38)
C33	0.5427(59)	0.1130(42)	0.4847(42)
C34	0.5272(63)	0.1054(44)	0.4103(46)
C35	0.5272(63)	0.1054(44)	0.4103(46)

TABLE 20

THERMAL PARAMETERS FOR BIS (RUBIDIUM (TRIS (2-(2-METHOXYETHOXY) ETHYL) AMINE)) HEXAIODO TETRACUPRATE (I)

ATOM	U11	U22	U33	U12	U13	U23
I1	48.(3)	72.(4)	50.(3)	-11.(3)	0.(3)	-11.(3)
I2	76.(4)	50.(3)	51.(3)	18.(3)	3.(3)	-4.(3)
I3	73.(6)	67.(6)	26.(4)	0.	0.	0.
I4	102.(7)	52.(5)	25.(4)	0.	0.	0.
Rb1	46.(5)	63.(5)	54.(5)	0.(5)	-5.(5)	0.(4)
Cu1	61.(8)	85.(9)	53.(7)	6.(7)	-3.(6)	-4.(6)
Cu2	96.(10)	80.(8)	44.(6)	-30.(7)	-5.(6)	0.(6)
O11	25.(41)	152.(70)	71.(45)	33.(43)	26.(33)	-31.(49)
O12	38.	38.	38.	0.	0.	0.
O21	28.(36)	83.(44)	51.(36)	30.(30)	-30.(27)	-3.(32)
O22	38.	38.	38.	0.	0.	0.
O31	1.(34)	62.(39)	77.(44)	-7.(27)	1.(30)	12.(35)
O32	0.(29)	54.(40)	111.(55)	-2.(29)	0.(33)	0.(39)
N1	38.	38.	38.	0.	0.	0.
C11	97.(80)	55.(58)	88.(73)	-27.(61)	62.(69)	2.(54)
C12	11.(46)	103.(77)	36.(50)	-9.(49)	18.(38)	8.(50)
C13	11.(48)	88.(75)	104.(79)	15.(53)	-33.(54)	-21.(63)
C14	38.	38.	38.	0.	0.	0.
C15	38.	38.	38.	0.	0.	0.
C21	24.(57)	123.(87)	41.(49)	53.(60)	-16.(45)	-29.(56)

TABLE 20 (Continued)

C22	14.(56)	124.(86)	21.(50)	-7.(59)	3.(44)	2.(55)
C23	38.	38.	38.	0.	0.	0.
C24	38.	38.	38.	0.	0.	0.
C25	38.	38.	38.	0.	0.	0.
C31	38.	38.	38.	0.	0.	0.
C32	1.(43)	58.(54)	53.(53)	-4.(40)	1.(39)	4.(49)
C33	3.(54)	85.(69)	70.(68)	-16.(46)	2.(45)	-13.(58)
C34	12.(47)	79.(72)	79.(72)	-28.(52)	10.(48)	2.(59)
C35	14.(48)	68.(62)	52.(57)	-29.(45)	-7.(41)	2.(50)

Anisotropic parameters are in the form:

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

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

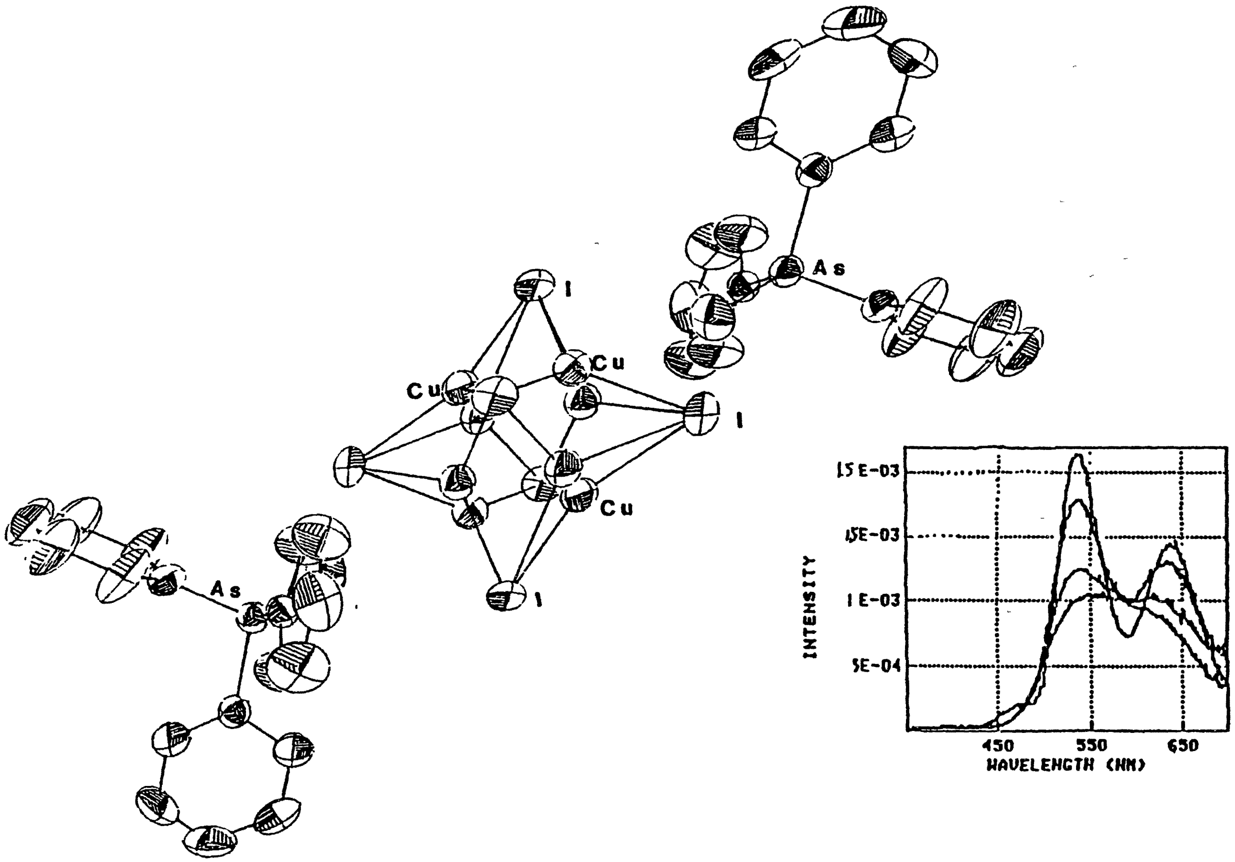


Figure 21. Bis(Methyltriphenylarsonium) Hexaiodotetracuprate

TABLE 21

CRYSTAL DATA FOR BIS (METHYLTRIPHENYLARSONIUM) HEXAIODOTETRACUPRATE (I)

Formula	$[CH_3(C_6H_5)_3As]_2(Cu_4I_6)$
MWT	1514.0 g mole^{-1}
a	15.743 (6) Å
b	15.743
c	15.743
α	52.77 (2)°
β	52.77
γ	52.77
V	2291 (1) Å^3
F(000)	1384
μMoK_α	72.85 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.194
Z	2
obs. refl.	3903
R	4.0%
R_w	5.5%
Space group	R3barc (Rhombohedral)
Octants meas.	+h, +k, +l

TABLE 22

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR BIS (METHYLTRIPHENYLARSONIUM) HEXAIODOTETRACUPRATE (I)

I1-Cu2	2.633(3)	Cu1-I1-Cu2	64.04(4)
I1-Cu1	2.548(2)	Cu1-I1-Cu2^{2}	43.64(4)
I1-Cu2^{2}	2.576(2)	Cu1-I1-Cu2^{4}	44.01(4)
I1-Cu2^{4}	2.535(2)	Cu2-I1-Cu2^{2}	44.93(6)
Cu2-I1^{2}	2.535(2)	Cu2-I1-Cu2^{4}	45.27(6)
Cu2-I1^{4}	2.576(2)	Cu2^{2}-I1-Cu2^{4}	65.33(5)
Cu1-I1^{1}	2.548(1)	I1-Cu2-I1^{2}	121.22(6)
Cu1-I1^{3}	2.548(1)	I1-Cu2-I1^{4}	119.66(6)
As1-C11	1.900(26)	I1^{2}-Cu2-I1^{4}	118.66(10)
As1-C21	1.934(41)	I1-Cu1-I1^{1}	119.27(5)
C11-C12	1.373(9)	I1-Cu1-I1^{3}	119.27(4)
C11-C16	1.354(13)	I1^{1}-Cu1-I1^{3}	119.27(4)
C12-C13	1.376(12)	C11-As1-C21	110.3(13)
C13-C14	1.364(12)	C11-As1-C11^{1}	108.6(17)
C14-C15	1.323(13)	C11-As1-C11^{3}	108.6(11)
C15-C16	1.385(11)	C11^{1}-As1-C11^{3}	108.6(13)

TABLE 22 (Continued)

Cu1-Cu2	2.748(3)	C21-As1-C11^1	110.3(11)
Cu1-Cu2^1	2.748(3)	C21-As1-C11^3	110.3(16)
Cu1-Cu2^3	2.748(3)	C12-C11-C16	119.2(5)
Cu2-Cu2^1	2.759(2)	C11-C12-C13	120.2(8)
Cu2-Cu2^3	2.759(2)	C12-C13-C14	118.7(7)
		C13-C14-C15	121.9(8)
		C14-C15-C16	119.6(10)
		C11-C16-C15	120.3(7)

1 = symmetry operation (z, x, y)
2 = symmetry operation (2-z, 2-x, 2-y)
3 = symmetry operation (y, z, x)
4 = symmetry operation (2-y, 2-z, 2-x)

TABLE 23

POSITIONAL PARAMETERS FOR BIS (METHYLTRIPHENYLARSONIUM) HEXAIODOTETRACUPRATE (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.84428 (4)	1.09749 (4)	1.19589 (4)
As1	1.17262 (2)	1.17262 (0)	1.17262 (0)
Cu1	1.0405 (1)	1.0405 (0)	1.0405 (0)
Cu2	0.8582 (1)	1.0195 (1)	1.0780 (1)
C11	1.1469 (5)	1.3320 (5)	1.0879 (5)
C12	1.1921 (7)	1.3744 (6)	0.9696 (6)
C13	1.1799 (8)	1.4881 (7)	0.9079 (6)
C14	1.1198 (8)	1.5578 (6)	0.9664 (8)
C15	1.0725 (8)	1.5192 (6)	1.0803 (8)
C16	1.0846 (7)	1.4047 (6)	1.1427 (6)
C21	1.1249 (2)	1.1249	1.1249
H1	1.2349	1.3211	0.9283
H2	1.2148	1.5196	0.8208
H3	1.1134	1.6401	0.9220
H4	1.0290	1.5727	1.1207
H5	1.0460	1.3749	1.2295

TABLE 24

THERMAL PARAMETERS FOR BIS (METHYLTRIPHENYLARSONIUM) HEXAIODOTETRACUPRATE (I)

ATOM	U11	U22	U33	U12	U13	U23
I1	51.6(3)	66.4(3)	50.2(3)	-18.2(2)	-14.7(2)	-32.6(2)
As1	41.8(3)	41.8	41.8	-16.9(2)	-16.9	-16.9
Cu1	53.0(2)	53.0	53.0	-21.6(1)	-21.6	-21.6
Cu2	46.7(9)	57.0(10)	51.3(9)	-20.9(8)	-15.5(8)	-24.8
C11	44.(3)	41.(3)	43.(3)	-13.(2)	-21.(3)	-16.(3)
C12	116.(6)	41.(4)	49.(4)	-28.(4)	-30.(4)	-9.(3)
C13	124.(7)	67.(5)	43.(4)	-50.(5)	-35.(4)	5.(4)
C14	118.(7)	44.(4)	94.(6)	-35.(4)	-70.(6)	5.(4)
C15	130.(8)	49.(4)	102.(7)	-24.(5)	-49.(6)	-35.(5)
C16	105.(6)	48.(4)	50.(4)	-30.(4)	-30.(4)	-9.(3)
C21	94.(5)	94.	94.	-44.(3)	-44.	-44.

Anisotropic parameters are in the form:

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

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

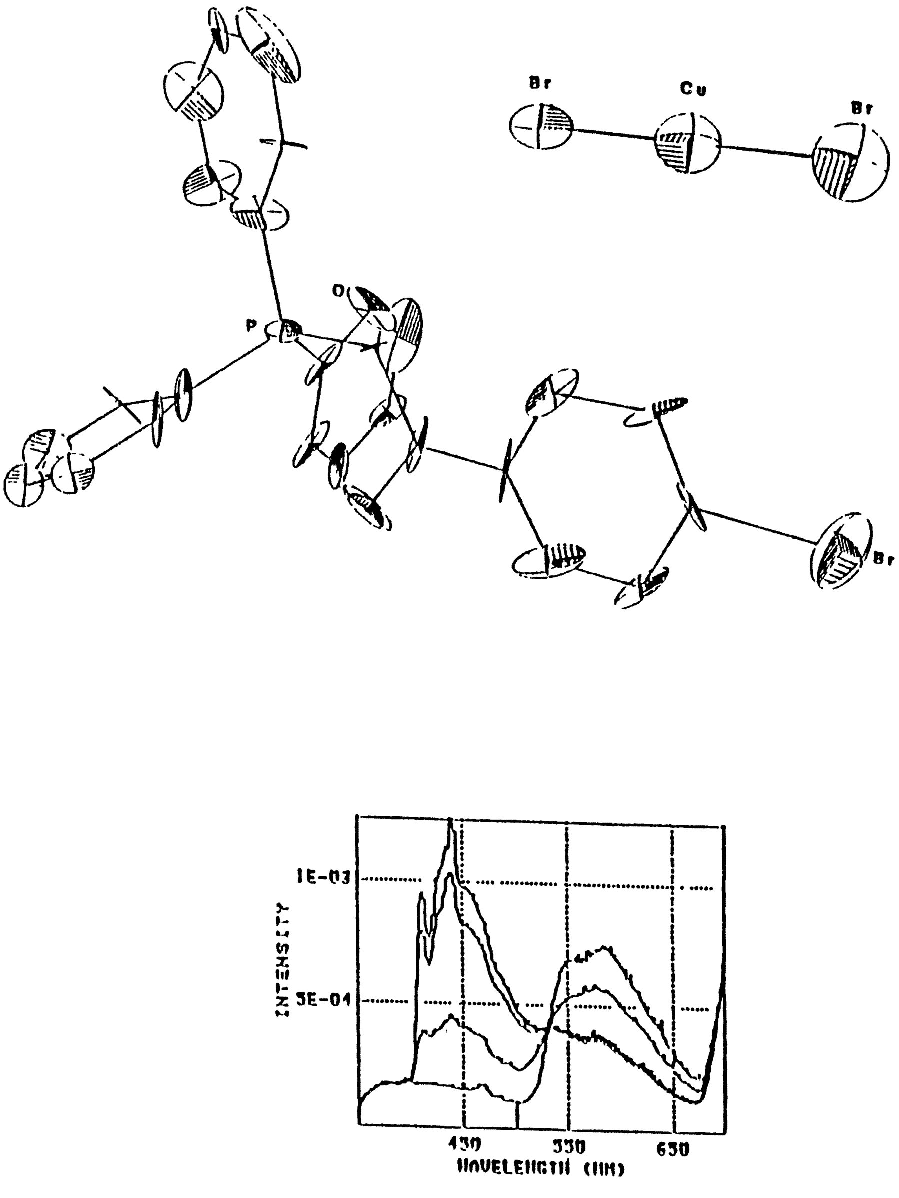


Figure 22. Parabromophenacyltriphenylphosphonium Dibromocuprate.

TABLE 25

CRYSTAL DATA FOR PARABROMOPHENACYLTRIPHENYL PHOSPHONIUM DIBROMOCUPRATE (I)

Formula	$C_{26}H_{21}BrOP(Cu\ Br_2)$
MWT	652.7 g $mole^{-1}$
a	9.722 (2) Å
b	21.96 (2)
c	12.516 (6)
α	90.0°
β	104.66 (3)
γ	90.0
V	2585. (2) Å^3
F(000)	1276
μMoK_α	54.53 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.677 g cm^{-3}
Z	4
Obs. refl.	910
R	7.2
R_w	9.0
Space group	$P2_1/n$ (Monoclinic)
Octants meas.	±h, +k, +l

TABLE 26

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR PARABROMOPHENACYLTRIPHENYL PHOSPHONIUM DIBROMOCUPRATE (I)

Br1-Cu1	2.207(8)	Br1-Cu1-Br2	178.0(5)
Br2-Cu1	2.229(8)	C11-P1-C21	109.(2)
Br3-C26	1.97(4)	C11-P1-C31	112.(2)
P1-C11	1.81(4)	C11-P1-C41	110.(2)
P1-C21	1.80(3)	C21-P1-C31	107.(2)
P1-C31	1.75(4)	C21-P1-C41	110.(2)
P1-C41	1.80(4)	C31-P1-C41	107.(2)
O1-C22	1.27(6)	P1-C11-C12	124.(4)
C11-C12	1.33(5)	P1-C11-C16	117.(3)
C11-C16	1.37(6)	C12-C11-C16	117.(4)
C12-C13	1.43(5)	C11-C12-C13	127.(4)
C13-C14	1.34(6)	C12-C13-C14	109.(4)
C14-C15	1.36(6)	C13-C14-C15	126.(4)
C15-C16	1.33(7)	C14-C15-C16	122.(4)
C21-C22	1.50(5)	C11-C16-C15	117.(5)
C22-C23	1.41(5)	P1-C21-C22	117.(3)
C23-C24	1.36(5)	O1-C22-C21	114.(3)
C23-C28	1.40(6)	O1-C22-C23	122.(4)
C24-C25	1.34(6)	C21-C22-C23	124.(4)
C25-C26	1.46(6)	C22-C23-C24	124.(4)
C26-C27	1.28(6)	C22-C23-C28	116.(4)
C27-C28	1.42(6)	C24-C23-C28	119.(4)

TABLE 26 (Continued)

C31-C32	1.44(6)	C23-C24-C25	126.(4)
C31-C36	1.37(7)	C24-C25-C26	112.(3)
C32-C33	1.43(7)	Br3-C26-C25	109.(3)
C33-C34	1.34(6)	Br3-C26-C27	124.(4)
C34-C35	1.34(6)	C25-C26-C27	126.(4)
C35-C36	1.43(7)	C26-C27-C28	119.(4)
C41-C42	1.35(6)	C23-C28-C27	117.(3)
C41-C46	1.35(7)	P1-C31-C32	119.(4)
C42-C43	1.31(7)	P1-C31-C36	125.(4)
C43-C44	1.41(7)	C32-C31-C36	117.(4)
C44-C45	1.36(8)	C31-C32-C33	120.(4)
C45-C46	1.39(7)	C32-C33-C34	116.(4)
		C33-C34-C35	128.(4)
		C34-C35-C36	114.(5)
		C31-C36-35	124.(4)
		P1-C41-C42	122.(4)
		P1-C41-C46	118.(4)
		C42-C41-C46	120.(4)
		C41-C42-C43	123.(5)
		C42-C43-C44	121.(4)
		C43-C44-C45	115.(4)
		C44-C45-C46	124.(5)
		C41-C46-C45	117.(5)

TABLE 27

POSITIONAL PARAMETERS FOR PARABROMOPHENACYL TRIPHENYL PHOSPHONIUM DIBROMOCUPRATE (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
Br1	-0.1114 (5)	0.6193 (3)	0.5178 (4)
Br2	0.0341 (6)	0.4936 (2)	0.8014 (5)
Br3	0.5367 (6)	0.4823 (2)	0.7944 (5)
Cu1	-0.0397 (6)	0.5554 (3)	0.6569 (5)
P1	0.1011 (11)	0.7057 (5)	0.2393 (9)
O1	0.3874 (30)	0.6636 (14)	0.3368 (24)
C11	0.1650 (41)	0.6898 (17)	0.11709 (28)
C12	0.1860 (39)	0.6339 (15)	0.0840 (28)
C13	0.2316 (33)	0.6174 (16)	-0.0117 (29)
C14	0.2410 (42)	0.6676 (16)	-0.0702 (35)
C15	0.2091 (43)	0.7250 (18)	-0.0445 (36)
C16	0.1643 (39)	0.7369 (17)	0.0457 (34)
C21	0.1514 (31)	0.6442 (14)	0.3359 (27)
C22	0.3072 (43)	0.6363 (17)	0.3875 (34)
C23	0.3622 (42)	0.5979 (17)	0.4784 (30)
C24	0.5027 (43)	0.5915 (20)	0.5279 (42)
C25	0.5579 (40)	0.5593 (19)	0.6194 (36)
C26	0.4481 (50)	0.5259 (17)	0.6566 (30)
C27	0.3141 (40)	0.5324 (16)	0.6184 (34)
C28	0.2628 (42)	0.5647 (19)	0.5176 (34)
C31	-0.0843 (43)	0.7119 (23)	0.2077 (38)

TABLE 27 (Continued)

C32	-0.1502 (51)	0.7660 (20)	0.1532 (40)
C33	-0.3010 (56)	0.7732 (19)	0.1286 (40)
C34	-0.3745 (38)	0.7262 (16)	0.1540 (28)
C35	-0.3246 (65)	0.6749 (19)	0.2086 (41)
C36	-0.1737 (43)	0.6679 (20)	0.2285 (34)
C41	0.1739 (46)	0.7764 (19)	0.3020 (35)
C42	0.3000 (45)	0.7979 (19)	0.2922 (35)
C43	0.3549 (44)	0.8492 (27)	0.3375 (35)
C44	0.2903 (44)	0.8817 (17)	0.4093 (35)
C45	0.1637 (70)	0.8587 (23)	0.4181 (39)
C46	0.1037 (46)	0.8050 (23)	0.3678 (40)
H11	0.1739	0.6001	0.1334
H12	0.2431	0.5747	-0.0381
H13	0.2889	0.6659	-0.1311
H14	0.2163	0.7585	-0.0975
H15	0.1304	0.7790	0.0581
H21	0.5747	0.6096	0.4889
H22	0.6596	0.5606	0.6549
H24	0.2444	0.5188	0.6551
H25	0.1580	0.5654	0.4777
H31	-0.0888	0.7994	0.1374
H32	-0.3530	0.8125	0.0878
H33	-0.4799	0.7267	0.1275
H34	-0.3833	0.6459	0.2438

TABLE 27 (Continued)

H35	-0.1259	0.6277	0.2620
H41	0.3568	0.7743	0.2496
H42	0.4420	0.8643	0.3201
H43	0.3379	0.9173	0.4508
H44	0.1078	0.8792	0.4672
H45	0.0105	0.7910	0.3771
H211	0.1009	0.6484	0.3978
H212	0.1103	0.6042	0.2999

TABLE 28

THERMAL PARAMETERS FOR PARABROMOPHENACYL TRIPHENYLPHOSPHONIUM DIBROMOCUPRATE (I)

ATOM	U11	U22	U33	U12	U13	U23
Br1	42.(3)	88.(4)	79.(4)	-7.(3)	19.(2)	3.(3)
Br2	102.(4)	42.(3)	98.(5)	-8.(3)	22.(3)	0.(3)
Br3	86.(4)	65.(3)	77.(4)	1.(3)	-15.(3)	33.(3)
Cu1	68.(4)	57.(3)	77.(4)	-3.(3)	20.(3)	0.(3)
P1	13.(7)	50.(8)	31.(7)	-8.(5)	6.(5)	4.(6)
O1	62.(23)	83.(24)	53.(23)	3.(18)	51.(19)	16.(18)
C11	58.(29)	47.(27)	5.(25)	-3.(24)	0.(22)	-11.(23)
C12	58.(28)	27.(25)	2.(25)	7.(22)	0.(21)	7.(20)
C13	29.(24)	31.(26)	37.(27)	0.(21)	2.(20)	33.(22)
C14	38.(31)	106.(46)	32.(31)	21.(31)	9.(24)	58.(32)
C15	47.(30)	12.(26)	55.(40)	18.(24)	12.(27)	19.(27)
C16	43.(28)	45.(28)	34.(33)	0.(23)	38.(25)	-1.(24)
C21	0.(21)	26.(23)	16.(24)	2.(17)	-1.(17)	0.(19)
C22	52.(32)	27.(28)	5.(26)	20.(24)	-12.(23)	-11.(23)
C23	60.(32)	16.(25)	3.(25)	-5.(23)	-11.(24)	3(.21)
C24	16.(28)	75.(38)	96.(44)	-9.(24)	0.(28)	-13.(34)
C25	22.(27)	46.(30)	37.(32)	6.(24)	-24.(25)	-25.(27)
C26	48.(32)	45.(28)	11.(25)	-8.(26)	22.(24)	-4.(21)
C27	5.(24)	43.(28)	63.(33)	-2.(21)	-11.(22)	-14.(24)
C28	36.(29)	41.(33)	58.(35)	26.(24)	-13.(25)	23.(27)

TABLE 28 (Continued)

C31	35.(33)	74.(39)	76.(40)	-44.(30)	25.(29)	0.(33)
C32	40.(36)	34.(32)	86.(43)	-5.(28)	-1.(31)	35.(30)
C33	89.(41)	25.(28)	86.(43)	-1.(30)	34.(35)	0.(28)
C34	58.(29)	40.(28)	8.(25)	-47.(23)	12.(21)	-6.(21)
C35	157.(61)	43.(33)	84.(45)	-65.(36)	89.(44)	-34.(30)
C36	8.(25)	69.(38)	51.(33)	-6.(26)	18.(24)	4.(27)
C41	23.(28)	42.(31)	49.(36)	-24.(27)	4.(26)	24.(27)
C42	31.(31)	34.(30)	33.(31)	-21.(24)	-28.(23)	7.(27)
C43	42.(33)	107.(49)	8.(30)	-14.(33)	-5.(24)	0(.30)
C44	20.(26)	13.(25)	35.(31)	-10.(23)	-12.(24)	-5.(23)
C45	145.(60)	45.(38)	43.(39)	42.(39)	-10.(39)	-34.(30)
C46	66.(40)	70.(39)	58.(39)	24.(32)	54.(32)	-8.(32)

Anisotropic parameters are in the form:

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

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

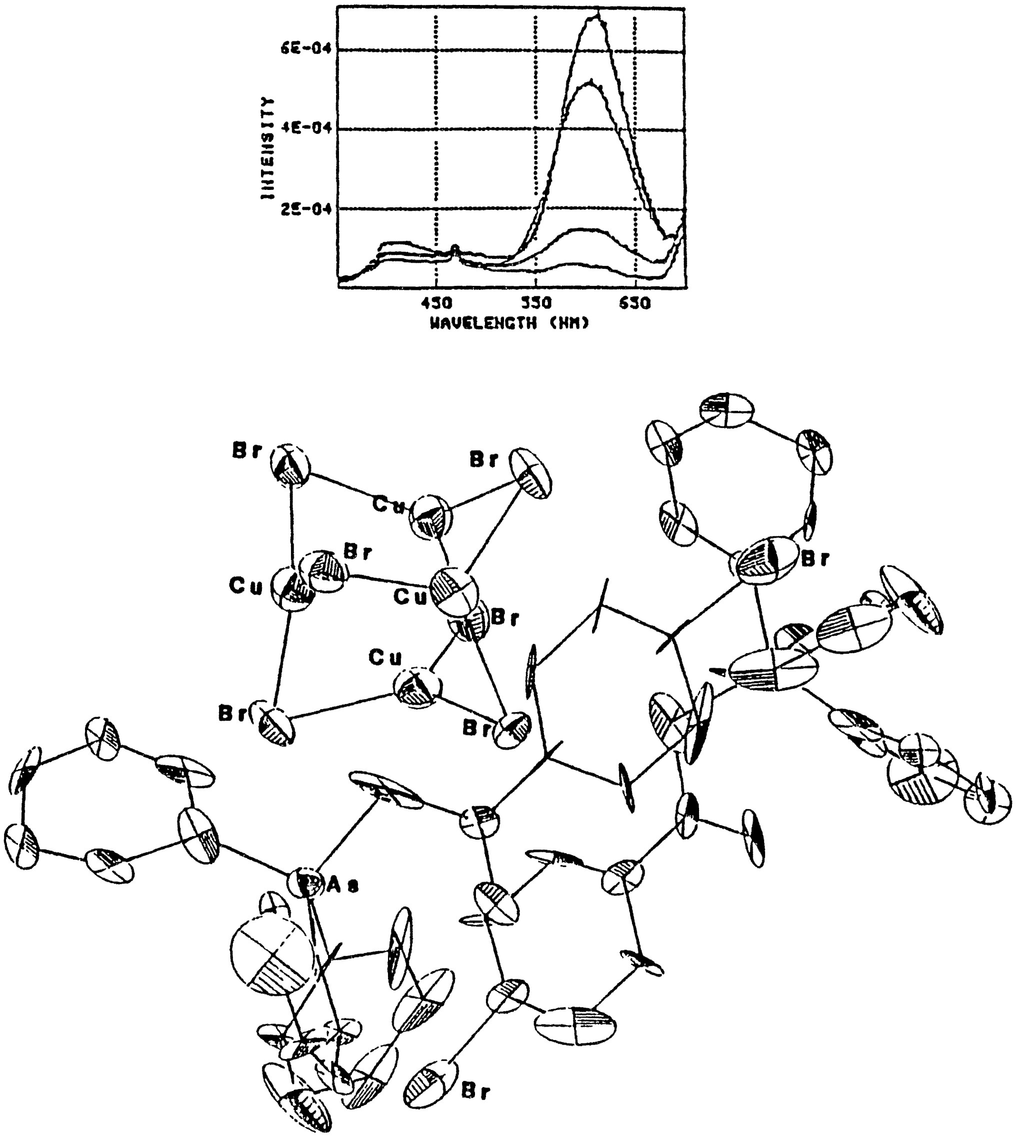


Figure 23. Bis(Parabromophenacyltriphenylarsonium) Hexabromotetracuprate.

TABLE 29

CRYSTAL DATA FOR BIS (PARABROMOPHENACYLTRIPHENYLARSONIUM) HEXABROMOTETRACUPRATE (I)

Formula	$C_{52}H_{42}As_2O_2Br_8Cu_4$
MWT	1742.2 g mole^{-1}
a	12.468 (4) Å
b	12.467 (4)
c	37.50 (5)
α	90.0 °
β	90.0
γ	90.0
V	5829. (8) Å^3
F(000)	3328
μMoK$_\alpha$	80.38 cm^{-1}
λMoK$_\alpha$	0.71069 Å
D_{calc}	1.985 g cm^{-3}
Z	4
Obs. refl.	1844
R	10.0
R_w	12.7
Space group	$P4_12_12$, #92 (Tetragonal)
Octants meas.	+h, +k, +l

TABLE 30

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR BIS (PARABROMOPHENACYL-TRIPHENYLARSONIUM) HEXABROMOTETRACUPRATE (I)

Br1-Cu2	2.380(7)	Cu2-Br1-Cu2'	72.9(2)
Br2-Cu1	2.40(2)	Cu1-Br2-Cu1'	70.1(3)
Br3-Cu1	2.39(1)	Cu1-Br3-Cu2	70.2(3)
Br3-Cu2	2.39(1)	Cu1-Br4-Cu2'	70.0(3)
Br4-Cu1	2.40(1)	C11-As1-C21	105.(2)
Br4-Cu2^{1}	2.4(1)	C11-As1-C31	114.(2)
Br5-C46	1.91(5)	C11-As1-C41	107.(3)
As1-C11	1.80(5)	C21-As1-C31	112.(3)
As1-C21	2.03(6)	C21-As1-C41	106.(3)
As1-C31	1.88(6)	C31-As1-C41	112.(3)
As1-C41	1.89(7)	Br2-Cu1-Br3	118.3(8)
O1-C42	1.24(6)	Br2-Cu1-Br4	121.3(9)
C11-C12	1.57(7)	Br3-Cu1-Br4	120.4(4)
C11-C16	1.38(7)	Br1-Cu2-Br3	121.1(3)
C12-C13	1.35(10)	Br1-Cu2-Br4'	117.4(3)
C13-C14	1.66(10)	Br3-Cu2-Br4'	121.5(3)
C14-C15	1.49(7)	As1-C11-C12	125.(4)
C15-C16	1.42(8)	As1-C11-C16	123.(4)
C21-C22	1.40(8)	C12-C11-C16	112.(4)
C21-C26	1.27(10)	C11-C12-C13	141.(6)
C22-C23	1.22(10)	C12-C13-C14	98.(6)

TABLE 30 (Continued)

C23-C24	1.58(11)	C13-C14-C15	129.(5)
C24-C25	1.45(10)	C14-C15-C16	116.(5)
C25-C26	1.37(12)	C11-C16-C15	124.(5)
C31-C32	1.32(8)	As1-C21-C22	110.(4)
C31-C36	1.61(8)	As1-C21-C26	117.(5)
C32-C33	1.61(7)	C22-C21-C26	120.(6)
C33-C34	1.37(8)	C21-C22-C23	121.(6)
C34-C35	1.37(9)	C22-C23-C24	112.(7)
C35-C36	1.38(9)	C23-C24-C25	126.(7)
C41-C42	1.57(9)	C24-C25-C26	109.(7)
C42-C43	1.46(8)	C21-C26-C25	121.(7)
C43-C44	1.33(8)	As1-C31-C32	119.(5)
C43-C44	1.41(8)	As1-C31-C36	124.(4)
C44-C45	1.51(7)	C32-C31-C36	116.(5)
C45-C46	1.30(6)	C31-C32-C33	110.(5)
C46-C47	1.38(8)	C32-C33-C34	132.(4)
C47-C48	1.50(8)	C33-C34-C35	117.(5)
Cu1-Cu2	2.75(1)	C34-C35-C36	115.(6)
Cu1-Cu1'	2.76(1)	C31-C36-C35	129.(5)
Cu1-Cu2'	2.76(1)	As1-C41-C42	110.(4)
Cu2-Cu1'	2.76(1)	O1-C42-C41	120.(5)
Cu2-Cu2'	2.83(1)	O1-C42-C43	120.(5)
		C41-C42-C43	119.(4)
		C42-C43-C44	123.(5)

TABLE 30 (Continued)

	C42-C43-C48	118.(5)
	C44-C43-C48	118.(5)
	C43-C44-C45	123.(5)
	C44-C45-C46	113.(4)
	C45-C46-C47	128.(5)
	C46-C47-C48	115.(5)
	C43-C48-C47	119.(5)

' = symmetry operation y, x, 2-z

TABLE 31

POSITIONAL PARAMETERS FOR BIS (PARABROMOPHENACYL-TRIPHENYLARSONIUM) HEXABROMOTETRACUPRATE (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
Br1	0.1065	0.1065	1.0000
Br2	0.4349 (5)	0.4349	1.0000
Br3	0.4358 (5)	0.1086 (5)	1.0154 (2)
Br4	0.3009 (5)	0.2334 (5)	0.9228 (2)
Br5	0.2043 (5)	0.9046 (5)	1.0622 (2)
As1	0.6122 (4)	0.3558 (4)	1.1208 (1)
Cu1	0.3880 (6)	0.2593 (6)	0.9792 (2)
Cu2	0.2607 (6)	0.1692 (6)	1.0310 (2)
O1	0.6308 (27)	0.5752 (31)	1.0927 (9)
C11	0.5571 (42)	0.2306 (38)	1.1358 (12)
C12	0.5917 (42)	0.1688 (45)	1.1704 (15)
C13	0.5689 (63)	0.0782 (53)	1.1887 (27)
C14	0.4830 (44)	0.0254 (40)	1.1599 (14)
C15	0.4459 (41)	0.0693 (44)	1.1252 (13)
C16	0.4835 (42)	0.1727 (46)	1.1160 (16)
C21	0.7146 (43)	0.3159 (43)	1.0807 (16)
C22	0.8089 (43)	0.2743 (45)	1.0951 (16)
C23	0.8876 (68)	0.2599 (61)	1.0764 (23)
C24	0.8677 (60)	0.2942 (52)	1.0370 (18)
C25	0.7732 (61)	0.3481 (52)	1.0237 (23)
C26	0.7025 (68)	0.3639 (44)	1.0511 (24)

TABLE 31 (Continued)

C31	0.6795 (53)	0.4350 (44)	1.1570 (17)
C32	0.7805 (41)	0.4639 (40)	1.1526 (15)
C33	0.8231 (37)	0.5223 (37)	1.1881 (12)
C34	0.7768 (41)	0.5399 (43)	1.2207 (16)
C35	0.6735 (62)	0.5057 (55)	1.2254 (18)
C36	0.6294 (42)	0.4544 (43)	1.1962 (15)
C41	0.4986 (47)	0.4321 (57)	1.0994 (20)
C42	0.5342 (38)	0.5509 (45)	1.0924 (12)
C43	0.4530 (40)	0.6315 (50)	1.0839 (12)
C44	0.3480 (47)	0.6118 (37)	1.0854 (13)
C45	0.2637 (40)	0.6926 (32)	1.0748 (12)
C46	0.3000 (37)	0.7901 (38)	1.0730 (13)
C47	0.4057 (56)	0.8226 (43)	1.0705 (14)
C48	0.4864 (43)	0.7394 (41)	1.0813 (14)
H11	0.6540	0.2094	1.1812
H12	0.5871	0.0547	1.2137
H13	0.4570	-0.0437	1.1680
H14	0.3982	0.0224	1.1090
H15	0.4567	0.2037	1.0928
H21	0.8088	0.2486	1.1206
H22	0.9649	0.2348	1.0725
H23	0.6354	0.4021	1.0487
H24	0.9452	0.2524	1.0407
H25	0.7506	0.3816	1.0002

TABLE 31 (Continued)

H31	0.8229	0.4501	1.1306
H32	0.8938	0.5572	1.1843
H33	0.8243	0.5670	1.2419
H34	0.6371	0.5282	1.2468
H35	0.5565	0.4198	1.2006
H41	0.3240	0.5407	1.0935
H42	0.2361	0.7569	1.0618
H44	0.3889	0.8927	1.0591
H45	0.5633	0.7618	1.0872
H411	0.4720	0.3931	1.0772
H412	0.4309	0.4272	1.1155

TABLE 32

THERMAL PARAMETERS FOR BIS (PARABROMO PHENACYL-TRIPHENYLARSONIUM) HEXABROMOTETRACUPRATE (I)

ATOM	U11	U22	U33	U12	U13	U23
Br1	56.(5)	56.	83.(7)	-7.(5)	-25.(7)	25.
Br2	38.(5)	38.	38.	-12.(4)	1.(5)	-1.
Br3	56.(4)	69.(4)	55.(4)	27.(4)	-11.(3)	12.(4)
Br4	70.(4)	45.(4)	51.(4)	9.(3)	-1.(3)	-2.(3)
Br5	59.(4)	61.(4)	99.(5)	-23.(4)	9.(4)	-33.(4)
As1	26.(3)	33.(3)	38.(3)	-2.(3)	-8.(3)	0.(2)
Cu1	48.(4)	66.(5)	50.(5)	8.(4)	12.(4)	1.(4)
Cu2	57.(5)	56.(5)	47.(5)	-2.(4)	-6.(4)	2.(4)
O1	49.(27)	97.(32)	63.(29)	-5.(24)	-47.(22)	45.(25)
C11	77.(40)	37.(34)	7.(31)	20.(32)	-10.(29)	-15.(26)
C12	31.(37)	47.(40)	47.(42)	-1.(32)	-36.(30)	-12.(33)
C13	105.(69)	42.(53)	279.(23)	-37.(50)	-34.(75)	-76.(68)
C14	56.(42)	33.(37)	36.(40)	-7.(31)	38.(32)	10.(29)
C15	48.(38)	60.(41)	5.(31)	9.(33)	-1.(29)	16.(30)
C16	23.(35)	58.(45)	86.(54)	33.(33)	3.(35)	-25.(42)
C21	34.(40)	30.(36)	67.(48)	-15.(32)	15.(35)	29.(34)
C22	14.(35)	35.(37)	74.(49)	20.(29)	2.(34)	-18.(34)
C23	110.(76)	126.(72)	116.(81)	98.(63)	-11.(63)	6.(58)
C24	94.(59)	63.(48)	57.(52)	-24.(46)	73.(47)	-21.(40)
C25	88.(61)	48.(49)	173.(87)	-2.(46)	122.(65)	-16.(50)

TABLE 32 (Continued)

C26	168.(86)	10.(40)	156.(86)	23.(45)	74.(72)	39.(46)
C31	84.(56)	31.(39)	82.(53)	6.(39)	1.(44)	50.(36)
C32	12.(33)	33.(37)	76.(50)	9.(30)	26.(32)	-11.(32)
C33	28.(33)	49.(36)	15.(30)	7.(27)	-18.(26)	2.(27)
C34	16.(34)	55.(42)	105.(56)	-2.(32)	37.(36)	16.(38)
C35	140.(74)	103.(61)	66.(58)	33.(54)	26.(54)	-68.(50)
C36	33.(40)	52.(38)	46.(41)	30.(32)	35.(34)	32.(32)
C41	30.(42)	97.(63)	169.(81)	54.(42)	-17.(47)	-25.(58)
C42	27.(35)	58.(41)	4.(30)	-6.(31)	-9.(24)	5.(28)
C43	11.(33)	86.(52)	6.(32)	4.(37)	-6.(25)	8.(32)
C44	76.(45)	8.(29)	34.(36)	7.(32)	30.(32)	14.(27)
C45	73.(40)	5.(26)	21.(33)	-8.(27)	23.(29)	4.(22)
C46	28.(33)	36.(35)	56.(42)	-22.(29)	16.(29)	17.(31)
C47	167.(71)	42.(40)	46.(45)	-11.(45)	55.(46)	30.(34)
C48	59.(43)	20.(36)	52.(44)	14.(33)	-4.(32)	26.(32)

Anisotropic parameters are in the form:

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

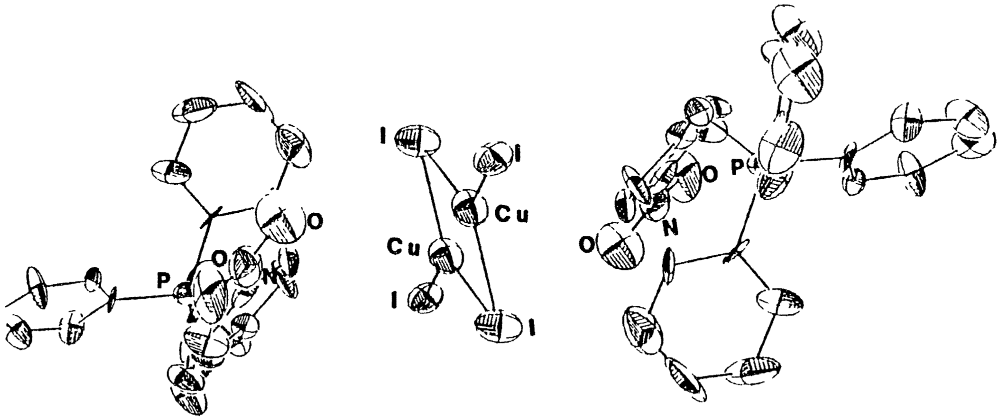


Figure 24. Bis(Paranitrobenzyltriphenylphosphonium) Tetraiododicuprate.

TABLE 33

CRYSTAL DATA FOR BIS (PARANITROBENZYLTRIPHENYL PHOSPHONIUM) TETRAIODODICUPRATE (I)

Formula	$C_{50}H_{42}N_2O_4P_2Cu_2I_4$
MWT	1431.5 g mole^{-1}
a	12.329 (9) Å
b	12.84 (1)
c	16.53 (1)
α	90.0°
β	96.62 (6)
γ	90.0
V	2600. (3) Å^3
F(000)	1376
μKoKα	32.73 Å^{-1}
λMoKα	0.71069 Å
D_{calc}	1.828 g cm^3
Z	2
Obs. refl.	1786
R	8.6
R_w	11.4
Space group	$P2_1/n$ (Monoclinic)
Octants meas.	±h, +k, +l

TABLE 34

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR BIS (PARANITROBENZYL TRIPHENYLPHOSPHONIUM) TETRAIODODICUPRATE (I)

I1-Cu1	2.574(5)	Cu-I1-Cu1'	64.9(1)
I1-Cu1'	2.564(5)	I1-Cu1-I2	123.3(2)
I2-Cu1	2.517(5)	I1-Cu1-I1'	115.1(2)
P1-C11	1.79(3)	I2-Cu1-I1'	121.6(2)
P1-C21	1.79(3)	C11-P1-C21	110.(1)
P1-C31	1.77(3)	C11-P1-C31	110.(1)
P1-C40	1.83(3)	C11-P1-C40	109.(1)
O1-N1	1.21(4)	C21-P1-C31	112.(1)
O1-N1	1.22(5)	C21-P1-C40	109.(1)
N1-C44	1.49(5)	C31-P1-C40	107.(1)
C11-C12	1.37(4)	O1-N1-O2	124.(3)
C11-C16	1.43(4)	01-N1-C44	118.(3)
C12-C13	1.34(4)	O2-N1-C44	118.(3)
C13-C14	1.35(5)	P1-C11-C12	120.(2)
C14-C15	1.42(5)	P1-C11-C16	120.(2)
C15-C16	1.30(4)	C12-C11-C16	119.(2)
C21-C22	1.36(5)	C11-C12-C13	117.(3)
C21-C26	1.38(4)	C12-C13-C14	126.(3)
C22-C23	1.45(5)	C13-C14-C15	116.(3)
C23-C24	1.37(7)	C14-C15-C16	122.(3)
C24-C25	1.31(7)	C11-C16-C15	120.(3)
C25-C26	1.36(6)	P1-C21-C22	121.(2)

TABLE 34 (Continued)

C31-C32	1.41(5)	P1-C21-C26	119.(2)
C31-C36	1.45(4)	C22-C21-C26	120.(3)
C32-C33	1.34(5)	C21-C22-C23	117.(3)
C33-C34	1.37(6)	C22-C23-C24	118.(4)
C34-C35	1.37(7)	C23-C24-C25	125.(4)
C35-C36	1.35(5)	C24-C25-C26	117.(4)
C40-C41	1.47(4)	C21-C26-C25	123.(3)
C41-C42	1.46(4)	P1-C31-C32	124.(2)
C41-C46	1.37(5)	P1-C31-C36	120.(2)
C42-C43	1.27(5)	C32-C31-C36	116.(3)
C43-C44	1.39(5)	C31-C32-C33	121.(3)
C44-C45	1.45(4)	C32-C33-C43	124.(4)
C45-C46	1.34(5)	C33-C34-C35	116.(4)
Cu1-Cu1'	2.755(6)	C34-C35-C36	124.(3)
		C31-C36-C35	119.(3)
		P1-C40-C41	116.(2)
		C40-C41-C42	121.(3)
		C40-C41-CC46	124.(3)
		C42-C41-C46	115.(3)
		C41-C42-C43	126.(3)
		C42-C43-C44	117.(3)
		C43-C44-C45	122.(3)
		N1-C44-C43	120.(3)
		N1-C44-C45	118.(3)

TABLE 34 (Continued)

	C44-C45-C46	117.(3)
	C41-C46-C45	124.(3)

TABLE 35

POSITIONAL PARAMETERS FOR BIS (PARANITROBENZYLTRIPHENYL PHOSPHONIUM) TETRAIODO DICUPRATE (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	-0.1647 (2)	0.9645 (2)	0.9464 (1)
I2	0.0774 (2)	1.0903 (2)	0.7892 (1)
Cu1	0.0264 (4)	1.0323 (3)	0.9252 (2)
P1	0.0578 (6)	0.7118 (6)	0.6699 (5)
O1	0.1276 (26)	0.5085 (18)	1.0839 (17)
O2	0.0029 (26)	0.6233 (22)	1.0929 (17)
N1	0.0761 (26)	0.5840 (28)	1.0590 (17)
C11	0.0703 (22)	0.5738 (19)	0.6599 (19)
C12	0.1105 (24)	0.5329 (22)	0.5930 (16)
C13	0.1191 (27)	0.4289 (23)	0.5890 (20)
C14	0.0980 (26)	0.3600 (26)	0.6469 (26)
C15	0.0608 (28)	0.4036 (22)	0.7174 (18)
C16	0.0462 (21)	0.5033 (20)	0.7243 (17)
C21	-0.0770 (22)	0.7435 (22)	0.6925 (20)
C22	-0.1568 (25)	0.6702 (31)	0.6869 (24)
C23	-0.2639 (25)	0.7041 (32)	0.7042 (28)
C24	-0.2774 (37)	0.8065 (42)	0.7231 (27)
C25	-0.1999 (37)	0.8767 (36)	0.7290 (23)
C26	-0.0994 (25)	0.8450 (23)	0.7131 (20)
C31	0.0901 (24)	0.7734 (21)	0.5799 (18)
C32	0.1955 (28)	0.7746 (26)	0.5552 (23)

TABLE 35 (Continued)

C33	0.2138 (35)	0.8204 (28)	0.4850 (22)
C34	0.1342 (41)	0.8674 (27)	0.4328 (25)
C35	0.0327 (35)	0.8716 (25)	0.4584 (21)
C36	0.0053 (27)	0.8227 (25)	0.5251 (17)
C40	0.1564 (23)	0.7575 (22)	0.7535 (20)
C41	0.1387 (21)	0.7203 (22)	0.8351 (17)
C42	0.1960 (24)	0.6295 (24)	0.8714 (22)
C43	0.1804 (26)	0.5875 (28)	0.9387 (18)
C44	0.1021 (26)	0.6323 (25)	0.9818 (19)
C45	0.0443 (26)	0.7259 (25)	0.9536 (22)
C46	0.0648 (29)	0.7639 (24)	0.8814 (22)
H11	0.1328	0.5801	0.5493
H12	0.1434	0.3994	0.5383
H13	0.1071	0.2835	0.6411
H14	0.0470	0.3563	0.7628
H15	0.0178	0.5306	0.7741
H21	-0.1423	0.5947	0.6703
H22	-0.3255	0.6528	0.7048
H23	-0.3530	0.8291	0.7336
H24	-0.2179	0.9505	0.7423
H25	-0.0373	0.8959	0.7180
H31	0.2599	0.7433	0.5930
H32	0.2889	0.8213	0.4678
H33	0.1492	0.8962	0.3787

TABLE 35 (Continued)

H34	-0.0262	0.9120	0.4246
H35	-0.0732	0.8247	0.5387
H41	0.2535	0.5982	0.8410
H42	0.2204	0.5235	0.9596
H44	-0.0069	0.7601	0.9872
H45	0.0244	0.8272	0.8591
H401	0.2304	0.7389	0.7419
H402	0.1542	0.8357	0.7538

TABLE 36

THERMAL PARAMETERS FOR BIS (PARANITRO BENZYLTRIPHENYL PHOSPHONIUM TETRAIODO DICUPRATE (I)

ATOM	U11	U22	U33	U12	U13	U23
I1	52.(1)	94.(1)	60.(1)	2.(1)	19.(1)	13.(1)
I2	51.(1)	57.(1)	55.(1)	-15.(1)	14.(1)	7.(1)
Cu1	69.(2)	53.(2)	61.(2)	0.(2)	23.(2)	2.(2)
P1	29.(4)	40.(5)	56.(5)	-2.(3)	9.(4)	4.(4)
O1	142.(28)	20.(13)	120.(24)	-1.(15)	36.(20)	14.(15)
O2	123.(26)	97.(24)	85.(20)	11.(19)	32.(19)	15.(17)
N1	80.(23)	71.(23)	55.(19)	-12.(20)	19.(17)	-26.(18)
C11	34.(17)	12.(16)	76.(22)	-5.(13)	-8.(16)	-24.(15)
C12	66.(21)	32.(16)	29.(16)	-14.(16)	17.(15)	3.(14)
C13	69.(24)	37.(21)	58.(22)	17.(16)	31.(19)	21.(17)
C14	37.(20)	40.(22)	120.(33)	20.(17)	-17.(22)	0.(23)
C15	93.(27)	15.(18)	44.(18)	-20.(17)	21.(18)	5.(15)
C16	31.(16)	11.(16)	48.(18)	-4.(12)	9.(14)	-3.(13)
C21	24.(17)	34.(19)	88.(26)	-26.(15)	4.(17)	-26.(17)
C22	35.(20)	97.(32)	103.(30)	-2.(21)	29.(20)	-20.(25)
C23	32.(21)	71.(30)	146.(38)	-11.(19)	8.(23)	28.(28)
C24	80.(33)	121.(44)	96.(33)	70.(30)	5.(27)	-50.(31)
C25	94.(33)	98.(38)	47.(23)	29.(26)	5.(23)	-26.(23)
C26	61.(22)	34.(19)	83.(24)	-18.(16)	26.(19)	-47.(18)
C31	49.(19)	29.(17)	45.(18)	-18.(15)	-7.(16)	-24.(15)

TABLE 36 (Continued)

C32	58.(23)	46.(22)	119.(32)	8.(18)	52.(23)	24.(21)
C33	122.(34)	58.(25)	69.(25)	28.(24)	61.(25)	22.(21)
C34	136.(39)	30.(22)	96.(31)	2.(23)	53.(31)	32.(21)
C35	98.(30)	46.(23)	54.(22)	-12.(20)	-3.(22)	19.(17)
C36	81.(26)	60.(24)	24.(16)	-31.(19)	-2.(18)	-4.(16)
C40	35.(18)	33.(19)	68.(22)	2.(14)	7.(16)	-10.(16)
C41	25.(16)	32.(17)	41.(17)	10.(13)	-18.(13)	5.(13)
C42	33.(18)	52.(22)	93.(27)	-9.(16)	41.(18)	-11.(20)
C43	54.(21)	89.(26)	29.(17)	13.(20)	18.(16)	17.(18)
C44	50.(21)	44.(21)	54.(20)	-23.(17)	-15.(17)	-12.(17)
C45	54.(21)	37.(19)	72.(24)	7.(17)	-1.(19)	-32.(18)
C46	83.(25)	32.(20)	77.(25)	9.(17)	61.(22)	-9.(18)

Anisotropic parameters are in the form:

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

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

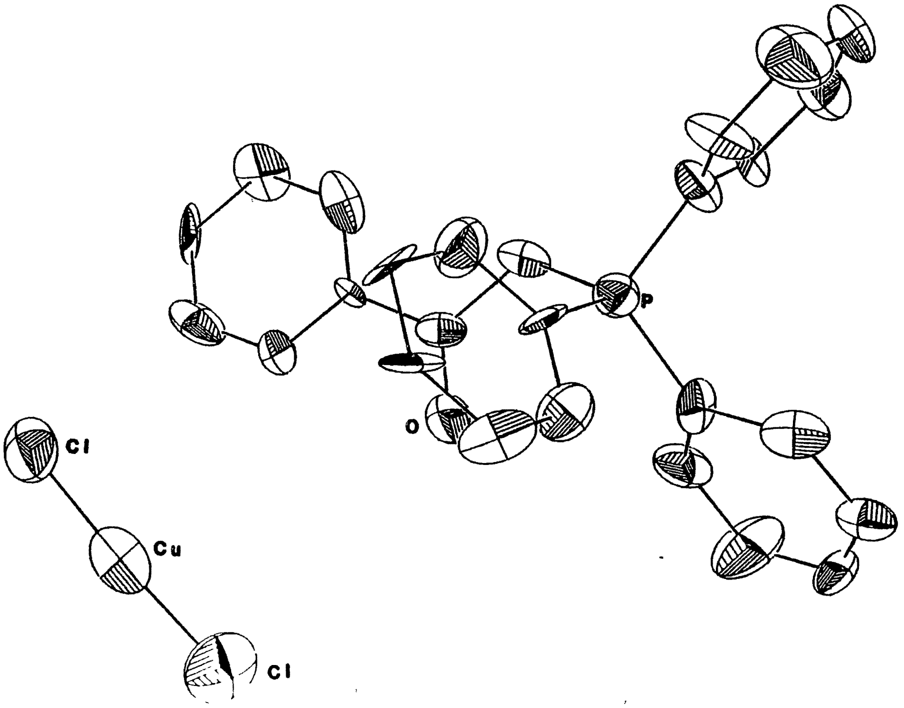


Figure 25. Phenacyltriphenylphosphonium Dichlorocuprate.

TABLE 37

CRYSTAL DATA FOR PHENACYLTRIPHENYL PHOSPHONIUM DICHLOROCUPRATE (I)

Formula	$C_{26}H_{22}OPCl_2$
MWT	515.9 g mole^{-1}
a	10.884 (3) Å
b	18.495 (4)
c	23.562 (9)
α	90.0°
β	90.0
γ	90.0
V	4742.(2) Å^{3}
F(000)	2112
μMoK_{α}	12.32 cm^{-1}
λMoK_{α}	0.71069 Å
D_{calc}	1.445 g cm^{-3}
Z	8
Obs. refl.	866
R	6.4
R_w	6.6
Space group	Pbca (Orthorhombic), #61
Octants meas.	+h, +k, +l

TABLE 38

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR PHENACYLTRIPHENYL PHOSPHONIUM DICHLOROCUPRATE (I)

Cu1-Cl1	2.095(8)	Cl1-Cu1-Cu2	175.0(4)
Cu1-Cl2	2.086(9)	C11-P1-C21	112.4(9)
P1-C11	1.77(2)	C11-P1-C31	110.5(9)
P1-C21	1.76(2)	C11-P1-C41	106.1(9)
P1-C31	1.78(2)	C21-P1-C31	109.(1)
P1-C41	1.79(2)	C21-P1-C41	113.(1)
C11-C12	1.37(3)	C31-P1-C41	106.(1)
C11-C16	1.36(3)	P1-C11-C12	121.(2)
C12-C13	1.41(3)	P1-C11-C16	122.(1)
C13-C14	1.33(3)	C12-C11-C16	117.(2)
C14-C15	1.30(3)	C11-C12-C13	123.(2)
C15-C16	1.40(3)	C12-C13-C14	115.(2)
C21-C22	1.36(3)	C13-C14-C15	127.(2)
C21-C26	1.46(3)	C14-C15-C16	118.(2)
C22-C23	1.34(3)	C11-C16-C15	121.(2)
C23-C24	1.35(3)	P1-C21-C22	129.(2)
C24-C25	1.30(3)	P1-C21-C26	115.(2)
C25-C26	1.37(3)	C22-C21-C26	116.(2)
C31-C32	1.40(3)	C21-C22-C23	122.(2)
C31-C36	1.35(3)	C22-C23-C24	118.(2)
C32-C33	1.33(3)	C23-C24-C25	126.(2)
C33-C34	1.38(4)	C24-C25-C26	118.(2)

TABLE 38 (Continued)

C34-C35	1.39(4)	C21-C26-C25	120.(2)
C35-C36	1.37(4)	P1-C31-C32	116.(2)
C41-C42	1.51(3)	P1-C31-C36	123.(2)
01-C42	1.21(3)	C32-C31-C36	120.(2)
C42-C43	1.49(3)	C31-C32-C33	122.(2)
C43-C44	1.36(3)	C32-C33-C34	121.(2)
C43-C48	1.33(2)	C34-C35-C36	125.(3)
C44-C45	1.38(3)	C31-C36-C35	117.(2)
C45-C46	1.39(3)	P1-C41-C42	114.(1)
C46-C47	1.36(3)	01-C42-C41	121.(2)
C47-C48	1.37(3)	01-C42-C43	120.(2)
		C41-C42-C43	119.(2)
		C42-C43-C44	122.(2)
		C42-C43-C48	119.(2)
		C44-C43-C48	120.(2)
		C43-C44-C45	121.(2)
		C44-C45-C46	118.(2)
		C45-C46-C47	120.(2)
		C46-C47-C48	120.(2)
		C43-C48-C47	122.(2)

TABLE 39

POSITIONAL PARAMETERS FOR PHENACYLTRIPHENYL PHOSPHONIUM DICHLOROCUPRATE (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
Cu1	1.0461 (3)	0.2014 (2)	0.0643 (1)
Cl1	0.9105 (6)	0.2382 (4)	0.0082 (3)
Cl2	1.1744 (7)	0.1706 (4)	0.1254 (3)
P1	0.6009 (5)	-0.0585 (3)	0.3322 (2)
O1	0.7727 (14)	0.0041 (8)	0.2475 (6)
C11	0.6043 (16)	-0.1274 (10)	0.2801 (8)
C12	0.5218 (22)	-0.1274 (13)	0.2364 (9)
C13	0.5247 (19)	-0.1792 (13)	0.1924 (9)
C14	0.6133 (17)	-0.2287 (13)	0.1974 (9)
C15	0.6916 (19)	-0.2343 (10)	0.2390 (10)
C16	0.6869 (19)	-0.1823 (11)	0.2820 (9)
C21	0.7328 (21)	-0.0592 (11)	0.3757 (8)
C22	0.8264 (20)	-0.0102 (12)	0.3781 (9)
C23	0.9235 (22)	-0.0184 (13)	0.4126 (10)
C24	0.9242 (19)	-0.0763 (11)	0.4474 (8)
C25	0.8383 (19)	-0.1247 (11)	0.4518 (9)
C26	0.7409 (20)	-0.1198 (11)	0.4152 (9)
C31	0.4686 (20)	-0.0679 (11)	0.3761 (8)
C32	0.4521 (22)	-0.0155 (12)	0.4179 (9)
C33	0.3646 (22)	-0.0214 (13)	0.4573 (10)
C34	0.2854 (24)	-0.0800 (17)	0.4578 (10)
C35	0.3037 (26)	-0.1301 (16)	0.4144 (12)

TABLE 39 (Continued)

C36	0.3959 (20)	-0.1271 (12)	0.3750 (10)
C41	0.5829 (18)	0.0249 (11)	0.2945 (8)
C42	0.6747 (20)	0.0352 (12)	0.2473 (10)
C43	0.6443 (16)	0.0854 (9)	0.1998 (7)
C44	0.5385 (21)	0.1250 (10)	0.1995 (8)
C45	0.5100 (21)	0.1692 (11)	0.1543 (10)
C46	0.5929 (25)	0.1734 (12)	0.1093 (9)
C47	0.6984 (21)	0.1345 (13)	0.1109 (10)
C48	0.7213 (17)	0.0900 (11)	0.16561 (7)
H11	0.4553	-0.0889	0.2350
H12	0.4644	-0.1786	0.1608
H13	0.6198	-0.2651	0.1658
H14	0.7521	-0.2745	0.2386
H15	0.7464	-0.1859	0.3147
H21	0.8199	0.0338	0.3525
H22	0.9890	0.0192	0.4135
H23	0.9987	-0.0830	0.4721
H24	0.8402	-0.1646	0.4815
H25	0.6783	-0.1587	0.4142
H31	0.5094	0.0286	0.4191
H32	0.3527	0.0158	0.4891
H33	0.2163	-0.0849	0.4851
H34	0.2411	-0.1736	0.4118
H35	0.4112	-0.1665	0.3459

TABLE 39 (Continued)

H41	0.4802	0.1216	0.2327
H42	0.4313	0.1995	0.1537
H43	0.5761	0.2046	0.0767
H44	0.7583	0.1380	0.0789
H45	0.7967	0.0589	0.1555
H411	0.4977	0.0282	0.2777
H412	0.5869	0.0670	0.3212

TABLE 40

THERMAL PARAMETERS FOR PHENACYL TRIPHENYL PHOSPHONIUM DICHLOROCUPRATE (I)

ATOM	U11	U22	U33	U12	U13	U23
Cu1	89.(2)	56.(2)	85.(2)	-14.(2)	23.(2)	-9.(2)
Cl1	80.(5)	122.(6)	69.(4)	-31.(5)	-4.(4)	-12.(4)
Cl2	100.(6)	67.(5)	125.(6)	3.(5)	-10.(5)	35.(5)
P1	35.(3)	38.(4)	35.(3)	4.(3)	0.(3)	-3.(3)
O1	47.(11)	60.(12)	45.(9)	9.(10)	8.(9)	13.(10)
C11	15.(11)	43.(14)	43.(13)	8.(11)	-15.(11)	10.(11)
C12	70.(19)	76.(19)	44.(15)	34.(15)	-9.(15)	1.(13)
C13	29.(14)	111.(22)	40.(13)	21.(15)	-33.(13)	-13.(15)
C14	9.(11)	134.(23)	60.(14)	24.(13)	-2.(12)	-5.(16)
C15	53.(16)	11.(15)	88.(19)	24.(12)	-13.(14)	0.(14)
C16	47.(15)	42.(17)	49.(15)	-5.(13)	-14.(13)	-1.(14)
C21	55.(18)	19.(17)	36.(13)	4.(13)	0.(13)	18.(13)
C22	33.(14)	40.(18)	70.(17)	-1.(14)	13.(14)	13.(14)
C23	55.(16)	85.(20)	95.(19)	-13.(15)	-48.(16)	4.(17)
C24	40.(14)	96.(18)	29.(12)	23.(12)	-15.(11)	3.(12)
C25	25.(12)	53.(17)	54.(15)	0.(12)	2.(13)	-2.(13)
C26	29.(13)	33.(16)	65.(16)	-13.(11)	-6.(13)	-18.(13)
C31	47.(16)	39.(16)	35.(12)	4.(14)	19.(13)	2.(13)
C32	39.(15)	60.(19)	36.(13)	-27.(14)	5.(14)	34.(14)
C33	61.(18)	96.(22)	58.(18)	-22.(15)	11.(15)	20.(16)
C34	60.(22)	187.(33)	38.(14)	22.(21)	27.(15)	30.(20)

TABLE 40 (Continued)

C35	59.(22)	135.(29)	68.(20)	-35.(19)	1.(18)	-21.(20)
C36	23.(13)	78.(21)	81.(18)	-35.(13)	14.(14)	18.(15)
C41	25.(13)	39.(15)	50.(15)	0.(11)	6.(13)	-7.(12)
C42	20.(13)	27.(16)	47.(15)	-4.(11)	-2.(15)	-8.(13)
C43	21.(12)	20.(13)	17.(10)	10.(10)	8.(10)	-10.(10)
C44	76.(16)	39.(14)	47.(14)	-21.(13)	22.(14)	21.(12)
C45	83.(19)	25.(16)	69.(17)	34.(13)	15.(16)	-10.(13)
C46	88.(23)	65.(20)	12.(11)	11.(16)	-1.(15)	21.(12)
C47	32.(17)	67.(20)	65.(18)	-22.(14)	18.(14)	-20.(15)
C48	37.(14)	78.(18)	31.(12)	1.(12)	7.(12)	14.(12)

Anisotropic parameters are in the form:

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

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

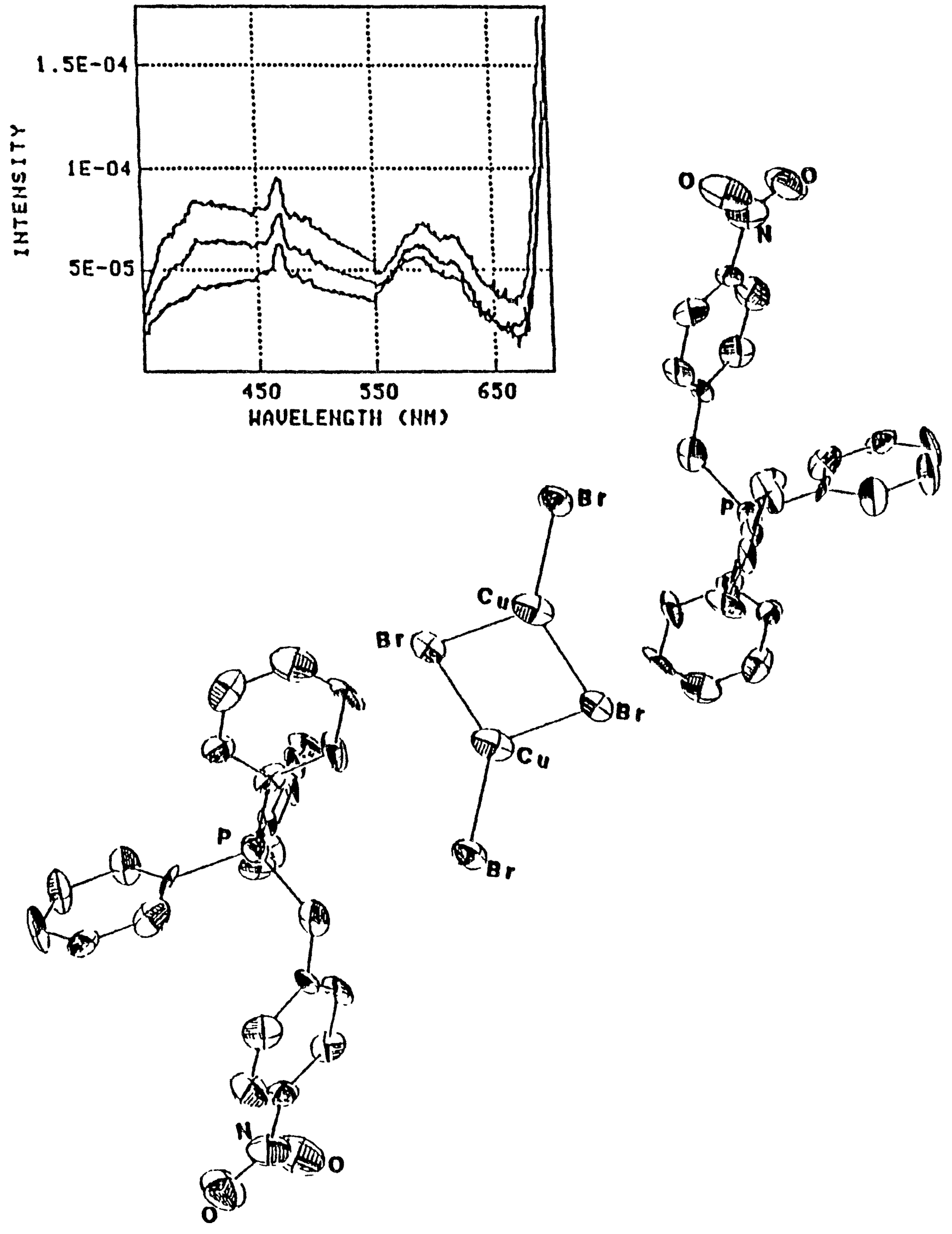


Figure 26. Bis(Paranitrobenzyltriphenylphosphonium) Tetrabromodicuprate.

TABLE 41

CRYSTAL DATA FOR BIS (PARANITROBENZYLTRIPHENYL PHOSPHONIUM) TETRABROMODICUPRATE (I)

Formula	$C_{50}H_{42}N_2O_4P_2Cu_2Br_4$
MWT	1243.5 g mole^{-1}
a	16.031 (5) Å
b	12.684 (2)
c	12.087 (3)
α	90.0°
β	96.12 (3)
γ	90.0
V	2443. (1) Å^3
F(000)	1232
μMoK$_{\alpha}$	42.20 cm^{-1}
lMoK$_{\alpha}$	0.71069 Å
D_{calc}	1.700 g cm^{-3}
Z	2
Obs. refl.	1358
R	5.6
R_w	6.7
Space group	$P2_1/n$ (Monoclinic)
Octants meas.	±h, +k, +l

TABLE 42

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR BIS (PARANITROBENZYLTRIPHENYLPHOSPHONIUM) TETRABROMODICUPRATE (I)

Br1-Cu1	2.382(3)	Cu1-Br1-Cu1'	75.4(1)
Br1-Cu1'	2.477(4)	Br1-Cu1-Br2	131.4(2)
Br2-Cu1	2.305(3)	Br1-Cu1-Br1'	104.6(1)
P1-C11	1.81(2)	Br2-Cu1-Br1'	124.0(1)
P1-C21	1.81(2)	C11-P1-C21	109.9(8)
P1-C31	1.80(2)	C11-P1-C31	109.7(8)
P1-C41	1.82(2)	C11-P1-C41	109.3(8)
O1-N1	1.23(3)	C21-P1-C31	110.9(8)
O2-N1	1.21(3)	C21-P1-C41	106.0(8)
N1-C45	1.50(3)	C31-P1-C41	110.9(8)
C11-C12	1.41(2)	O1-N1-O2	121.(2)
C11-C16	1.38(2)	O1-N1-C45	117.(2)
C12-C13	1.40(3)	O2-N1-C45	122.(2)
C13-C14	1.35(3)	P1-C11-C12	118.(1)
C14-C15	1.32(3)	P1-C11-C16	119.(1)
C15-C16	1.40(3)	C12-C11-C16	124.(2)
C21-C22	1.36(2)	C11-C12-C13	114.(2)
C21-C26	1.39(2)	C12-C13-C14	123.(2)
C22-C23	1.40(3)	C13-C14-C15	120.(2)
C23-C24	1.39(3)	C14-C15-C16	123.(2)
C24-C25	1.36(2)	C11-C16-C15	116.(2)

TABLE 42 (Continued)

C25-C26	1.36(3)	P1-C21-C22	121.(1)
C31-C32	1.43(2)	P1-C21-C26	120.(1)
C31-C36	1.38(2)	C22-C21-C26	119.(2)
C32-C33	1.37(2)	C21-C22-C23	123.(2)
C33-C34	1.37(3)	C22-C23-C24	115.(2)
C34-C35	1.39(3)	C23-C24-C25	123.(2)
C35-C36	1.38(3)	C24-C25-C26	119.(2)
C41-C42	1.51(3)	C21-C26-C25	121.(2)
C42-C43	1.40(3)	P1-C31-C32	120.(1)
C42-C47	1.33(3)	P1-C31-C-36	121.(1)
C43-C44	1.40(3)	C32-C31-C36	119.(1)
C44-C45	1.34(3)	C31-C32-C33	120.(2)
C45-C46	1.40(3)	C32-C33-C34	121.(2)
C46-C47	1.41(2)	C33-C34-C35	121.(2)
Cu1-Cu1'	2.974(4)	C34-C35-C36	119.(2)
		C31-C36-C35	121.(2)
		P1-C41-C42	115.(1)
		C41-C42-C43	116.(2)
		C41-C42-C47	123.(2)
		C43-C42-C47	121.(2)
		C42-C43-C44	119.(2)
		C43-C44-C45	117.(2)
		N1-C45-C44	119.(2)
		N1-C45-C46	114.(2)

TABLE 42 (Continued)

C44-C45-C46	127.(2)
C45-C46-C47	113.(2)
C42-C47-C46	123.(2)

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

TABLE 43

POSITIONAL PARAMETERS FOR BIS (PARANITROBENZYLTRIPHENYLPHOSPHONIUM) TETRABROMODICUPRATE (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG))
Br1	0.5516 (1)	0.0327 (2)	0.1469 (2)
Br2	0.2878 (1)	0.0859 (2)	0.0790 (2)
Cu1	0.4191 (2)	0.0361 (2)	0.0369 (2)
P1	0.3376 (3)	0.2075 (4)	0.4355 (4)
O1	0.0978 (9)	0.8675 (13)	0.4979 (13)
O2	0.0910 (9)	0.9890 (13)	0.6176 (15)
N1	-0.0633 (10)	0.0911 (16)	0.4271 (17)
C11	0.3144 (9)	0.2430 (13)	0.5744 (13)
C12	0.2861 (12)	0.3462 (15)	0.5907 (17)
C13	0.2661 (11)	0.3666 (18)	0.6991 (19)
C14	0.2762 (15)	0.2949 (24)	0.7821 (17)
C15	0.3058 (14)	0.2007 (18)	0.7628 (16)
C16	0.3261 (12)	0.1688 (14)	0.6578 (15)
C21	0.4314 (10)	0.2759 (12)	0.4025 (14)
C22	0.4797 (10)	0.3309 (15)	0.4818 (15)
C23	0.5548 (12)	0.3809 (16)	0.4620 (16)
C24	0.5774 (11)	0.3687 (16)	0.3547 (18)
C25	0.5300 (11)	0.3153 (16)	0.2731 (16)
C26	0.4566 (12)	0.2699 (15)	0.2962 (15)
C31	0.3506 (10)	0.0673 (12)	0.4266 (13)
C32	0.2844 (11)	-0.0009 (13)	0.4519 (16)

TABLE 43 (Continued)

C33	0.2920 (11)	-0.1076 (12)	0.4384 (15)
C34	0.3623 (11)	-0.1494 (14)	0.3995 (13)
C35	0.4251 (11)	-0.0837 (15)	0.3676 (16)
C36	0.4183 (11)	0.0242 (15)	0.3809 (14)
C41	0.2527 (11)	0.2532 (14)	0.3342 (15)
C42	0.1670 (10)	0.2105 (15)	0.3510 (14)
C43	0.1202 (12)	0.2695 (15)	0.4204 (17)
C44	0.0429 (13)	0.2303 (15)	0.4464 (17)
C45	0.0168 (10)	0.1396 (16)	0.3983 (15)
C46	0.0584 (10)	0.0788 (14)	0.3245 (16)
C47	0.1363 (11)	0.1215 (15)	0.3039 (15)
H11	0.2793	0.3987	0.5275
H12	0.2431	0.4393	0.7121
H13	0.2618	0.3206	0.8574
H14	0.3105	0.1515	0.8281
H15	0.3490	0.0959	0.6451
H21	0.4612	0.3358	0.5587
H22	0.5895	0.4242	0.5208
H23	0.6318	0.4004	0.3370
H24	0.5485	0.3090	0.1974
H25	0.4196	0.2316	0.2360
H31	0.2319	0.0291	0.4807
H32	0.2460	-0.1565	0.4587
H33	0.3670	-0.2282	0.3920

TABLE 43 (Continued)

H34	0.4750	-0.1141	0.3369
H35	0.4634	0.0736	0.3584
H41	0.1424	0.3394	0.4509
H42	0.0074	0.2671	0.4991
H44	0.0345	0.0132	0.2894
H45	0.1709	0.0820	0.2538
H411	0.2515	0.3326	0.3366
H412	0.2666	0.2359	0.2583

TABLE 44

THERMAL PARAMETERS FOR BIS (PARANITROBENZYLTRIPHENYL PHOSPHONIUM) TETRABROMODICUPRATE (I)

ATOM	U11	U22	U33	U12	U13	U23
Br1	48.(1)	79.(1)	52.(1)	6.(1)	16.(1)	-2.(1)
Br2	44.(1)	73.(1)	58.(1)	12.(1)	14.(1)	-18.(1)
Cu1	52.(1)	54.(1)	85.(2)	7.(1)	27.(1)	9.(1)
P1	33.(2)	41.(3)	32.(3)	-4.(2)	9.(2)	-2.(2)
O1	57.(10)	100.(14)	88.(12)	-18.(9)	34.(9)	-6.(11)
O2	67.(11)	66.(12)	128.(16)	-10.(9)	44.(11)	-3.(11)
N1	46.(12)	46.(13)	89.(16)	12.(10)	9.(11)	0.(12)
C11	30.(10)	32.(11)	13.(9)	-5.(8)	-14.(8)	10.(9)
C12	55.(13)	36.(13)	58.(15)	-5.(11)	-12.(11)	-10.(13)
C13	30.(11)	80.(19)	45.(14)	9.(11)	-12.(11)	-27.(14)
C14	88.(18)	116.(24)	19.(13)	0.(18)	26.(13)	-8.(17)
C15	89.(17)	55.(16)	24.(13)	10.(14)	13.(12)	-6.(12)
C16	74.(14)	28.(13)	41.(13)	24.(11)	9.(11)	0.(10)
C21	32.(10)	11.(10)	44.(12)	-15.(8)	-6.(9)	9.(9)
C22	31.(11)	51.(14)	40.(12)	-7.(11)	1.(9)	17.(11)
C23	63.(15)	61.(17)	52.(15)	-9.(12)	-15.(12)	5.(12)
C24	46.(13)	73.(17)	87.(17)	-18.(11)	23.(12)	5.(14)
C25	45.(12)	73.(16)	56.(14)	-19.(12)	43.(11)	-5.(13)
C26	70.(14)	61.(15)	26.(11)	-15.(12)	22.(11)	10.(11)
C31	37.(10)	16.(12)	20.(10)	0.(8)	4.(8)	-17.(8)
C32	33.(11)	31.(13)	61.(14)	14.(9)	4.(10)	21.(10)

TABLE 44 (Continued)

C33	76.(14)	3.(10)	48.(12)	-12.(9)	28.(11)	1.(9)
C34	57.(12)	49.(13)	11.(9)	14.(10)	4.(8)	-21.(9)
C35	44.(12)	54.(14)	67.(14)	9.(11)	31.(11)	-22.(13)
C36	45.(11)	53.(13)	23.(10)	-1.(11)	16.(9)	-19.(10)
C41	63.(14)	27.(12)	42.(13)	14.(10)	9.(11)	-14.(10)
C42	27.(10)	31.(13)	28.(11)	6.(9)	11.(9)	-6.(10)
C43	50.(13)	33.(14)	67.(15)	5.(11)	5.(12)	9.(12)
C44	59.(13)	47.(15)	63.(15)	6.(12)	20.(12)	-12.(12)
C45	20.(9)	81.(16)	43.(12)	-1.(11)	7.(9)	17.(13)
C46	36.(11)	25.(11)	58.(13)	-9.(9)	-4.(10)	-17.(11)
C47	42.(12)	39.(14)	46.(13)	6.(10)	18.(10)	-27.(11)

Anisotropic parameters are in the form:

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

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

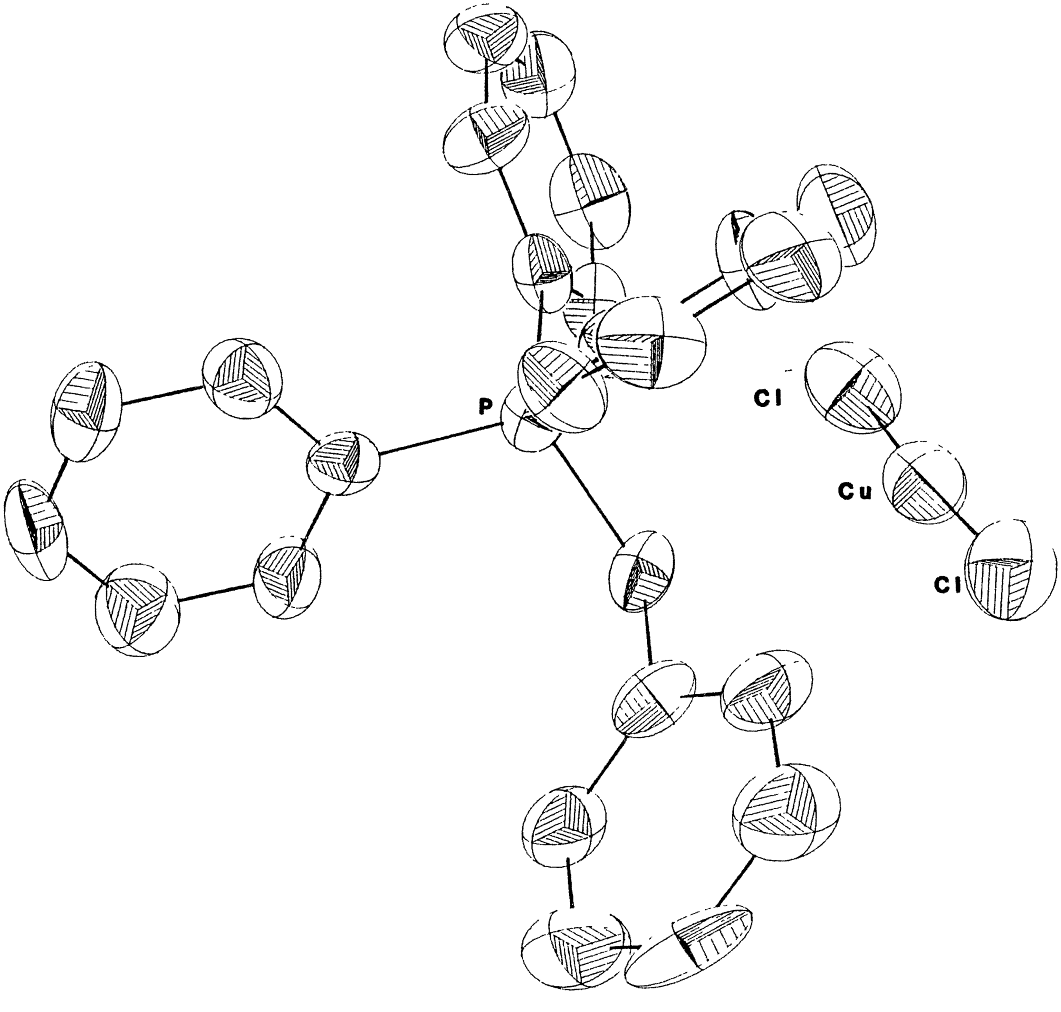


Figure 27. Benzyltriphenylphosphonium Dichlorocuprate.

TABLE 45

CRYSTAL DATA FOR BENZYLTRIPHENYL PHOSPHONIUM DICHLOROCUPRATE (I)

Formula	$C_{25}H_{22}PCuCl_2$
MWT	487.9 g mole^{-1}
$\underline{a}$	9.571 (2) Å
$\underline{b}$	14.000 (3)
$\underline{c}$	17.093 (4)
α	90.0°
β	93.29 (2)
γ	90.0
V	2286.6 (8) Å^3
F(000)	1000
μMoK_{α}	12.70 cm^{-1}
λMoK_{α}	0.71069 Å
D_{calc}	1.417 g cm^{-3}
Z	4
Obs. refl.	1826
R	6.0
R_w	7.6
Space group	$P2_1/n$ (Monoclinic)
Octants meas.	±h, +k, +l

TABLE 46

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR BENZYLTRIPHENYL PHOSPHONIUM DICHLOROCUPRATE (I)

Cu1-Cl1	2.088(3)	Cl1-Cu1-Cl2	1.75.4(2)
Cu1-Cl2	2.097(3)	C11-P1-C21	112.0(4)
P1-C11	1.792(9)	C11-P1-C31	108.0(4)
P1-C21	1.776(9)	C11-P1-C40	107.4(4)
P1-C31	1.802(9)	C21-P1-C31	107.6(4)
P1-C40	1.803(9)	C21-P1-C40	111.1(4)
C11-C12	1.39(1)	C31-P1-C40	110.6(4)
C11-C16	1.37(1)	P1-C11-C12	121.2(7)
C12-C13	1.39(1)	P1-C11-C16	118.1(7)
C13-C14	1.36(2)	C12-C11-C16	120.0(9)
C14-C15	1.39(2)	C11-C12-C13	118.5(9)
C15-C16	1.36(2)	C12-C13-C14	121.(1)
C21-C22	1.39(1)	C13-C14-C15	119.(1)
C21-C26	1.39(1)	C14-C15-C16	120.(1)
C22-C23	1.37(2)	C11-C16-C15	120.6(9)
C23-C24	1.37(2)	P1-C21-C22	119.9(7)
C24-C25	1.36(2)	P1-C21-C26	121.6(7)
C25-C26	1.38(1)	C22-C21-C26	118.3(8)
C31-C32	1.38(1)	C21-C22-C23	120.6(9)
C31-C36	1.40(1)	C22-C23-C24	121.(1)
C33-C33	1.38(1)	C23-C24-C25	120.(1)

TABLE 46 (Continued)

C33-C34	1.36(2)	C24-C25-C26	120.(1)
C34-C35	1.36(2)	C21-C26-C25	120.6(9)
C35-C36	1.39(1)	P1-C31-C32	119.1(6)
C40-C41	1.51(1)	P1-C31-C36	121.2(7)
C41-C42	1.37(1)	C32-C31-C36	119.6(8)
C41-C46	1.40(1)	C31-C32-C33	119.8(9)
C42-C43	1.35(2)	C32-C33-C34	120.2(9)
C43-C44	1.39(2)	C33-C34-C35	121.(1)
C44-C45	1.39(2)	C34-C35-C36	120.4(9)
C45-C46	1.36(2)	C31-C36-C35	118.9(9)
		P1-C40-C41	113.3(6)
		C40-C41-C42	123.4(9)
		C40-C41-C46	118.3(9)
		C42-C41-C46	118.3(9)
		C41-C42-C43	122.(1)
		C42-C43-C44	120.(1)
		C43-C44-C45	119.(1)
		C44-C45-C46	120.(1)
		C41-C46-C45	120.(1)

TABLE 47

POSITIONAL PARAMETERS FOR BENZYLTRIPHENYL PHOSPHONIUM DICHLOROCUPRATE (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
Cu1	0.4472 (1)	0.1703 (1)	0.5305 (1)
Cl1	0.5242 (3)	0.2490 (2)	0.6273 (2)
Cl2	0.3548 (3)	0.0970 (2)	0.4338 (2)
P1	0.3872 (2)	-0.0390 (2)	0.7740 (1)
C11	0.3165 (9)	0.0355 (7)	0.8472 (5)
C12	0.3569 (10)	0.0245 (7)	0.9259 (6)
C13	0.3149 (11)	0.0929 (8)	0.9784 (6)
C14	0.2369 (11)	0.1693 (8)	0.9542 (7)
C15	0.1963 (12)	0.1788 (8)	0.8753 (7)
C16	0.2369 (11)	0.1128 (7)	0.8228 (5)
C21	0.4390 (8)	-0.1525 (6)	0 8119 (5)
C22	0.5510 (10)	-0.1998 (7)	0.7818 (6)
C23	0.5861 (11)	-0.2903 (8)	0.8062 (7)
C24	0.5105 (13)	-0.3359 (7)	0.8608 (7)
C25	0.3979 (12)	-0.2915 (8)	0.8902 (6)
C26	0.3622 (10)	-0.1998 (7)	0.8662 (5)
C31	0.2523 (10)	-0.0584 (6)	0.6977 (5)
C32	0.1234 (10)	-0.0925 (7)	0.7176 (5)
C33	0.0218 (9)	-0.1128 (7)	0.6598 (6)
C34	0.0474 (12)	-0.0991 (8)	0.5831 (7)
C35	0.1734 (13)	-0 0660 (8)	0.5622 (5)

TABLE 47 (Continued)

C36	0.2783 (10)	-0.0451 (7)	0.6188 (6)
C40	0.5334 (9)	0.0237 (6)	0.7361 (5)
C41	0.6446 (10)	0.0501 (7)	0.7985 (5)
C42	0.7644 (11)	-0.0024 (7)	0.8137 (6)
C43	0.8616 (12)	0.0233 (9)	0.8705 (8)
C44	0.8428 (12)	0.1053 (10)	0.9143 (6)
C45	0.7324 (13)	0.1600 (9)	0.8993 (7)
C46	0.6256 (10)	0.1330 (8)	0.8426 (6)
H11	0.4155	-0.0311	0.9441
H12	0.3428	0.0849	1.0365
H13	0.2065	0.2175	0.9922
H14	0.1378	0.2350	0.8577
H15	0.2097	0.1206	0.7667
H21	0.6047	-0.1676	0.7405
H22	0.6683	-0.3231	0.7831
H23	0.5368	-0.4012	0.8786
H24	0.3415	-0.3249	0.9304
H25	0.2792	-0.1672	0.8882
H31	0.1042	-0.1014	0.7735
H32	-0.0717	-0.1364	0.6749
H33	-0.0268	-0.1142	0.5412
H34	0.1925	-0.0585	0.5060

TABLE 47 (Continued)

H35	0.3696	-0.0205	0.6037
H41	0.7808	-0.0602	0.7821
H42	0.9453	-0.0184	0.8829
H43	0.9153	0.1257	0.9547
H44	0.7095	0.2201	0.9307
H45	0.5382	0.1712	0.8332
H401	0.5765	-0.0165	0.6968
H402	0.5002	0.0822	0.7095

TABLE 48

THERMAL PARAMETERS FOR
BENZYLTRIPHENYL PHOSPHONIUM DICHLOROCUPRATE (I)

ATOM	U11	U22	U33	U12	U13	U23
Cu1	69.5(9)	79.(1)	70.(1)	9.7(8)	18.1(7)	16.9(8)
Cl1	95.(2)	82.(2)	92.(2)	-2.(1)	6.(1)	8.(1)
Cl2	90.(2)	104.(2)	73.(2)	23.(2)	14.(1)	-3.(1)
P1	47.(1)	39.(1)	30.(1)	-4.(1)	0.(1)	2.(1)
C11	39.(5)	49.(6)	42.(5)	-7.(4)	-10.(4)	2.(4)
C12	60.(6)	59.(7)	47.(6)	15.(5)	0.(5)	-5.(5)
C13	59.(6)	78.(8)	54.(6)	2.(6)	6.(5)	-22.(6)
C14	60.(7)	59.(7)	99.(9)	14.(6)	26.(6)	-38.(7)
C15	78.(8)	48.(6)	84.(8)	15.(6)	-8.(7)	2.(6)
C16	79.(7)	36.(5)	43.(5)	16.(5)	-7.(5)	-3.(5)
C21	35.(5)	41.(5)	39.(5)	-4.(4)	-3.(4)	-8.(4)
C22	57.(6)	44.(6)	66.(7)	0.(5)	18.(5)	13.(5)
C23	72.(7)	57.(7)	77.(8)	8.(6)	13.(6)	-2.(6)
C24	84.(7)	32.(7)	72.(7)	16.(6)	-11.(6)	5.(5)
C25	81.(8)	49.(6)	49.(6)	-10.(6)	1.(5)	14.(5)
C26	51.(6)	57.(7)	49.(6)	6.(5)	5.(5)	8.(5)
C31	57.(6)	32.(5)	32.(4)	5.(4)	-15.(4)	-1.(4)
C32	51.(6)	69.(7)	44 (6)	-15.(5)	7.(4)	2.(5)
C33	44.(6)	61.(7)	70.(7)	-10.(5)	-8.(5)	-10.(6)
C34	72.(7)	54.(7)	61.(7)	-6.(6)	-20.(6)	-4.(6)
C35	93.(9)	70.(8)	32.(5)	13.(7)	-13.(5)	0.(5)

TABLE 48 (Continued)

C36	63.(6)	39.(5)	48.(5)	0.(5)	5.(5)	2.(4)
C40	57.(6)	34.(5)	45.(5)	-7.(4)	14.(4)	-4.(4)
C41	49.(6)	58.(6)	40.(5)	-19.(5)	17.(4)	0.(5)
C42	52.(6)	47.(6)	89.(8)	-6.(5)	11.(6)	-20.(6)
C43	57.(7)	88.(9)	103.(9)	-9.(7)	-21.(6)	-11.(8)
C44	58.(7)	113.(11)	69.(7)	-56.(7)	-8.(6)	-22.(7)
C45	69.(7)	76.(9)	96.(9)	-7.(7)	5.(7)	-28.(7)
C46	52.(6)	62.(7)	73.(7)	-17.(5)	-1.(5)	-9.(6)

Anisotropic parameters are in the form:

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

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

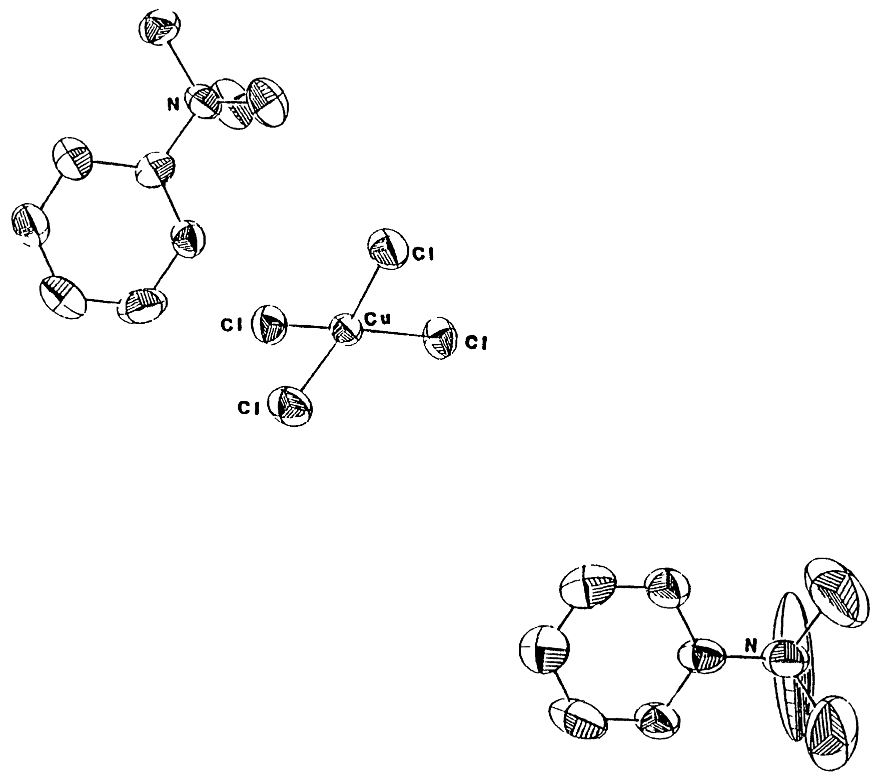


Figure 28 Bis(Trimethylphenylammonium) Tetrachlorocuprate

TABLE 49

CRYSTAL DATA FOR BIS (TRIMETHYLPHENYL AMMONIUM) TETRACHLOROCUPRATE (II)

Formula	$C_{18}H_{28}N_2CuCl_4$
MWT	477.8 g mole^{-1}
a	9.369 (2) Å
b	8.985 (2)
c	9.124 (2)
α	115.10(1)°
β	124.25 (1)
γ	85.96 (2)
V	560.3 Å^3
F(000)	247
μMoK_α	14.62 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.416 g cm^{-3}
Z	1
Obs. refl.	1315
R	5.3
R_w	7.0
Space group	P1 (Triclinic)
Ocatants meas.	±h, +k, +l

TABLE 50

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR BIS (TRIMETHYLPHENYLAMMONIUM) TETRACHLOROCUPRATE (II)

Cu1-Cl1	2.213(6)	Cl1-Cu1-Cl2	98.1(2)
Cu1-Cl2	2.259(4)	Cl1-Cu1-Cl3	99.5(2)
Cu1-Cl3	2.247(3)	Cl1-Cu1-Cl4	135.3(3)
Cu1-Cl4	2.290(5)	Cl2-Cu1-Cl3	133.9(2)
N1-C11	1.59(2)	Cl2-Cu1-Cl4	99.1(2)
N1-C21	1.47(3)	Cl3-Cu1-Cl4	97.6(2)
N1-C31	1.53(3)	C11-N1-C21	111.(1)
N1-C41	1.50(2)	C11-N1-C31	106.(1)
N2-C211	1.51(5)	C11-N1-C41	107.(1)
N2-C221	1.40(3)	C21-N1-C31	109.(2)
N2-C231	1.51(5)	C21-N1-C41	110.(1)
N2-C241	1.49(3)	C31-N1-C41	114.(1)
C41-C42	1.33(3)	C211-N2-C221	110.(3)
C41-C46	1 45(3)	C211-N2-C231	104.(3)
C42-C43	1.43(2)	C211-N2-C241	114.(2)
C43-C44	1.39(3)	C221-N2-C231	103.(3)
C44-C45	1.37(4)	C221-N2-C241	113.(2)
C45-C46	1.37(2)	C231-N2-C241	112.(2)
C241-C242	1.38(4)	N1-C41-C42	120.(2)
C241-C246	1.36(2)	N1-C41-C46	118.(2)
C242-C243	1.38(3)	C42-C41-C46	122.(1)
C243-C244	1.32(3)	C41-C42-C43	120.(2)

TABLE 50 (Continued)

C244-C245	1.38(4)	C42-C43-C44	118.(2)
C245-C246	1.38(4)	C43-C44-C45	120.(2)
		C44-C45-C46	123.(2)
		C41-C46-C45	116.(2)
		N2-C241-C242	121.(2)
		N2-C241-C246	120.(2)
		C242-C241-C246	119.(2)
		C241-C242-C243	120.(2)
		C242-C243-C244	121.(3)
		C243-C244-C245	120.(2)
		C244-C245-C246	120.(2)
		C241-C246-C245	120.(2)

TABLE 51

POSITIONAL PARAMETERS FOR BIS (TRIMETHYLPHENYL AMMONIUM TETRACHLOROCUPRATE (II)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
Cu1	0.3219	0 1430	0.3070
Cl1	0.3471 (5)	-0.0920 (5)	0.3348 (6)
Cl2	0.1694 (5)	0.0248 (5)	-0.0294 (5)
Cl3	0.5977 (5)	0.2986 (6)	0.5660 (6)
Cl4	0.1724 (6)	0.3505 (6)	0.3532 (6)
N1	0.1636 (15)	0.4403 (15)	0.8626 (17)
N2	0.6216 (17)	0.8973 (18)	0.8646 (20)
C11	0.0648 (24)	0.2605 (20)	0.6695 (25)
C21	0.1308 (25)	0.5754 (22)	0.8045 (29)
C31	0.0837 (20)	0.4580 (23)	0.9751 (21)
C41	0.3572 (19)	0.4422 (16)	0.9794 (20)
C42	0.4452 (18)	0.4386 (18)	0.9035 (20)
C43	0 6315 (23)	0.4437 (23)	0.0164 (27)
C44	0.7163 (22)	0.4564 (22)	0.2058 (29)
C45	0.6204 (23)	0.4527 (23)	0.2752 (25)
C46	0.4424 (20)	0.4484 (19)	0.1727 (23)
C211	0.4592 (46)	0.9694 (57)	0.8175 (50)
C221	0.5800 (72)	0.7446 (37)	0.7005 (38)
C231	0.7352 (37)	1.0150 (38)	0.8709 (48)
C241	0.7165 (19)	0.8854 (21)	0.0545 (22)
C242	0.6403 (22)	0.9057 (22)	0.1519 (25)
C243	0.7312 (25)	0 8960 (21)	0.3284 (26)

TABLE 51 (Continued)

C244	0.8877 (27)	0.8582 (23)	0.4016 (25)
C245	0.9660 (24)	0.8329 (30)	0.3043 (30)
C246	0.8780 (21)	0.8460 (23)	0.1295 (24)
H41	0 5620	0.4305	1.0038
H42	0.6080	0.4396	-0.1040
H43	0.8434	0.4656	0.2854
H44	0.6809	0.4540	0.4050
H45	0.3569	0.4472	0.0431
H241	0.5191	0.9266	0.0938
H242	0.6792	0 9152	0.4015
H243	0.9472	0.8446	0.5239
H244	1.0846	0.8047	0.3590
H245	0.9360	0.8277	0.0626

TABLE 52

THERMAL PARAMETERS FOR BIS (TRI-METHYLPHENYL AMMONIUM) TETRACHLOROCUPRATE (II)

ATOM	U11	U22	U33	U12	U13	U23
Cu1	39.(1)	49.(1)	37.(1)	12.(1)	22.(1)	18.(1)
Cl1	58.(2)	66.(2)	67.(2)	15.(2)	33.(2)	42.(2)
Cl2	59.(2)	58.(2)	33.(2)	11.(2)	21.(1)	16.(1)
Cl3	42.(2)	73.(2)	48.(2)	2.(1)	19.(1)	16.(2)
Cl4	65.(2)	77.(3)	53.(2)	36.(2)	40.(2)	29.(2)
N1	38.(7)	51.(7)	39.(6)	16.(5)	20.(6)	17.(5)
N2	45.(7)	78.(9)	56.(8)	12.(6)	33.(6)	27.(7)
C11	60.(10)	38.(9)	45.(9)	6.(7)	14.(8)	4.(7)
C21	74.(12)	55.(10)	83.(12)	36.(9)	43.(10)	49.(9)
C31	46 (9)	88.(12)	36.(8)	8.(8)	26.(7)	19.(8)
C41	52.(8)	33.(7)	39.(9)	5.(6)	31.(7)	7.(6)
C42	42.(8)	47.(8)	36.(7)	11.(6)	20.(6)	18.(6)
C43	63.(11)	84.(12)	70.(11)	14.(9)	51.(21)	29.(10)
C44	42.(9)	59.(11)	69.(12)	19.(8)	25.(9)	31.(9)
C45	47.(10)	69.(11)	44.(9)	16.(8)	21.(8)	28.(8)
C46	51.(10)	53.(9)	47.(8)	16.(7)	24.(8)	22.(7)
C211	156.(30)	350.(58)	163.(32)	176.(36)	125.(28)	177.(38)
C221	567.(88)	125.(25)	70.(17)	193.(41)	159.(35)	66.(18)
C231	117.(22)	151.(26)	167.(27)	-24.(19)	30.(19)	119.(23)
C241	35.(8)	66.(10)	38.(8)	-1.(7)	21.(7)	10.(7)

TABLE 52 (Continued)

C242	52.(9)	74.(11)	57.(10)	21.(8)	37.(8)	30.(8)
C243	76.(12)	60.(10)	56.(10)	8.(9)	52.(10)	5.(8)
C244	65.(12)	63.(11)	42.(9)	5.(9)	32.(9)	7.(8)
C245	39.(10)	113.(17)	58.(12)	12.(10)	26.(9)	20.(11)
C246	43.(9)	98.(14)	47.(9)	21.(9)	32.(8)	32.(9)

Anisotropic parameters are in the form:

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

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

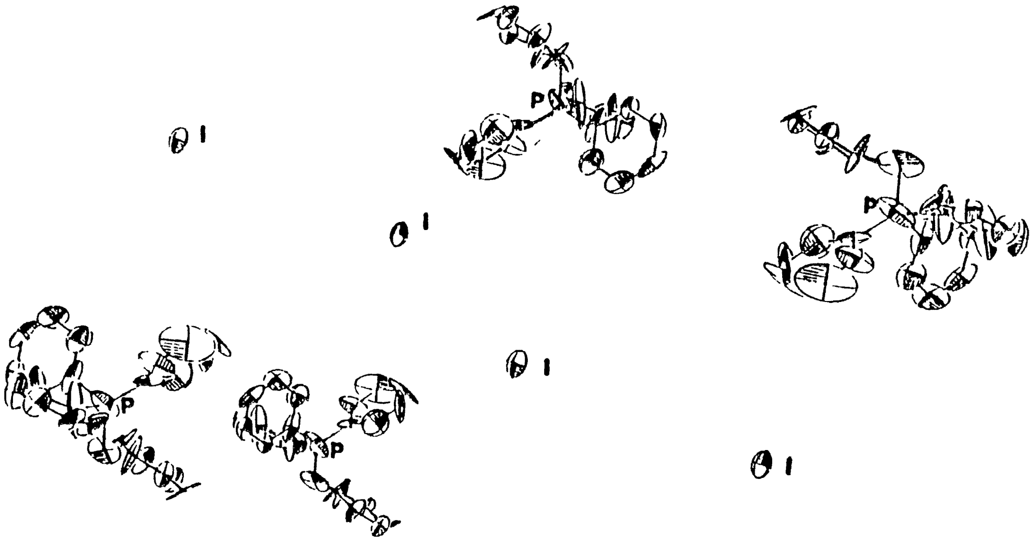


Figure 29. Packing Diagram of Benzyltriphenylphosphonium Iodide.

TABLE 53
CRYSTAL DATA FOR BENZYLTRIPHENYL PHOSPHONIUM IODIDE

Formula	$C_{25}H_{22}PI$
MWT	480.3 g mole^{-1}
a	11.718 (6) Å
b	10.440 (3)
c	18.45 (1)
α	90.0°
β	104.79 (4)
γ	90.0
V	2182. (2) Å^{3}
F(000)	960
μKoK$_{\alpha}$	15.287 cm^{-1}
λMoK$_{\alpha}$	0.71069 Å
D_{calc}	1.461 g cm^{3}
Z	4
Obs. refl.	1083
R	8.9
R_w	11.5
Space group	$P2_1/n$ (Monoclinic)
Octants meas.	+h, +k, +l

TABLE 54

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR BENZYLTRIPHENYL PHOSPHONIUM IODIDE

P1-C11	1.71(4)	C11-P1-C21	116.(2)
P1-C21	1.76(4)	C11-P1-C31	102.(2)
P1-C31	2.20(5)	C11-P1-C40	120.(2)
P1-C40	1.63(5)	C21-P1-C31	105.(2)
C11-C12	1.42(7)	C21-P1-C40	123.(3)
C11-C16	1.35(6)	C31-P1-C40	75.(3)
C12-C13	1.36(9)	P1-C11-C12	124.(4)
C13-C14	1.4(1)	P1-C11-C16	116.(3)
C14-C15	1.4(1)	C12-C11-C16	119.(5)
C15-C16	1.4(1)	C11-C12-C13	124.(6)
C21-C22	1.39(6)	C12-C13-C14	112.(7)
C21-C26	1.43(7)	C13-C14-C15	129.(7)
C22-C23	1.36(5)	C14-C15-C16	113.(6)
C23-C24	1.42(7)	C11-C16-C15	122.(5)
C24-C25	1.41(8)	P1-C21-C22	121.(4)
C25-C26	1.47(6)	P1-C21-C26	116.(3)
C31-C32	1.48(7)	C22-C21-C26	123.(4)
C31-C36	1.34(6)	C21-C22-C23	119.(4)
C32-C33	1.33(6)	C22-C23-C24	120.(4)
C33-C34	1.34(5)	C23-C24-C25	124.(4)
C34-C35	1.33(5)	C24-C25-C26	115.(4)

TABLE 54 (Continued)

C35-C36	1.43(6)	C21-C26-C25	118.(4)
C40-C41	1.89(8)	P1-C31-C32	118.(3)
C41-C42	1.30(4)	P1-C31-C36	119.(4)
C42-C46	1.52(5)	C32-C31-C36	122.(3)
C42-C43	1.44(4)	C31-C32-C33	121.(4)
C43-C44	1.47(5)	C32-C33-C34	117.(4)
C44-C45	1.29(5)	C33-C34-C35	122.(4)
C45-C46	1.43(5)	C34-C35-C36	123.(4)
		C31-C36-C35	115.(4)
		P1-C40-C41	90.(4)
		C40-C41-C42	108.(3)
		C40-C41-C46	131.(3)
		C42-C41-C46	121.(3)
		C41-C42-C43	118.(3)
		C42-C43-C44	119.(3)
		C43-C44-C45	123.(3)
		C44-C45-C46	119.(3)
		C41-C46-C45	118.(3)

TABLE 55

POSITIONAL PARAMETERS FOR BENZYL TRIPHENYL PHOSPHONIUM IODIDE

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.9432 (2)	0.1296 (3)	0.8162 (1)
P1	0.2351 (14)	0.8532 (17)	0.9697 (7)
C11	0.2750 (27)	0.8846 (38)	0.8886 (22)
C12	0.2662 (53)	0.7914 (65)	0.8342 (46)
C13	0.3027 (64)	0.7977 (111)	0.7762 (33)
C14	0.3398 (82)	0.9114 (110)	0.7610 (42)
C15	0.3640 (83)	1.0122 (60)	0.8167 (66)
C16	0.3246 (52)	0.9880 (64)	0.8749 (38)
C21	0.3291 (45)	0.7511 (34)	1.0326 (23)
C22	0.3007 (30)	0.7068 (31)	1.0966 (21)
C23	0.3752 (38)	0.6292 (43)	1.1451 (17)
C24	0.4845 (42)	0.5985 (40)	1.1304 (31)
C25	0.5162 (40)	0.6358 (55)	1.0688 (32)
C26	0.4350 (44)	0.7136 (45)	1.0189 (25)
C31	0.2572 (65)	1.0390 (44)	1.0266 (24)
C32	0.3311 (67)	1.0512 (47)	1.0993 (27)
C33	0.3569 (42)	1.1595 (37)	1.1345 (23)
C34	0.3204 (33)	1.2628 (31)	1.0960 (22)
C35	0.2474 (31)	1.2589 (40)	1.0311 (23)
C36	0.2099 (30)	1.1435 (48)	0.9927 (25)
C40	0.1047 (42)	0.8759 (76)	0.9731 (29)
C41	0.0573 (41)	0.7242 (40)	0.9178 (22)

TABLE 55 (Continued)

C42	-0.0183 (31)	0.7545 (34)	0.8562 (20)
C43	-0.0926 (24)	0.6581 (27)	0.8177 (24)
C44	-0.0643 (35)	0.5279 (36)	0.8381 (21)
C45	0.0124 (36)	0.4958 (35)	0.8964 (23)
C46	0.0866 (32)	0.5889 (37)	0.9370 (25)
H11	0.2214	0.7088	0.8452
H12	0.2999	0.7186	0.7397
H13	0.3537	0.9232	0.7115
H14	0.4090	1.0910	0.8019
H15	0.3394	1.0642	0.9133
H21	0.2222	0.7285	1.1056
H22	0.3525	0.5973	1.1902
H23	0.5387	0.5453	1.1704
H24	0.5940	0.6051	1.0595
H25	0.4557	0.7485	0.9712
H31	0.3840	0.9740	1.1221
H32	0.3947	1.1627	1.1909
H33	0.3526	1.3488	1.1187
H34	0.2186	1.3440	1.0061
H35	0.1497	1.1458	0.9433
H41	-0.0225	0.8441	0.8370
H42	-0.1638	0.6810	0.7771
H43	-0.1089	0.4584	0.8045
H44	0.0200	0.4028	0.9131

TABLE 55 (Continued)

H45	0.1574	0.5644	0.9783
H401	0.0920	0.8908	1.0267
H402	0.0695	0.9683	0.9505

TABLE 56

THERMAL PARAMETERS FOR BENZYL TRIPHENYL PHOSPHONIUM IODIDE

ATOM	U11	U22	U33	U12	U13	U23
I1	88.(1)	48.(1)	53.(1)	0.(2)	-4.(1)	3.(2)
P1	135.(12)	177.(15)	101.(10)	110.(12)	86.(9)	88.(11)
C11	19.(19)	17.(19)	120.(33)	-2.(19)	22.(19)	16.(25)
C12	137.(56)	142.(56)	148.(71)	-54.(44)	27.(53)	-40.(58)
C13	158.(61)	446.(57)	25.(35)	122.(76)	0.(37)	-46.(61)
C14	166.(76)	312.(36)	127.(62)	149.(87)	136.(59)	164.(78)
C15	194.(81)	51.(43)	384.(56)	-4.(49)	143.(1)	94.(65)
C16	112.(50)	92.(48)	164.(62)	-12.(39)	95.(44)	-6.(42)
C21	126.(41)	38.(24)	57.(29)	58.(27)	-43.(28)	-1.(21)
C22	61.(26)	31.(21)	45.(25)	42.(20)	5.(21)	-3.(19)
C23	96.(32)	38.(20)	44.(21)	-28.(30)	1.(22)	20.(26)
C24	64.(36)	54.(32)	118.(41)	26.(26)	-46.(31)	5.(29)
C25	75.(33)	131.(44)	132.(43)	71.(37)	24.(34)	41.(43)
C26	87.(35)	89.(33)	90.(34)	24.(31)	1.(29)	16.(29)
C31	358.(90)	67.(35)	28.(27)	-52.(43)	14.(39)	17.(23)
C32	324.(90)	69.(38)	46.(33)	114.(49)	5.(43)	20.(27)
C33	141.(37)	47.(32)	59.(28)	20.(26)	-8.(25)	-13.(22)
C34	86.(31)	39.(22)	92.(31)	3.(22)	1.(25)	-14.(21)
C35	47.(23)	100.(34)	84.(31)	47.(23)	-12.(21)	7.(27)
C36	38.(23)	112.(38)	120.(38)	-17.(29)	-27.(23)	-47.(35)
C40	99.(41)	347.(95)	130.(46)	19.(59)	73.(36)	175.(63

TABLE 56 (Continued)

C41	129.(41)	69.(31)	57.(27)	-37.(28)	-73.(27)	29.(23)
C42	62.(27)	56.(24)	48.(23)	-57.(22)	-5.(20)	15.(20)
C43	9.(20)	22.(23)	146.(37)	3.(14)	-27.(22)	18.(21)
C44	62.(29)	46.(24)	63.(32)	7.(23)	-11.(23)	-9.(21)
C45	73.(31)	35.(21)	78.(32)	1.(21)	-23.(25)	-13.(22)
C46	51.(27)	79.(32)	119.(37)	-35.(22)	-73.(25)	45.(27)

Anisotropic parameters are in the form:

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

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

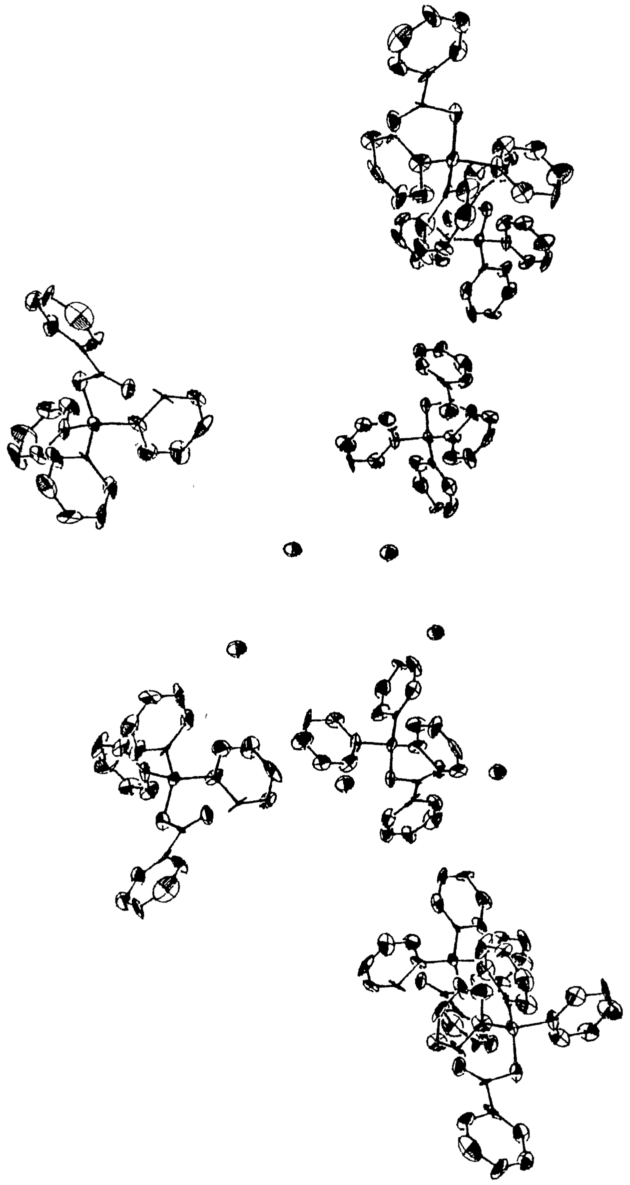


Figure 30. Packing Diagram of Phenacyltriphenylphsophonium Iodide.

TABLE 57

CRYSTAL DATA FOR PHENACYLTRIPHENYL PHOSPHONIUM IODIDE

Formula	$C_{26}H_{22}OPI$
MWT	508.3 g $mole^{-1}$
a	19.078 (5) Å
b	10.901 (3)
c	22.164 (5)
α	90.0°
β	90.0
γ	90.0
V	4609. (2) $Å^3$
F(000)	2032
μMoK_{α}	14.55 cm^{-1}
λMoK_{α}	0.71069 Å
D_{calc}	1.465 g cm^{-3}
Z	8
Obs. refl.	1215
R	7.4
R_w	9.7
Space group	Pcab (Orthorhombic)
Octants meas.	±h, +k, +l

TABLE 58

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR PHENACYLTRIPHENYL PHOSPHONIUM IODIDE

P1-C11	1.73(3)	C11-P1-C21	104.9(9)
P1-C21	1.76(3)	C11-P1-C31	109.(1)
P1-C31	1.82(2)	C11-P1-C40	107.(1)
P1-C40	1.81(3)	C21-P1-C31	106.(1)
O1-C41	1.18(3)	C21-P1-C40	115.(1)
C11-C12	1.44(4)	C31-P1-C40	105.(1)
C11-C16	1.37(4)	P1-C11-C12	120.(2)
C12-C13	1.40(5)	P1-C11-C16	122.(2)
C13-C14	1.35(5)	C12-C11-C16	118.(3)
C14-C15	1.39(5)	C11-C12-C13	118.(3)
C15-C16	1.37(5)	C12-C13-C14	122.(3)
C21-C22	1.43(4)	C13-C14-C15	119.(3)
C21-C26	1.39(4)	C14-C15-C16	120.(3)
C22-C23	1.41(4)	C11-C16-C15	122.(3)
C23-C24	1.38(5)	P1-C21-C22	123.(2)
C24-C25	1.32(5)	P1-C21-C26	118.(2)
C25-C26	1.37(5)	C22-C21-C26	118.(2)
C31-C32	1.37(4)	C21-C22-C23	118.(2)
C31-C36	1.37(4)	C22-C23-C24	120.(3)
C32-C33	1.37(4)	C23-C24-C25	121.(3)
C33-C34	1.33(5)	C24-C25-C26	122.(3)
C34-C35	1.31(6)	C21-C26-C25	120.(3)

TABLE 58 (Continued)

C35-C36	1.40(5)	P1-C31-C32	118.(2)
C40-C41	1.50(3)	P1-C31-C36	124.(2)
C41-C42	1.50(3)	C32-C31-C36	118.(2)
C42-C43	1.36(4)	C31-C32-C33	122.(3)
C42-C47	1.41(4)	C32-C33-C34	118.(3)
C43-C44	1.39(5)	C33-C34-C35	124.(3)
C44-C45	1.37(5)	C34-C35-C36	119.(3)
C45-C46	1.36(5)	C31-C36-C35	119.(3)
C46-C47	1.36(4)	P1-C40-C41	112.(2)
		O1-C41-C40	123.(2)
		O1-C41-C42	123.(2)
		C40-C41-C42	114.(2)
		C41-C42-C43	124.(3)
		C41-C42-C47	118.(3)
		C43-C42-C47	118.(3)
		C42-C43-C44	120.(3)
		C43-C44-C45	121.(3)
		C44-C45-C46	119.(3)
		C45-C46-C47	120.(3)
		C42-C47-C46	122.(3)

TABLE 59

POSITIONAL PARAMETERS FOR PHENACYL TRIPHENYL PHOSPHONIUM IODIDE

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
I1	0.1506 (1)	0.1558 (2)	0.1069 (1)
P1	0.6173 (4)	0.3717 (6)	0.6704 (3)
O1	0.6806 (10)	0.2046 (18)	0.7586 (9)
C11	0.5508 (12)	0.3720 (21)	0.7238 (12)
C12	0.4908 (18)	0.2932 (26)	0.7164 (13)
C13	0.4365 (18)	0.3014 (31)	0.7589 (16)
C14	0.4371 (14)	0.3845 (30)	0.8042 (16)
C15	0.4958 (19)	0.4582 (32)	0.8115 (15)
C16	0.5498 (17)	0.4535 (31)	0.7706 (14)
C21	0.6166 (14)	0.2445 (25)	0.6218 (10)
C22	0.6715 (12)	0.1550 (28)	0.6198 (11)
C23	0.6671 (15)	0.0617 (30)	0.5762 (14)
C24	0.6118 (20)	0.0588 (32)	0.5360 (15)
C25	0.5617 (19)	0.1425 (33)	0.5383 (15)
C26	0.5616 (17)	0.2342 (33)	0.5806 (16)
C31	0.6082 (16)	0.5051 (22)	0.6219 (9)
C32	0.6518 (18)	0.5143 (28)	0.5732 (12)
C33	0.6470 (15)	0.6101 (27)	0.5334 (11)
C34	0.5981 (18)	0.6945 (35)	0.5437 (15)
C35	0.5548 (23)	0.6923 (28)	0.5893 (20)
C36	0.5565 (17)	0.5919 (31)	0.6285 (14)
C40	0.6989 (14)	0.3949 (22)	0.7108 (10)

TABLE 59 (Continued)

C41	0.7101 (11)	0.2995 (23)	0.7588 (11)
C42	0.7593 (13)	0.3381 (29)	0.8079 (12)
C43	0.8013 (17)	0.4390 (28)	0.8051 (13)
C44	0.8455 (19)	0.4666 (27)	0.8531 (15)
C45	0.8517 (18)	0.3897 (25)	0.9017 (16)
C46	0.8128 (20)	0.2855 (33)	0.9035 (14)
C47	0.7684 (14)	0.2581 (27)	0.8574 (13)
H11	0.4889	0.2343	0.6815
H12	0.3947	0.2458	0.7558
H13	0.3967	0.3935	0.8331
H14	0.4998	0.5157	0.8468
H15	0.5919	0.5107	0.7751
H21	0.7125	0.1610	0.6478
H22	0.7041	-0.0037	0.5761
H23	0.6113	-0.0059	0.5025
H24	0.5236	0.1356	0.5087
H25	0.5201	0.2904	0.5821
H31	0.6913	0.4508	0.5663
H32	0.6775	0.6188	0.4981
H33	0.5937	0.7687	0.5138
H34	0.5215	0.7600	0.5962
H35	0.5205	0.5803	0.6609
H41	0.8024	0.4935	0.7670
H42	0.8760	0.5420	0.8522

TABLE 59 (Continued)

H43	0.8834	0.4108	0.9359
H44	0.8165	0.2290	0.9391
H45	0.7404	0.1803	0.8577
H401	0.7340	0.3662	0.6806
H402	0.7029	0.4857	0.7112

TABLE 60

THERMAL PARAMETERS FOR PHENACYL TRIPHENYL PHOSPHONIUM IODIDE

ATOM	U11	U22	U33	U12	U13	U23
I1	45.4(9)	63.(1)	47.(1)	-1.(1)	-7.(1)	2.(1)
P1	32.(3)	22.(3)	37.(4)	6.(3)	-2.(3)	5.(3)
O1	63.(14)	25.(10)	54.(13)	-5.(10)	-15.(11)	-4.(9)
C11	20.(15)	13.(15)	50.(17)	14.(12)	24.(12)	10.(13)
C12	79.(24)	42.(18)	32.(18)	8.(18)	-12.(18)	-31.(15)
C13	92.(28)	36.(20)	78.(26)	-31.(19)	48.(23)	-43.(19)
C14	22.(15)	63.(23)	87.(28)	-12.(17)	24.(17)	43.(21)
C15	79.(28)	58.(23)	62.(25)	22.(23)	25.(21)	-2.(20)
C16	65.(24)	60.(22)	52.(22)	27.(20)	15.(17)	-34.(19)
C21	39.(18)	30.(14)	22.(18)	-24.(15)	6.(11)	14.(13)
C22	29.(15)	45.(16)	45.(19)	36.(15)	20.(11)	21.(16)
C23	38.(21)	64.(22)	57.(19)	14.(16)	34.(15)	-25.(19)
C24	83.(26)	47.(21)	63.(25)	-48.(22)	-8.(22)	17.(19)
C25	92.(27)	48.(22)	57.(22)	20.(24)	-38.(20)	23.(19)
C26	47.(23)	75.(26)	79.(26)	1.(20)	-4.(18)	-34.(22)
C31	68.(21)	20.(14)	2.(15)	1.(15)	-9.(12)	-3.(10)
C32	59.(19)	69.(22)	31.(16)	21.(21)	1.(18)	-5.(15)
C33	47.(16)	79.(21)	19.(13)	5.(20)	11.(15)	24.(13)
C34	69.(22)	104.(31)	68.(25)	25.(23)	21.(20)	4.(21)
C35	109.(22)	21.(19)	168.(46)	39.(20)	42.(31)	32.(24)
C36	53.(22)	61.(23)	65.(24)	11.(18)	48.(17)	-25.(18)

TABLE 60 (Continued)

C40	55.(18)	25.(14)	5.(12)	1.(14)	-7.(12)	10.(11)
C41	3.(11)	16.(13)	33.(16)	-6.(10)	4.(10)	-14.(11)
C42	36.(16)	39.(16)	48.(17)	37.(17)	-7.(13)	-15.(17)
C43	69.(22)	38.(18)	39.(19)	5.(18)	-26.(17)	-11.(16)
C44	60.(21)	40.(19)	81.(24)	-4.(21)	-20.(22)	-1.(18)
C45	60.(19)	34.(16)	93.(27)	-24.(18)	-2.(22)	-34.(17)
C46	109.(29)	96.(27)	52.(23)	27.(23)	-19.(21)	39.(20)
C47	49.(21)	47.(17)	35.(15)	-23.(16)	-20.(16)	-7.(16)

Anisotropic parameters are in the form:

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

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

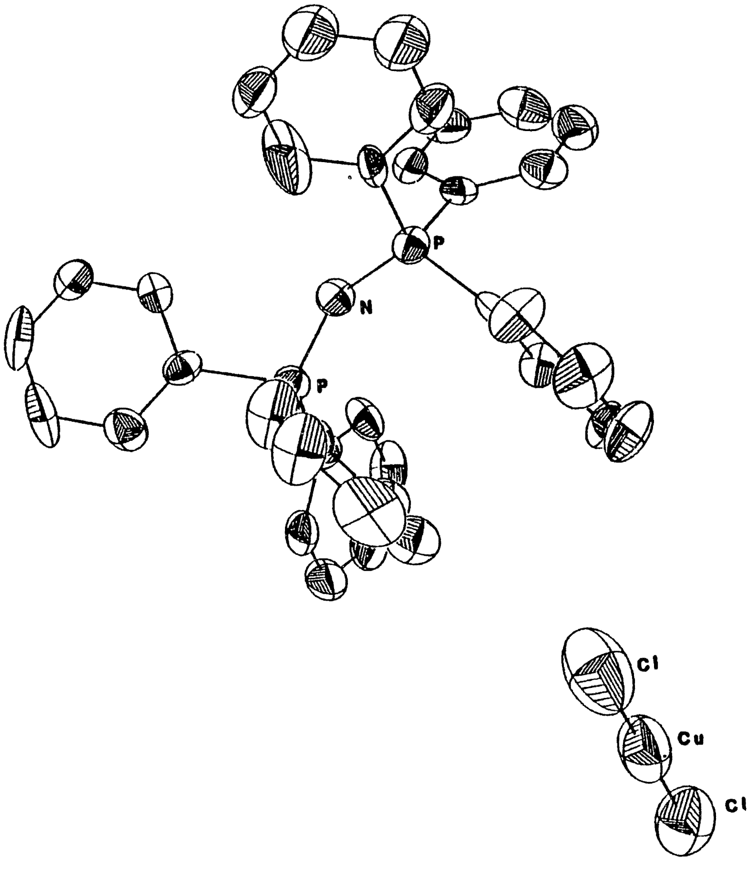


Figure 31. Bis(Triphenylphosphoranyl)Ammonium Dichlorocuprate.

TABLE 61

CRYSTAL DATA FOR BIS (TRIPHENYLPHOSPHORANYL) AMMONIUM DICHLOROCUPRATE (I)

Formula	$C_{36}H_{38}NP_2CuCl_2$
MWT	673.0 g $mole^{-1}$
a	10.891 (8) Å
b	16.91 (1)
c	9.773 (2)
α	84.32 (4)°
β	96.78 (5)
γ	70.09 (5)
V	1662. (2) $Å^3$
F(000)	692
μMoK_α	9.39 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	1.345 g cm^{-3}
Z	2
Obs. refl.	1895
R	5.9
R_w	7.6
Space group	P1bar (Triclinic)
Octants meas.	±h, +k, ±l

TABLE 62

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR BIS (TRIPHENYLPHOSPHORANYL) AMMONIUM DICHLOROCUPRATE (I)

Cu1-Cl11	2.086(5)	Cl1-Cu1-Cl2	178.9(6)
Cu1-Cl12	2.084(6)	N1-P11-C111	108.6(5)
P11-N1	1.568(9)	N1-P11-C121	109.2(5)
P11-C111	1.79(1)	N1-P11-C131	114.0(5)
P11-C121	1.80(2)	C111-P11-C121	108.5(6)
P11-C131	1.79(1)	C111-P11-C131	108.6(6)
P12-N1	1.560(9)	C121-P11-C131	108.6(6)
P12-C211	1.79(1)	N1-P12-C211	114.1(5)
P12-C221	1.79(9)	N1-P12-C221	107.3(5)
P12-C231	1.78(2)	N1-P12-C231	111.1(6)
C111-C112	1.37(2)	C211-P12-C221	107 1(5)
C111-C116	1.39(2)	C211-P12-C231	109.0(5)
C112-C113	1.39(2)	C221-P12-C231	108.0(5)
C113-C114	1.37(2)	P11-N1-P12	137.2(5)
C114-C115	1 35(2)	P11-C111-C112	123 (1)
C115-C116	1.38(2)	P11-C111-C116	118.1(8)
C121-C122	1 38(2)	C112-C111-C116	119.(1)
C121-C126	1.39(2)	C111-C112-C113	121.(1)
C122-C123	1.38(2)	C112-C113-C114	118.(1)
C123-C124	1.35(2)	C113-C114-C115	122.(1)
C124-C125	1.36(2)	C114-C115-C116	120.(1)
C125-C126	1.39(2)	C111-C116-C115	119.(1)

TABLE 62 (Continued)

C131-C132	1.38(2)	P11-C121-C122	121.0(9)
C131-C136	1.39(2)	P11-C121-C126	121.(1)
C132-C133	1.38(2)	C122-C121-C126	118.(1)
C133-C134	1.37(3)	C121-C122-C123	121.(1)
C134-C135	1.31(3)	C122-C123-C124	119.(1)
C135-C136	1.35(2)	C123-C124-C125	122.(2)
C211-C212	1.38(1)	C124-C125-C126	119.(1)
C211-C216	1.38(1)	C121-C126-C125	120.(1)
C212-C213	1.35(2)	P11-C131-C132	121.3(9)
C213-C214	1.36(2)	P11-C131-C136	120.(1)
C214-C215	1.37(2)	C132-C131-C136	119.(1)
C215-C216	1.38(2)	C131-C132-C133	119.(1)
C221-C222	1.41(1)	C132-C133-C134	119.(2)
C221-C226	1.39(2)	C133-C134-C135	122.(1)
C222-C223	1.40(1)	C134-C135-C136	120.(2)
C223-C224	1.37(2)	C131-C136-C135	121.(1)
C224-C225	1 38(2)	P12-C311-C312	125.(1)
C225-C226	1.35(1)	P12-C211-C216	117.7(7)
C231-C232	1.38(2)	C212-C211-C216	117.(1)
C231-C236	1.34(2)	C211-C212-C213	121.(1)
C232-C233	1.37(3)	C212-C213-C214	122.(1)
C233-C234	1.35(3)	C213-C214-C215	119.(1)
C234-C235	1.34(4)	C214-C215-C216	119.(1)
C235-C236	1 37(3)	C211-C216-C215	122.(1)

TABLE 62 (Continued)

P12-C221-C222	120.1(8)
P12-C221-C226	121.4(8)
C222-C221-C226	118.4(9)
C221-C222-C223	121.(1)
C222-C223-C224	118.(1)
C223-C224-C225	122.(1)
C224-C225-C226	120.(1)
C221-C226-C225	121.(1)
P12-C231-C232	120.(1)
P12-C231-C236	121.(1)
C232-C231-C236	118.(2)
C231-C232-C233	121.(1)
C232-C233-C234	120.(2)
C233-C234-C235	119.(2)
C234-C235-C236	122.(2)
C231-C236-C235	120.(2)

TABLE 63

POSITIONAL PARAMETERS FOR BIS (TRIPHENYLPHOSPHORANYL) AMMONIUM DICHLOROCUPRATE (I)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
Cu1	0.6149 (2)	0.2321 (1)	1.0233 (2)
Cl11	0.7021 (4)	0 3319 (2)	0.9551 (4)
Cl12	0.5826 (5)	0.1314 (3)	1.0880 (5)
P11	0.1414 (3)	0.2424 (2)	0.3208 (3)
P12	-0.0807 (3)	0.3058 (2)	0.4738 (3)
N1	-0.0051 (8)	0.2848 (5)	0.3448 (9)
C111	0.1458 (11)	0.1694 (7)	0.1997 (11)
C112	0.2619 (12)	0.1120 (7)	0.1743 (12)
C113	0.2624 (14)	0.0571 (8)	0.0775 (13)
C114	0.1430 (16)	0.0607 (8)	0.0098 (13)
C115	0.0270 (12)	0.1175 (8)	0.0312 (13)
C116	0.0266 (11)	0.1726 (7)	0.1266 (12)
C121	0.1976 (12)	0.3234 (8)	0.2469 (12)
C122	0.3282 (12)	0.3050 (7)	0.2322 (13)
C123	0.3726 (13)	0.3673 (9)	0.1798 (14)
C124	0.2861 (16)	0.4481 (10)	0.1423 (14)
C125	0.1557 (15)	0.4695 (7)	0.1534 (13)
C126	0.1104 (12)	0.4062 (7)	0.2042 (12)
C131	0.2545 (11)	0.1849 (8)	0.4755 (12)
C132	0.3266 (12)	0.2224 (8)	0.5532 (13)
C133	0.3988 (13)	0.1801 (12)	0.6810 (17)

TABLE 63 (Continued)

C134	0.3976 (14)	0.1010 (11)	0.7277 (15)
C135	0.3309 (19)	0.0642 (10)	0.6525 (17)
C136	0.2610 (15)	0.1040 (8)	0.5265 (14)
C211	0.0170 (10)	0.3212 (6)	0.6219 (10)
C212	0.0613 (13)	0.2667 (8)	0.7469 (12)
C213	0.1428 (15)	0.2801 (9)	0.8494 (12)
C214	0.1843 (13)	0.3475 (9)	0.8351 (12)
C215	0 1434 (12)	0.4028 (8)	0.7131 (13)
C216	0.0606 (11)	0.3891 (7)	0.6069 (11)
C221	-0.2185 (10)	0.4034 (7)	0.4180 (11)
C222	-0.2834 (11)	0.4235 (8)	0.2791 (12)
C223	-0.3936 (12)	0.4984 (8)	0.2353 (13)
C224	-0.4348 (12)	0.5512 (8)	0.3318 (14)
C225	-0.3754 (12)	0.5302 (8)	0.4700 (13)
C226	-0.2688 (11)	0.4582 (7)	0.5115 (12)
C231	-0.1435 (12)	0.2253 (8)	0.5257 (12)
C232	-0.2107 (14)	0.2306 (8)	0.6376 (14)
C233	-0.2572 (16)	0.1683 (11)	0.6796 (16)
C234	-0.2437 (24)	0.1028 (13)	0.6074 (21)
C235	-0.1773 (27)	0.0975 (12)	0.4993 (26)
C236	-0.1277 (19)	0.1585 (10)	0.4579 (17)
H111	0.3479	0.1106	0.2275
H112	0.3463	0.0173	0.0564

TABLE 63 (Continued)

H113	0.1436	0.0187	-0.0544
H114	-0.0591	0.1197	-0.0231
H115	-0.0581	0.2156	0.1434
H121	0.3928	0.2454	0.2600
H122	0.4684	0.3515	0.1706
H123	0.3192	0.4940	0.1058
H124	0.0926	0.5289	0.1236
H125	0.0135	0.4210	0.2121
H131	0.3254	0.2805	0.5162
H132	0.4548	0.2052	0.7405
H133	0.4490	0.0723	0.8218
H134	0.3374	0.0046	0.6019
H135	0.2097	0.0745	0.4680
H211	0.0319	0.2168	0.7615
H212	0.1765	0.2395	0.9375
H213	0.2447	0.3569	0.9143
H214	0.1744	0.4522	0.7007
H215	0.0293	0.4288	0.5148
H221	-0.2517	0.3847	0.2096
H222	0.4378	0.5126	0.1395
H223	-0.5095	0.6068	0.2977
H224	-0.4108	0.6590	0.5403
H225	-0.2247	0.4431	0.6114
H231	-0.2272	0.2813	0.6865

TABLE 63 (Continued)

H232	-0.2999	0.1722	0.7657
H233	-0.2793	0.0570	0.6393
H234	-0.1702	0.0487	0.4482
H235	-0.0797	0.1528	0.3730

TABLE 64

THERMAL PARAMETERS FOR BIS (TRIPHENYLPHOSPHORANYL) AMMONIUM DICHLOROCUPRATE (I)

ATOM	U11	U22	U33	U12	U13	U23
Cu1	76.(1)	56.(1)	63.(1)	-5.(1)	8.(1)	-15.(0)
C111	97.(3)	68.(2)	67 (2)	-21.(2)	-6.(2)	-6.(2)
C112	127.(4)	70.(2)	119.(3)	-31.(2)	51.(3)	-23.(2)
P11	35.(2)	37.(1)	34.(1)	-12.(1)	7.(1)	-5.(1)
P12	42.(2)	37.(1)	32.(1)	-20.(1)	8.(1)	-4.(1)
N1	43.(6)	44.(5)	31.(5)	-20.(5)	9.(4)	-3.(4)
C111	40.(7)	44.(7)	30.(6)	-25.(6)	4.(5)	-2.(5)
C112	39.(8)	48.(8)	49.(8)	-5.(6)	1.(6)	-4.(6)
C113	83.(10)	40 (8)	44.(8)	15.(7)	10.(7)	-15.(6)
C114	110.(12)	48 (8)	45.(8)	-26.(8)	6.(8)	-28.(7)
C115	57.(8)	64.(9)	59.(8)	-35.(7)	15.(7)	-25.(7)
C116	44.(7)	45 (7)	52.(7)	-13.(6)	13.(6)	-20.(6)
C121	47.(8)	58 (9)	43 (7)	-29.(7)	16.(6)	-13(. 6)
C122	58.(9)	34 (7)	62.(9)	-18.(6)	17 (7)	-21.(6)
C123	59.(9)	60 (9)	90.(11)	-35.(8)	38.(8)	-30.(8)
C124	87.(12)	79 (11)	57 (9)	-55.(10)	42.(8)	-33.(8)
C125	98.(11)	28.(7)	53.(8)	-27.(7)	21.(8)	-5.(6)
C126	48.(8)	32 (7)	60.(8)	-4.(6)	22.(6)	-9.(6)
C131	37.(7)	55.(8)	41.(7)	-12.(6)	10.(6)	-21.(6)
C132	49.(8)	59.(9)	49.(8)	-13.(7)	2.(7)	1.(7)
C133	42.(9)	175 (18)	82.(12)	-46.(11)	9.(9)	-43.(12)

TABLE 64 (Continued)

C134	66.(10)	132.(15)	54.(10)	25.(10)	-25.(8)	36.(9)
C135	146.(17)	83.(12)	83.(13)	-11.(11)	-13.(11)	36.(9)
C136	97.(11)	50.(9)	58.(9)	-14.(8)	-10.(8)	1.(7)
C211	27.(6)	29.(6)	30.(6)	-1.(5)	14.(5)	1.(4)
C212	76.(9)	50.(8)	38.(8)	-37.(7)	-7.(7)	14.(6)
C213	96.(12)	105.(12)	19.(7)	-42.(10)	-9.(7)	7.(7)
C214	83.(10)	81.(10)	35.(7)	-38.(8)	-15.(7)	-11.(7)
C225	65.(9)	57.(8)	58.(8)	-41.(7)	14.(7)	-30.(7)
C216	57.(8)	34.(7)	33.(6)	-24.(6)	11.(6)	0.(5)
C221	29.(6)	42.(7)	50.(7)	-20.(5)	16.(5)	-13.(5)
C222	47.(7)	63.(8)	44.(7)	-30.(7)	13.(6)	-23.(6)
C223	46.(8)	54.(8)	81.(10)	-20.(7)	15.(7)	2.(7)
C224	44.(8)	50.(8)	80.(10)	0.(6)	10.(7)	2.(7)
C225	52.(8)	51.(8)	75.(9)	-11.(7)	16.(7)	-16.(7)
C226	35.(7)	53.(7)	48.(8)	-8.(6)	0.(6)	1.(6)
C231	58.(8)	57.(8)	48.(8)	-32 (7)	34.(7)	-35.(6)
C232	81.(10)	65.(9)	69.(10)	-48.(8)	24.(8)	-28.(8)
C233	120.(14)	129.(14)	79.(11)	-90.(12)	55.(10)	-46.(10)
C234	287.(28)	152.(18)	141.(17)	189.(20)	145.(19)	-78.(15)
C235	348.(34)	115.(16)	243.(26)	180.(21)	214.(27)	117.(17)
C236	190.(19)	89.(12)	103 (13)	-81.(13)	119.(14)	-47.(10)

TABLE 64 (Continued)

Anisotropic parameters are in the form:

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

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

PART 2

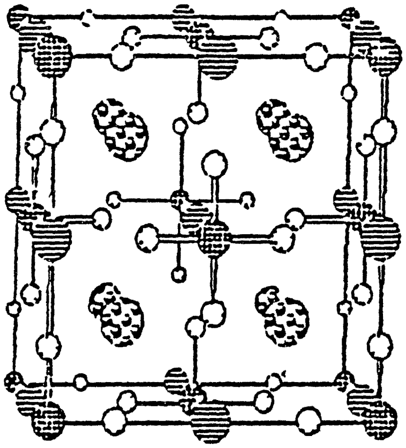
POLYMERIC CUPRIC FLUORIDE COMPLEXES

CHAPTER VI

POLYMERIC CUPRIC FLUORIDE COMPLEXES

Anionic copper (I) halide complexes are known for X = Cl, Br and I, but unknown for X = F. However copper (III) is known to exist in complexes with fluoride. $CsCuF_4$ (93), K_3CuF_6 (94), Cs_2NaCuF_6 (95), and Cs_2KCuF_6 (95) for example, exist with copper (III) stabilized by coordination to fluoride. While copper (II) complexes commonly exist with copper octahedrally coordinated to six fluoride atoms, and with fluorides bridging pairs of copper atoms, copper (III) complexes display isolated $Cu(III)F_6^{-3}$ octahedra. Cs_2KCuF_6 (Figure 32) and Cs_2NaCuF_6 (Figure 33) exist with isolated octahedra of CuF_6^{-3}. These materials were reported to form light colored crystals.

It was of interest to observe the properties of copper fluoride complexes in higher oxidation states. There are no reports of emission from copper (III) halide complexes. However, there are very few structural observations of copper (III) complexes in the solid state. Thus it seemed a logical extension of the work with copper (I) halides to explore the synthesis of mixed copper state materials with fluorides, to see if copper (III) or mixed copper (II) copper (III) systems might be produced under the synthetic conditions used and to ascertain if emission exists for copper (III).

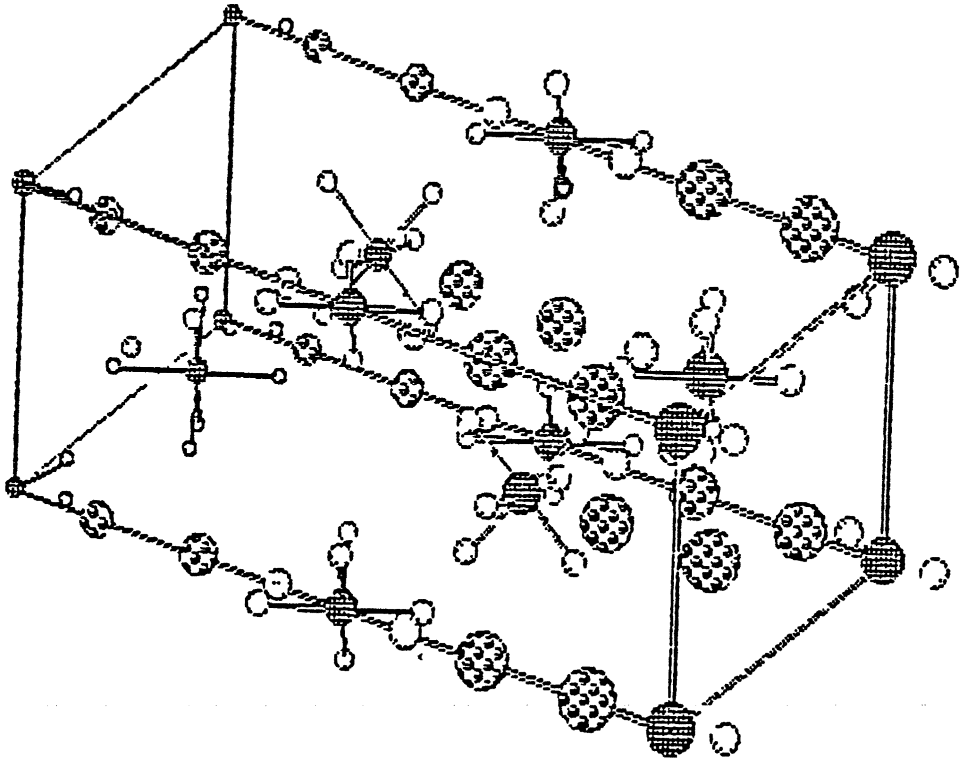


Cs_2KCuF_6

Cu(III) isolated octahedra

Cu-F 1.832Å

Figure 32. Dicesium Potassium Hexafluorocuprate (III)



Cs_2NaCuF_6
Copper(III) isolated octahedra
Cu-F 1.904Å

Figure 33. Dicesium Sodium Hexafluorocuprate (III).

There are several common methods of synthesizing inorganic fluoride complexes. (96) The synthesis of fluoride containing solid materials takes place more readily under conditions of high pressure and temperature and thereby requires a system that is relatively inert to attack by the fluorinating agent under these conditions.

Fluorine gas may be allowed to react with solid, liquid or gaseous reactants. The strongly oxidizing character of F_2 gas normally leads to high oxidation state products. For copper, these products include complexes of copper (III) and (IV). The use of fluorine gas requires safety measures because of its high reactivity and extreme toxicity. (97)

A solution of aqueous hydrogen fluoride can serve as the fluorinating reagent. (98) At room temperature and atmospheric pressure, this method requires fewer precautions. However, its use at elevated temperatures and pressures requires gold tubing as a reaction vessel. (99)

Liquid hydrogen fluoride has been used as the solvent in the preparation of $(KrF)(AgF_3)$ from AgF_2 and KrF_2. (100)

Halogen fluorides such as BrF_3, BrF_5 and IF_5 may be used as fluorinating agents without added solvent. (101, 102, 103) Teflon or other inert plastic containers are suitable reaction vessels at room temperature and atmospheric pressure.

The compounds synthesized in this study were prepared by the fusion of solid fluorides of group 1 or group 2 metals with cupric fluoride in an atmosphere of anhydrous hydrogen fluoride. The product was cooled slowly in an atmosphere of argon to remove excess absorbed hydrogen fluoride.

<u>Synthesis</u> All fluoride salts used were purchased from Aesar Chemicals and were used without further purification. The 3/4 inch graphite rods used for the boats were purchased from Poco Graphite Company. The graphite boats were prepared by the Oklahoma State University, Chemistry and Physics Machine Shop.

The graphite boats were placed in an oven to bake at 120°C overnight prior to their use. The materials to be fused were mixed, then ground to a fine powder. The mixture was then placed in the dry graphite boat. The inconel reaction tube in the Lindeburg tube furnace was lined with graphite foil. The samples were then placed in the oven as shown in Figure 34. The oven was flushed with anhydrous argon and the samples heated to the desired reaction temperature. Upon reaching the reaction temperature anhydrous hydrogen fluoride gas at atmospheric pressure was passed through the inconel reaction tube for a specified length of time. The tube furnace was then slowly cooled to room temperature before the samples were removed. Temperature control for the reaction was achieved through the use of an Omega 2011 programable temperature controller. The programming as well as overseeing the fusion of the samples was done by Mr. C. A. Hunt and Dr. J. J. Martin in the Oklahoma State University, Solid State Materials Laboratory. The products of these reactions were heterogeneous mixtures of dark charred materials and sometimes light colored solids.

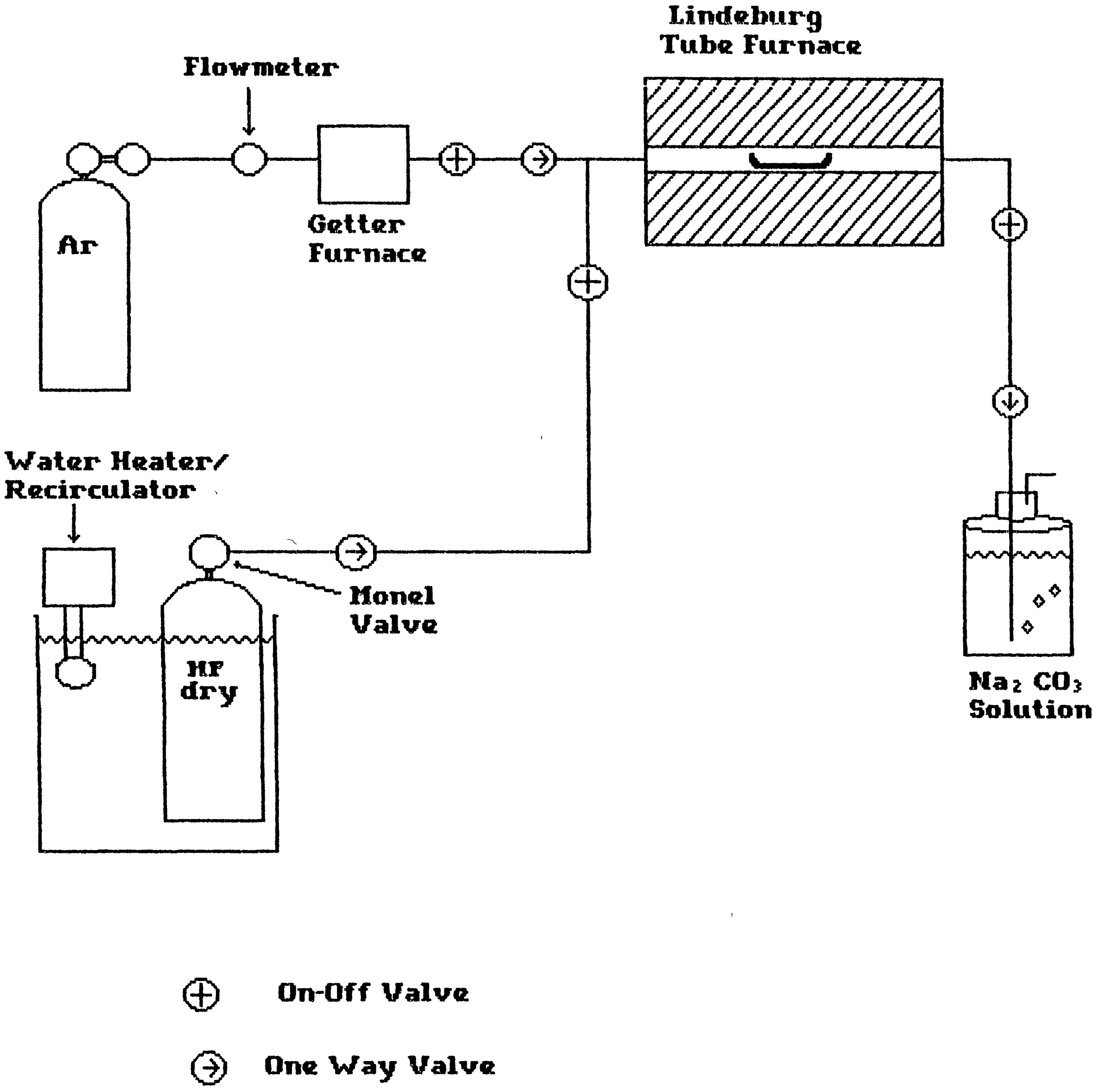


Figure 34. HF Oven.

In a few cases, the solid materials were found to be suitably crystalline for further study.

Tetracesium [Catena-Decafluoro Tricuprate (II)].

A finely ground mixture of 2.66 g (17.5 mmol) cesium fluoride and 1.34 g (13.2 mmol) cupric fluoride was placed in a graphite boat. The boat was then placed into the inconel reaction tube of the furnace. The reaction tube was flushed with argon gas at room temperature for 100 minutes. The sample was heated to 675°C over an 18 hour period. The sample was then exposed to an atmosphere of anhydrous hydrogen fluoride for three hours. The chamber was flushed with argon and the temperature lowered to room temperature over a 24 hour period.

Heptacesium [Catena-Nonadecafluoro Hexacuprate (II)].

A finely ground mixture of 2.54 g (16.7 mmol) cesium fluoride and 1.46 g (14.4 mmol) cupric fluoride was placed in a graphite boat. The boat was then placed into the inconel reaction tube of the furnace. The reaction tube was flushed with argon gas at room temperature for 100 minutes. The sample was heated to 675°C over an 18 hour period. The sample was then exposed to an atmosphere of anhydrous hydrogen fluoride for three hours. The chamber was flushed with argon and the temperature lowered to room temperature over a 24 hour period.

Dirubidium [Catena-Tetrafluorocuprate (II)].

A finely ground mixture of 2.69 g (21.8 mmol) rubidium fluoride and 1.31 g (12.9 mmol) cupric fluoride was placed in a graphite boat. The boat was then placed into the inconel reaction tube of the furnace. The reaction tube was flushed with argon gas at room temperature for 35 minutes. The sample was heated to 675°C over an 18 hour period. The sample was then exposed to an atmosphere of anhydrous hydrogen fluoride for two and one half hours. The chamber was flushed with argon and the temperature lowered to room temperature over a 24 hour period.

Barium [Tetrafluorocuprate (II)].

A finely ground mixture of 3.49 g (19.9 mmol) barium fluoride and 0.51 g (5.0 mmol) cupric fluoride was placed in a graphite boat. The boat was then placed into the inconel reaction tube of the furnace. The reaction tube was flushed with argon gas at room temperature for 20 minutes. The sample was heated to 770°C over a five hour period. The sample was then exposed to an atmosphere of anhydrous hydrogen fluoride for three hours. The chamber was flushed with argon and the temperature lowered to room temperature over a 24 hour period.

Discussion

All of the compounds prepared in this study exhibit an octahedral arrangement of fluoride atoms around copper (II). Fluoride atoms may be bridging or terminal. The compounds differ in the arrangement of bridging fluoride atoms.

Tetracesium catenadecafluorotricuprate (II) crystallized with copper (II) atoms in linear groups of three (Cu-Cu 2.78(2),2.77(2)Å). Each pair of copper atoms is bridged by three fluoride atoms. Copper atoms at the ends of the linear group of three copper atoms are linked by bridging fluoride atoms to four other end copper atoms. (Figure 35)

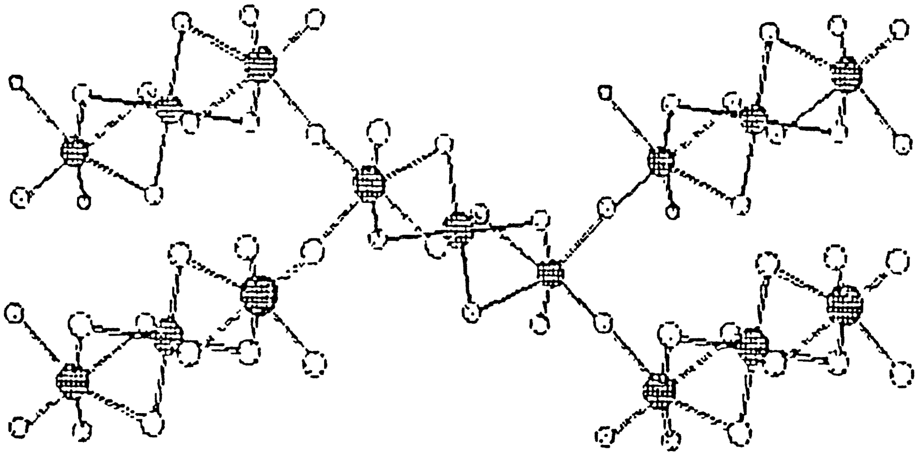


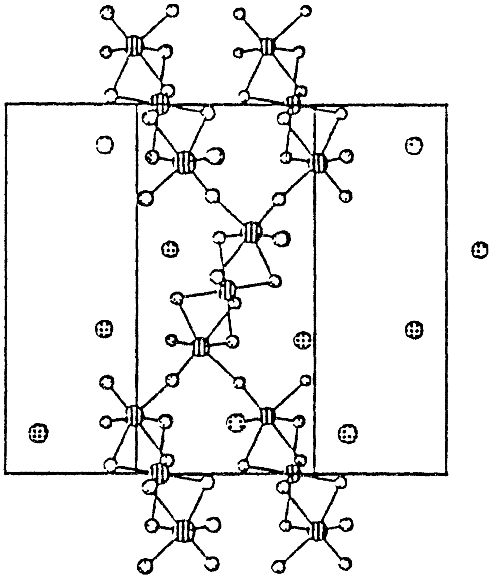
Figure 35. Cupric Fluoride Cluster from Tetracesium Catenadecafluorotricuprate (II).

Each terminal copper atom is bound to one terminal fluoride atom. These puckered layers show a herringbone pattern of alternating linked copper trimers. The copper fluoride layers are separated by cesium atoms. (Figure 36) This structure is similar to that seen in tetracesium catenadecafluorotrinickel and tetracesium catenadecafluorotrimagnesium. (104, 105, 106)

Heptacesium catena-nonadecafluorohexacuprate (II) displays a similar repeat unit of three linear copper atoms (Cu-Cu, 2.82(1),2.83(1)Å) bridged in pairs by three fluoride atoms and with the end most copper atoms linked by bridging fluoride atoms to other repeat units. (Figure 37) However, in this solid material, trimeric copper units are parallel and only one copper atom bears a terminal fluoride atom. Each copper trimer is thus bridged to five other trimeric units. (Figure 38) Cesium atoms lie in the interstices of the three dimensional matrix formed.

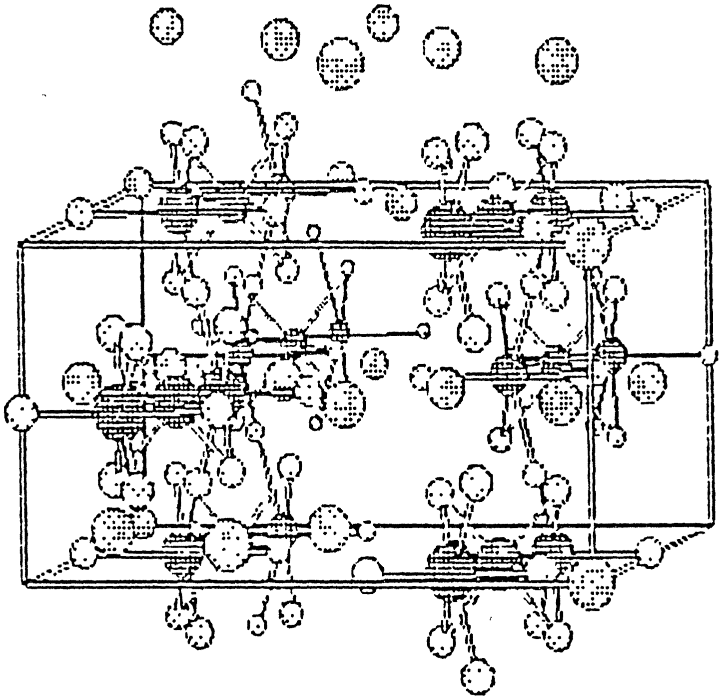
Dirubidium tetrafluorocuprate (II) displays a structure similar to that of K_2NiF_4 of the 1D-disconnected perovskite family. The CuF_6 octahedra share equatorial fluoride atoms to form a sheet. (Figure 39) The axial and terminal fluoride atoms project upward and downward from this plane.

$BaCuF_4$ (Figures 40 and 41) shows a series of CuF_6 octahedra linked by the sharing of one fluoride atom between them. These chains are cross linked to other chains by similar sharing. Two of the fluoride atoms bound to each copper (II) atom are terminal.



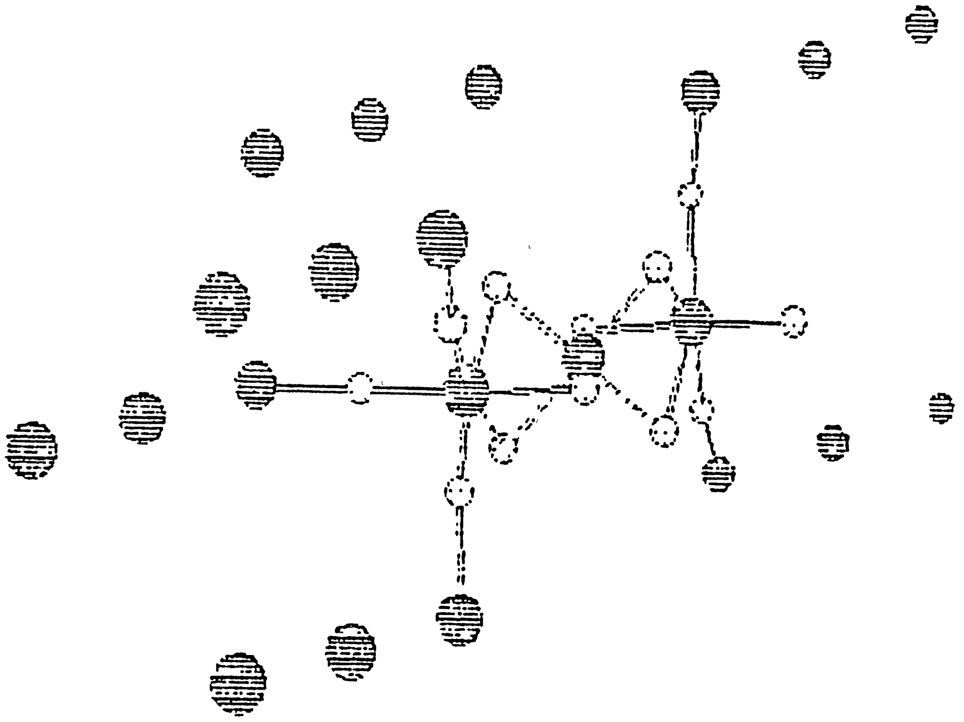
$Cs_4Cu_3F_{10}$

Figure 36. Packing Diagram of Tetracesium Catenadecafluorotricuprate (II).



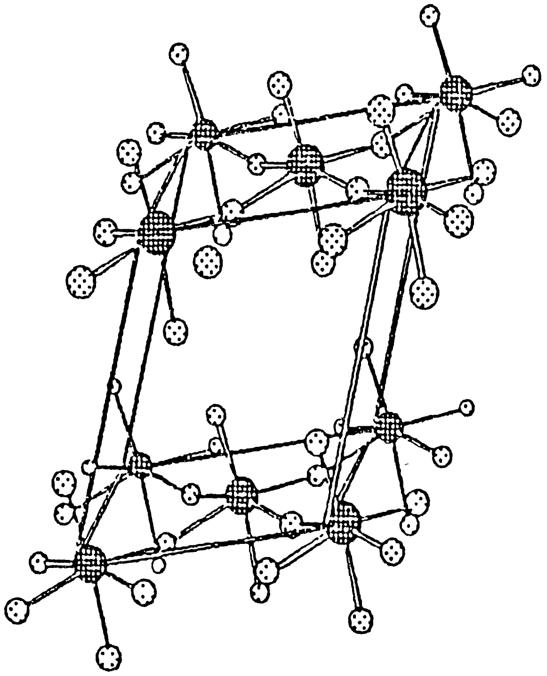
$Cs_7Cu_6F_{19}$

Figure 37. Packing diagram of Heptacesium Catenanonadecafluorohexacuprate(II).



$Cs_7Cu_6F_{19}$ monoclinic space group A2/m
a = 11.731, b = 6.274, c = 15.700 β = 99.05°
Copper(II) on mirror
one terminal fluoride

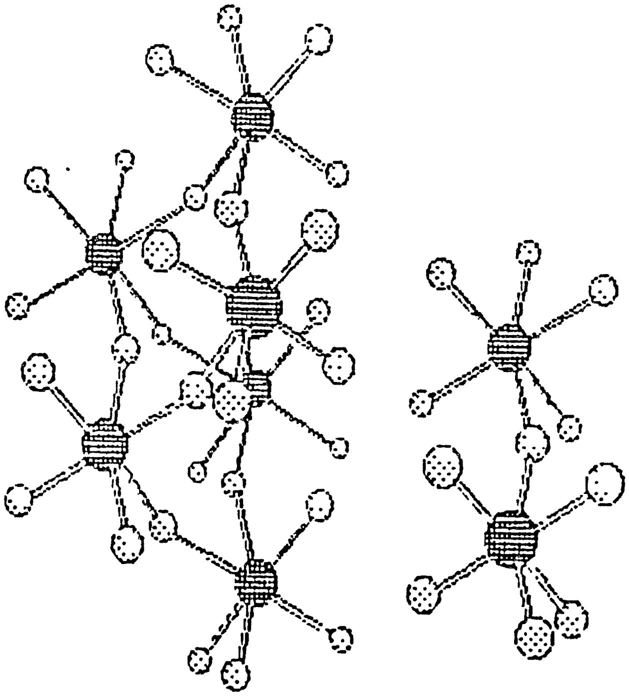
Figure 38. Heptacesium Catenanonadecafluorohexacuprate (II).



$Rb_4Cu_2F_8$

Cu(II) on mirror plane
Cu-F bridging - 2.176Å
2.120
terminal - 1.780
2.128

Figure 39. Packing Diagram of Dirubidium Catenatetrafluorocuprate (II).

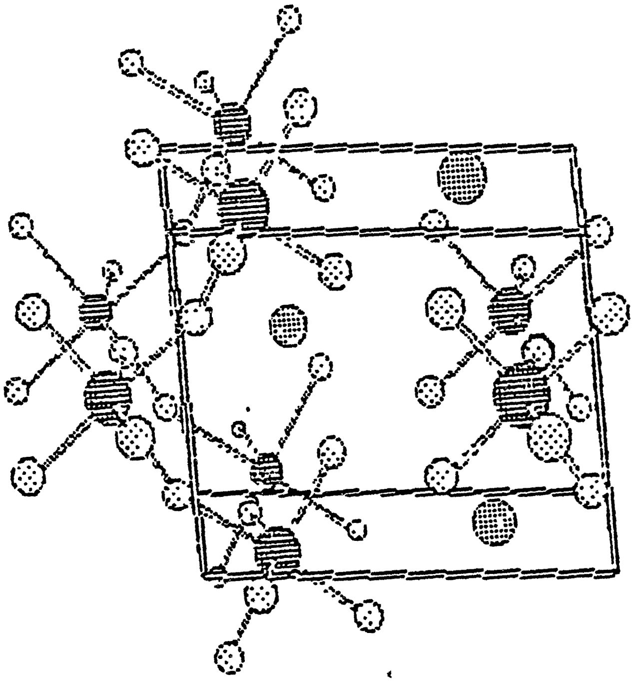


BaCuF$_4$

Copper(II) - condensed chain

Cu - F	2.213Å	along chain
	2.228	
	1.907	terminal
	1.869	
	1.915	cross linking
	1.952	

Figure 40. Cupric Fluoride Cluster from Barium Catenatetrafluorocuprate (II).



BaCuF4

Figure 41. Barium Catenatetrafluorocuprate (II).

The complexes prepared in this study contained only copper (II) and no copper (III) was observed. There was no evidence of mixed oxidation states in the crystalline materials studied. The stoichiometry observed in the crystalline materials established them to contain copper only in oxidation state (II). Fluoride exhibits only terminal or bidentate binding capacity unlike iodine which is observed to exhibit tetra, tri, bi and monodentate binding to copper (I). Thus variation in anionic CuF cluster formation is limited compared to the range of complexes observed in anionic CuX (X = I, Br, Cl) complexes. Copper (II) exhibits a tendency to form bridged, linked copper trimers with all halides and thus the structures observed here, while previously unreported, are not unprecedented.

The Cu (II) fluoride complexes prepared display patterns of elongation of copper-fluoride bonds along the trimer that may indicate interesting magnetic properties. Such magnetic behavior in fluorides has not been reported.

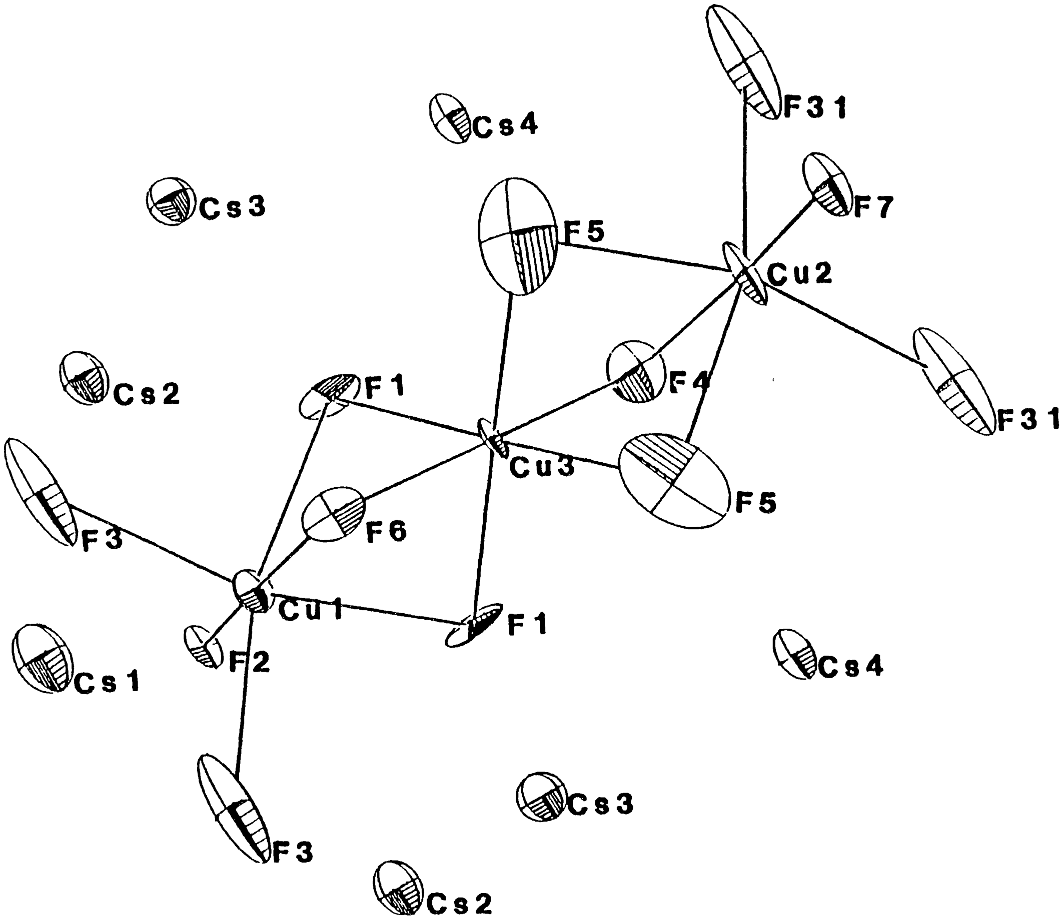


Figure 42. Tetracesium Catenadecafluorotricuprate.

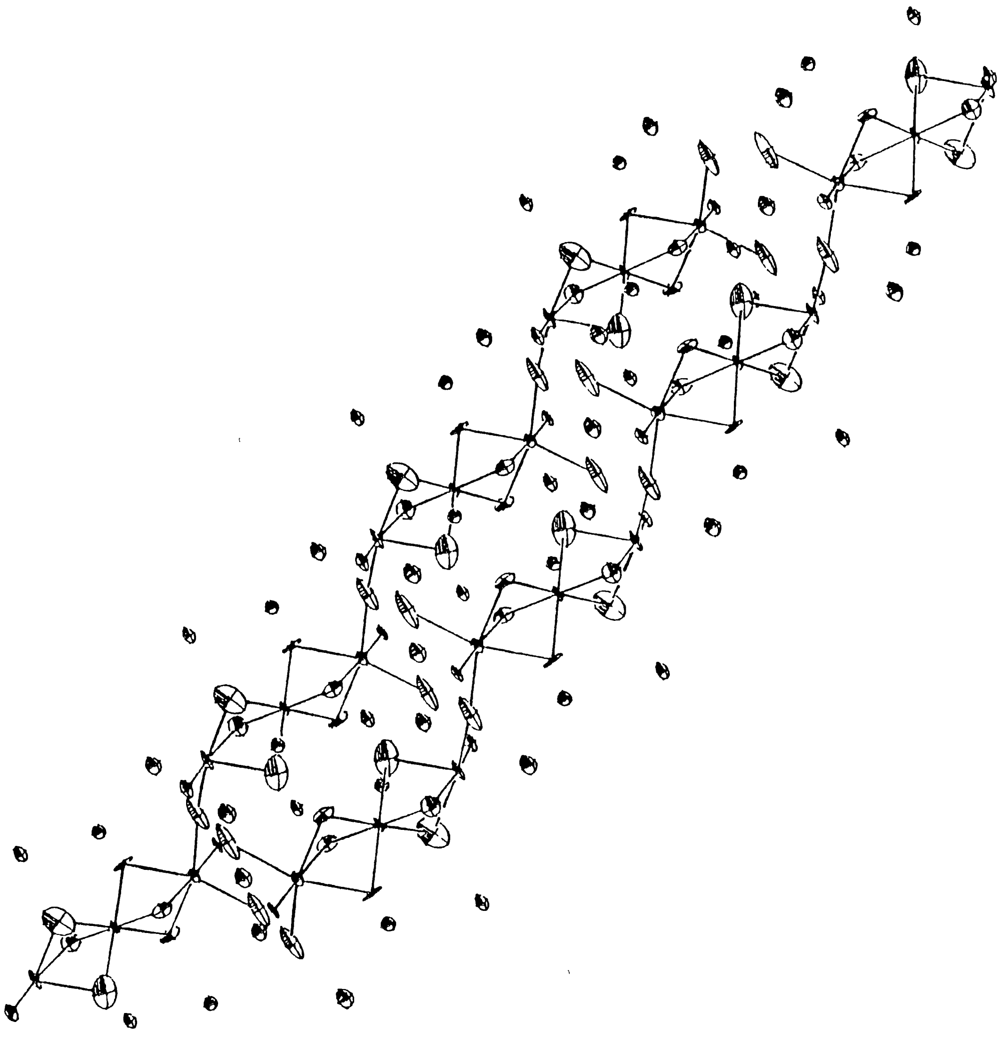


Figure 43. Packing Diagram of Tetracesium Catenadecafluorotricuprate (II).

TABLE 66

CRYSTAL DATA FOR TETRA CESIUM (CATENA-DECAFLUOROTRICUPRATE (II))

Formula	$Cs_4Cu_3F_{10}$
MWT	912.2 g mole $^{-1}$
a	11.68 (1) Å
b	14.255 (9)
c	6.279 (4)
α	90.0°
β	142.73 (6)
γ	90.0
V	633.1 (5) Å ^{3}
F(000)	397
μMoK_α	83.16 cm^{-1}
λMoK_α	0.71069 Å
D_{calc}	2.431 g cm^{-3}
Z	1
Obs. refl.	641
R	14.7
R_w	18.3
Space group	P2/c (Monoclinic)
Octants meas.	±h, +k, +l

TABLE 65

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR TETRA CESIUM (CATENA-DECAFLUOROTRICUPRATE (II))

Cu1-F1	1.98(4)	F1-Cu1-F2	166.(3)
Cu1-F2	1.89(5)	F1-Cu1-F3	74.(3)
Cu1-F3	2.44(9)	F1-Cu1-F4	91.(3)
Cu1-F4	1.87(10)	F1-Cu1-F5	75.(3)
Cu1-F5	2.22(11)	F1-Cu1-F4^1	92.(3)
Cu1-F4^1	2.25(11)	F2-Cu1-F3	96.(4)
Cu2-F1	2.04(5)	F2-Cu1-F4	95.(3)
Cu2-F3	1.87(12)	F2-Cu1-F5	92.(3)
Cu2-F5	2.07(9)	F2-Cu1-F4^1	99.(4)
Cu1-Cu2	2.82(1)	F3-Cu1-F4	160.(4)
		F3-Cu1-F5	74.(3)
		F3-Cu1-F4^1	95.(1)
		F4-Cu1-F5	89.(4)
		F4-Cu1-F4^1	99.(4)
		F5-Cu1-F4	165.(2)
		F1-Cu2-F3	87.(2)
		F1-Cu2-F5	78.(2)
		F1-Cu2-F1^2	180.(4)
		F1-Cu2-F3^2	93.(3)

TABLE 66 (Continued)

F1-Cu2-F5^2	102.(2)
F3-Cu2-F5	91.(5)
F3-Cu2-F1^2	93.(3)
F3-Cu2-F3^2	180.(3)
F3-Cu2-F5^2	88.(5)
Cu1-F1-Cu2	89.(4)
Cu1-F3-Cu2	81.(5)
Cu1^2-F4-Cu1^3	173.(6)
Cu1-F5-Cu2	82.(4)

^{1} = symmetry operation 1-x, 0.5+y, 0.5-z

^{2} = symmetry operation 1-x, 1-y, 1-z

^{3} = symmetry operation 1-x, -0.5+y, 0.5-z

TABLE 67

POSITIONAL PARAMETERS FOR TETRA CESIUM (CATENA-DECAFLUOROTRICUPRATE (II))

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
Cs1	0.5811 (8)	0.3612 (5)	0.1123 (15)
Cs2	0.9877 (9)	0.3905 (5)	1.2205 (17)
Cu1	0.7443 (14)	0.6566 (7)	0.8798 (29)
Cu2	0.5000	0.5000	0.5000
F1	0.4660 (57)	0.64128 (36)	0.4695 (114)
F2	0.9916 (76)	0.3615 (47)	0.7179 (147)
F3	0.6778 (86)	0.5231 (43)	0.5494 (177)
F4	0.2667 (85)	0.2465 (49)	-0.1461 (149)
F5	0.6922 (97)	0.5359 (41)	1.0185 (200)

TABLE 68

THERMAL PARAMETERS FOR TETRA CESIUM (CATENA-DECAFLUOROTRICUPRATE (II))

ATOM	U11	U22	U33	U12	U13	U23
Cs1	12.(2)	8.(2)	10.(2)	5.(2)	5.(2)	3.(2)
Cs2	12.(3)	30.(3)	11.(3)	7.(2)	5.(2)	6.(2)
Cu1	6.(5)	4.(6)	11.(5)	-2.(3)	5.(5)	0.(4)
Cu2	4.(6)	4.(7)	4.(7)	-3.(5)	2.(6)	-3.(5)
F1	1.(22)	10.(22)	2.(22)	3.(19)	0.(21)	0.(22)
F2	9.(27)	50.(41)	6.(28)	3.(32)	-6.(25)	0.(34)
F3	32.(36)	39.(41)	38.(42)	34.(30)	26.(37)	23.(33)
F4	40.(39)	34.(35)	2.(29)	7.(31)	8.(31)	4.(26)
F5	41.(43)	14.(34)	45.(49)	21.(29)	17.(41)	19.(33)

Anisotropic parameters are in the form:

exπ(-2p2(U11h2a*2 + U22k2b*2 + U33l2c*2 + 2U12hka*b* +

2U13hla*c* + 2U23klb*c*)) * 103

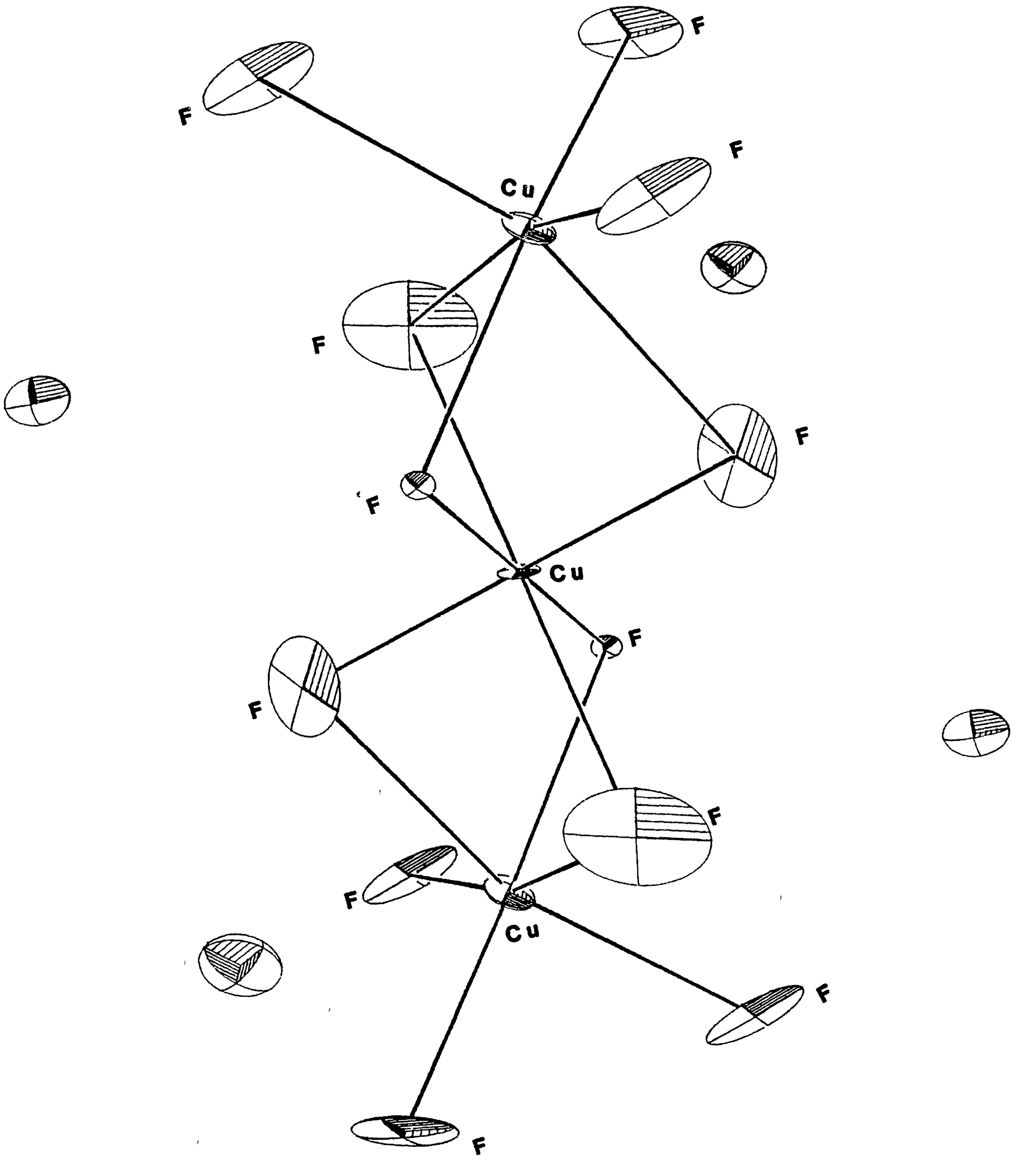


Figure 44. Heptacecium Catenanonadecafluorohexacuprate

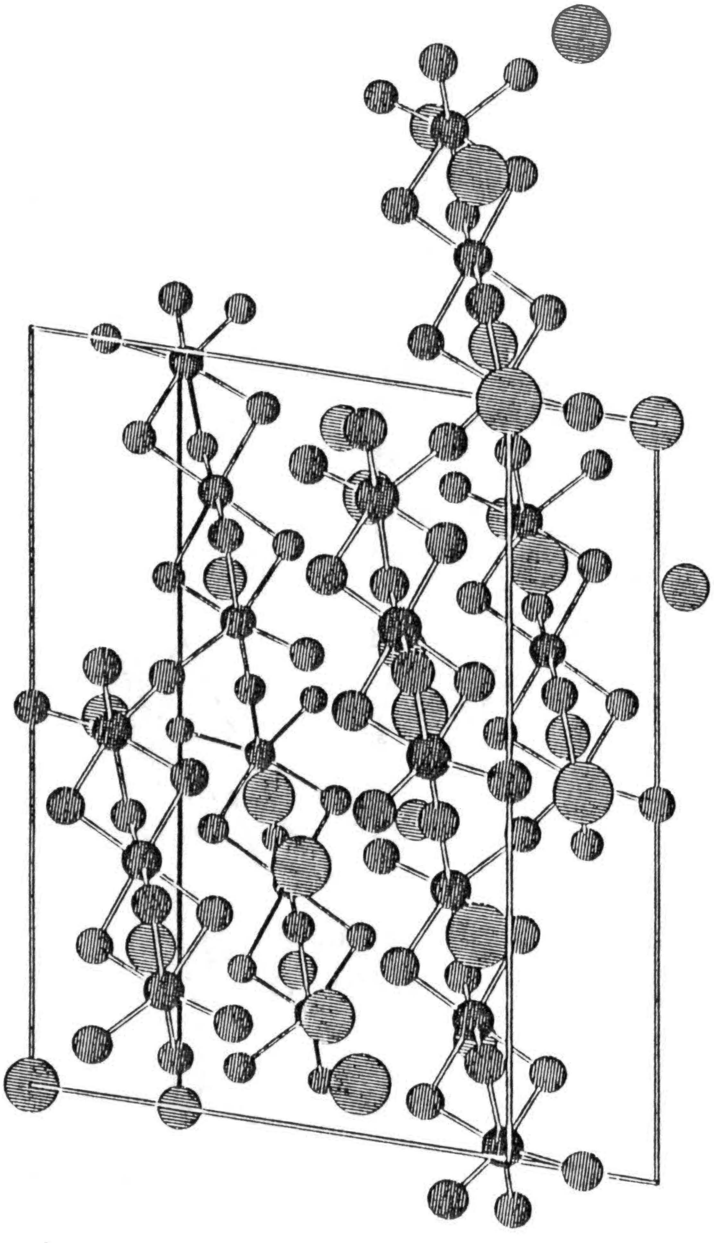


Figure 45. Packing Diagram of Heptacesium Catenanonadecafluorohexacuprate(II).

TABLE 69

CRYSTAL DATA FOR HEPTA CESIIUM (CATENANONA DECAFLUORO HEXACUPRATE (II))

Formula	$Cs_7Cu_6F_{19}$
MWT	1311.6 g mole^{-1}
a	11.731 (3) Å
b	6.274 (2)
c	15.700 (6)
α	90.0°
β	99.05 (3)
γ	90.0
V	1141.1 (6) Å^3
F(000)	559
μMoKα	82.11 cm^{-1}
λMoKα	0.71069 Å
D_{calc}	1.900 g cm^{-1}
Z	2
Obs. refl.	529
R	7.3
R_w	8.8
Space Group	A2/m (Monoclinic)
Octants meas.	±h, +k, +l

TABLE 70

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR HEPTA CESIIUM (CATENA-NONA DECAFLUORO HEXACUPRATE (II))

Cu1-F1	2.20(3)	F1-Cu1-F2	96.(1)
Cu1-F2	1.84(4)	F1-Cu1-F3	91.(1)
Cu1-F3	2.28(4)	F1-Cu1-F6	78.(1)
Cu1-F6	1.94(4)	F1-Cu1-F1^1	75.(1)
Cu2-F3	1.90(4)	F1-Cu1-F3^1	163.(1)
Cu2-F4	2.11(5)	F2-Cu1-F3	94.(1)
Cu2-F5	2.12(4)	F2-Cu1-F6	173.(2)
Cu2-F7	2.02(4)	F2-Cu1-F1^1	96.(1)
Cu3-F1	1.97(2)	F2-Cu1-F3^1	94.(1)
Cu3-F4	2.04(3)	F3-Cu1-F6	90.(1)
Cu3-F5	1.99(4)	F3-Cu1-F1^1	163.(1)
Cu3-F6	2.00(4)	F3-Cu1-F3^1	101.(1)
Cu1-Cu3	2.78(2)	F6-Cu1-F1^1	78.(1)
Cu2-Cu3	2.77(2)	F6-Cu1-F3^1	90.(1)
		F1^1-Cu1-F3^3	91.(1)
		F4-Cu2-F5	76.(1)
		F4-Cu2-F5^1	76.(1)

TABLE 70 (Continued)

$F4-Cu2-F3^2$	93.(1)
$F4-Cu2-F7^2$	168.(1)
$F4-Cu2-F3^3$	93.(1)
$F5-Cu2-F5^1$	76.(2)
$F5-Cu2-F3^2$	168.(1)
$F5-Cu2-F7^2$	93.(1)
$F5-Cu2-F3^3$	95.(2)
$F5^1-Cu2-F7^2$	93.(1)
$F5^1-Cu2-F3^3$	168.(1)
$F3^2-Cu2-F7^2$	96.(1)
$F3^2-Cu2-F3^3$	93.(2)
$F7^2-Cu2-F3^3$	96.(1)
F1-Cu3-F4	98.(1)
F1-Cu3-F5	96.(1)
F1-Cu3-F6	179.(2)
$F1-Cu3-F1^1$	86.(1)
$F1-Cu3-F1^1$	178.(1)
F4-Cu3-F5	50.(1)

TABLE 70 (Continued)

F4-Cu3-F6	179.(1)
F4-Cu3-F1[1]	98.(1)
F4-Cu3-F5[1]	82.(1)
F5-Cu3-F6	99.(1)
F5-Cu3-F1[1]	178.(1)
F5-Cu3-F5[1]	82.(2)
F6-Cu3-F1[1]	81.(1)
F6-Cu3-F5[1]	99.(1)
F1[1]-Cu3-F5[1]	96.(1)
Cu1-F1-Cu3	83.(1)
Cu1-F3-Cu2[4]	174.(1)
Cu2-F4-Cu3	84.(2)
Cu2-F5-Cu3	85.(2)
Cu1-F6-Cu3	87.(1)
Cu2[4]-F7-Cu2[5]	180.(3)

[1] = Symmetry operation (x, -y, z)
[2] = Symmetry operation (x, -0.5+y, 0.5+z)
[3] = Symmetry operation (x, 0.5-y, 0.5+z)
[4] = Symmetry operation (x, 0.5+y, -0.5+z)
[5] = Symmetry operation (-x, 0.5-y, 0.5-z)

TABLE 71

POSITIONAL PARAMETERS FOR HEPTA CESIUM (CATENA-NONA DECAFLUORO HEXACUPRATE (II))

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
Cs1	0.000	0.000	0.000
Cs2	0.4462 (4)	0.500	0.1533 (3)
Cs3	0.0944 (3)	0.500	0.2085 (3)
Cs4	0.3416 (4)	0.500	0.4305 (3)
Cu1	0.2761 (6)	0.000	0.1535 (5)
Cu2	0.1678 (7)	0.000	0.4847 (5)
Cu3	0.2293 (6)	0.000	0.3213 (5)
F1	0.316 (2)	0.213 (4)	0.266 (2)
F2	0.422 (3)	0.000	0.124 (2)
F3	0.214 (2)	0.281 (8)	0.066 (2)
F4	0.328 (4)	0.000	0.440 (3)
F5	0.137 (2)	0.208 (7)	0.377 (2)
F6	0.131 (3)	0.000	0.199 (2)
F7	0.000	0.500	0.000

TABLE 72

THERMAL PARAMETERS FOR HEPTA CESIIUM (CATENA-NONA DECAFLUORO HEXACUPRATE (II))

ATOM	U11	U22	U33	U12	U13	U23
Cs1	25.(3)	44.(4)	24.(3)	0.	6.(0)	0.
Cs2	25.(2)	37.(3)	24.(2)	0.	8.(1)	0.
Cs3	23.(2)	20.(2)	23.(2)	0.	8.(1)	0.
Cs4	21.(2)	31.(3)	14.(2)	0.	6.(1)	0.
Cu1	16.(4)	23.(5)	16.(5)	0.	11.(3)	0.
Cu2	31.(4)	48.(6)	6.(4)	0.	8.(3)	0.
Cu3	19.(3)	22.(3)	6.(3)	0.	9.(2)	0.
F1	33.(14)	7.(16)	44.(16)	-11.(12)	-3.(12)	-5.(12)
F2	53.(25)	28.(26)	16.(18)	0.	29.(17)	0.
F3	26.(13)	147.(40)	15.(12)	-10.(20)	6.(10)	-2.(19)
F4	47.(25)	41.(31)	33.(24)	0.	6.(19)	0.
F5	19.(13)	113.(37)	58.(20)	10.(19)	-9.(13)	29.(22)
F6	4.(16)	22.(24)	39.(22)	0.	-2.(14)	0.
F7	31.(28)	38.(40)	10.(26)	0.	6.(0)	0.

Anisotropic parameters are in the form:

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

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

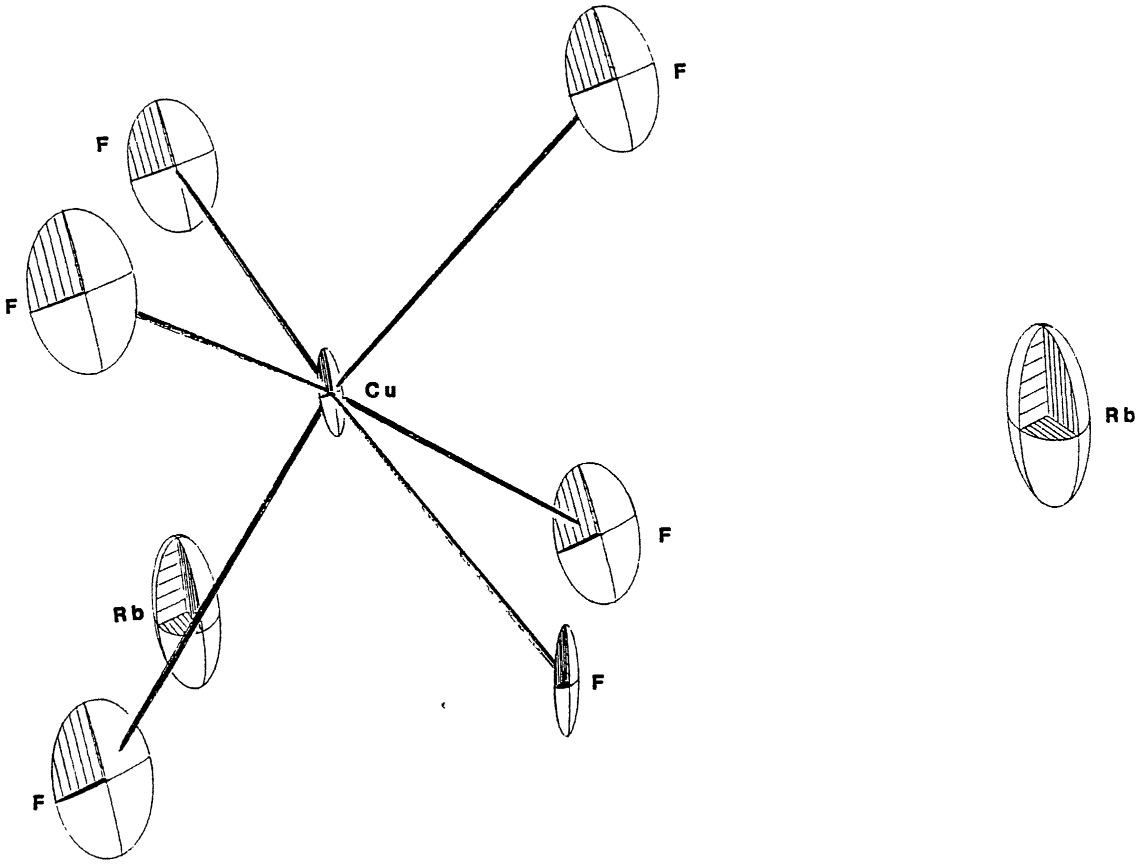
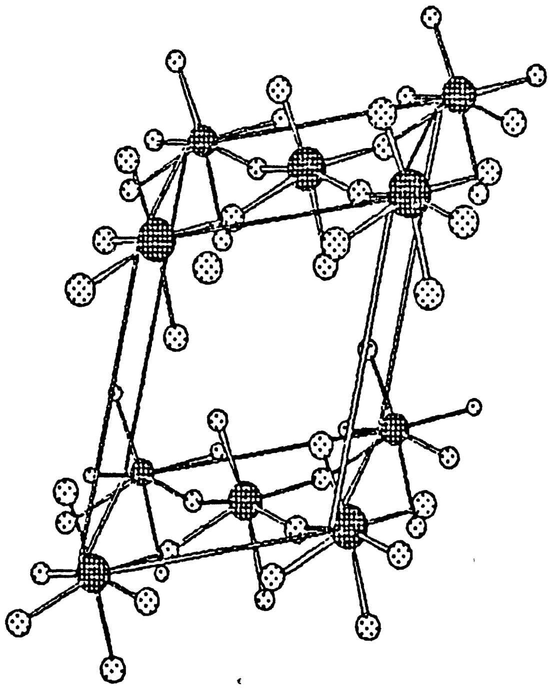


Figure 46. Dirubidium Catenatetrafluorocuprate



$Rb_4Cu_2F_8$

Cu(II) on mirror plane
Cu-F bridging - 2.176Å
2.120
terminal - 1.780
2.128

Figure 47. Packing Diagram of Dirubidium Catenatetrafluorocuprate

TABLE 73

CRYSTAL DATA FOR DIRUBIDIUM (CATENA-TETRAFLUOROCUPRATE (II))

Formula	Rb_2CuF_4
MWT	310.5 g mole^{-1}
a	6.016 (4) Å
b	6.016 (4)
c	7.321 (5)
α	90.0°
β	114.30 (4)
γ	90.0
V	241.5 (3) Å^3
F(000)	278
μMoK_α	239.83 cm^{-1}
λMoK_α	0.71069Å
D_{calc}	4.269 g cm^{-3}
Z	2
Obs. refl.	224
R	12.3
R_w	16.1
Space group	A2/m (Monoclinic)
Octants meas.	±h, +k, +l

TABLE 74

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR DIRUBIDIUM (CATENA-TETRAFLUOROCUPRATE (II))

Cu1-F1	2.1(1)	F1-Cu1-F2	172.(6)
Cu1-F2	1.8(1)	F1-Cu1-F3	82.(3)
Cu1-F3	2.2(1)	F1-Cu1-F3^{1}	82.(4)
Cu1-F3^{1}	2.1(1)	F1-Cu1-F3^{2}	82.(3)
Cu1-F3^{2}	2.2(1)	F1-Cu1-F3^{3}	82.(4)
Cu1-F3^{3}	2.1(1)	F2-Cu1-F3	93.(4)
		F2-Cu1-F3^{1}	104.(4)
		F2-Cu1-F3^{2}	93.(4)
		F2-Cu1-F3^{3}	104.(4)
		F3-Cu1-F3^{1}	163.(4)
		F3-Cu1-F3^{2}	87.(5)
		F3-Cu1-F3^{3}	89.(5)
		F3^{1}-Cu1-F3^{2}	89.(5)
		F3^{1}-Cu1-F3^{3}	91.(5)
		F3^{2}-Cu1-F3^{3}	163.(4)
		Cu1-F3-Cu^{4}	163.(5)

TABLE 74 (Continued)

[1] = symmetry operation (0.5 + x, 0.5 + y, z)

[2] = symmetry operation (x, -y, z)

[3] = symmetry operation (0.5 + x, 0.5-y, z)

[4] = symmetry operation (-0.5 + x, 0.5+y, z)

TABLE 75

POSITIONAL PARAMETERS FOR DIRUBIDIUM (CATENA-TETRAFLUOROCUPRATE (II))

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
Rb1	0.7201	0.0000	0.3051
Rb2	1.4397 (42)	0.0000	-0.2656 (28)
Cu1	1.0667 (41)	0.0000	-0.0011 (40)
F1	1.224 (20)	0.0000	0.318 (12)
F2	0.895 (21)	0.0000	-0.266 (16)
F3	0.832 (19)	0.250 (21)	0.045 (14)

TABLE 76

THERMAL PARAMETERS FOR DIRUBIDIUM (CATENA-TETRAFLUOROCUPRATE (II))

ATOM	U11	U22	U33	U12	U13	U23
Rb1	1.(3)	7.(6)	3.(5)	0.	2.	0.
Rb2	101.(15)	15.(11)	21.(9)	0.	22.(8)	0.
Cu1	24.(9)	1.(6)	2.(10)	0.	-6.(6)	0.
F1	35.(38)	1.(33)	0.(38)	0.	2.(30)	0.
F2	58.(30)	29.(63)	14.(51)	0.	-28.(49)	0.
F3	56.(30)	54.(32)	15.(40)	-10.(28)	-18.(25)	26.(33)

Anisotropic parameters are in the form:

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

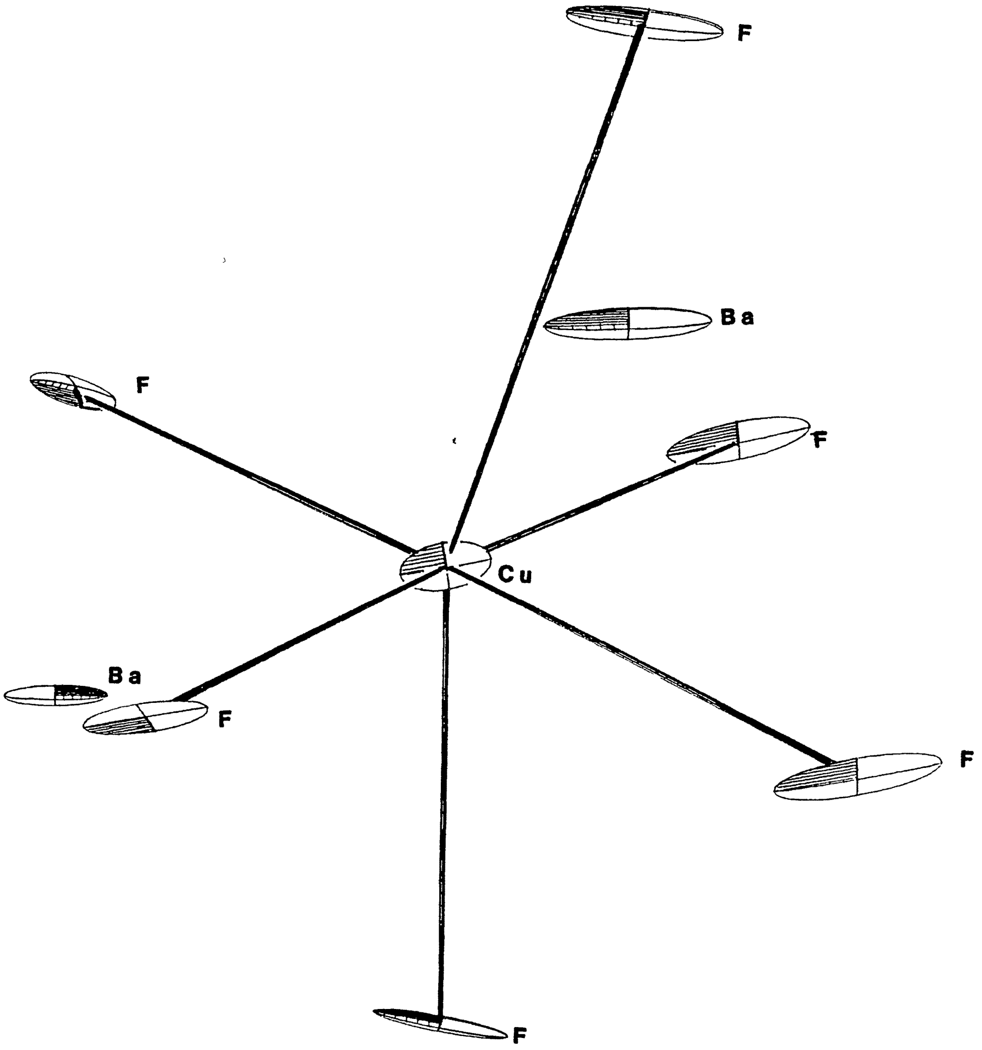


Figure 48. Barium Catenatetrafluorocuprate

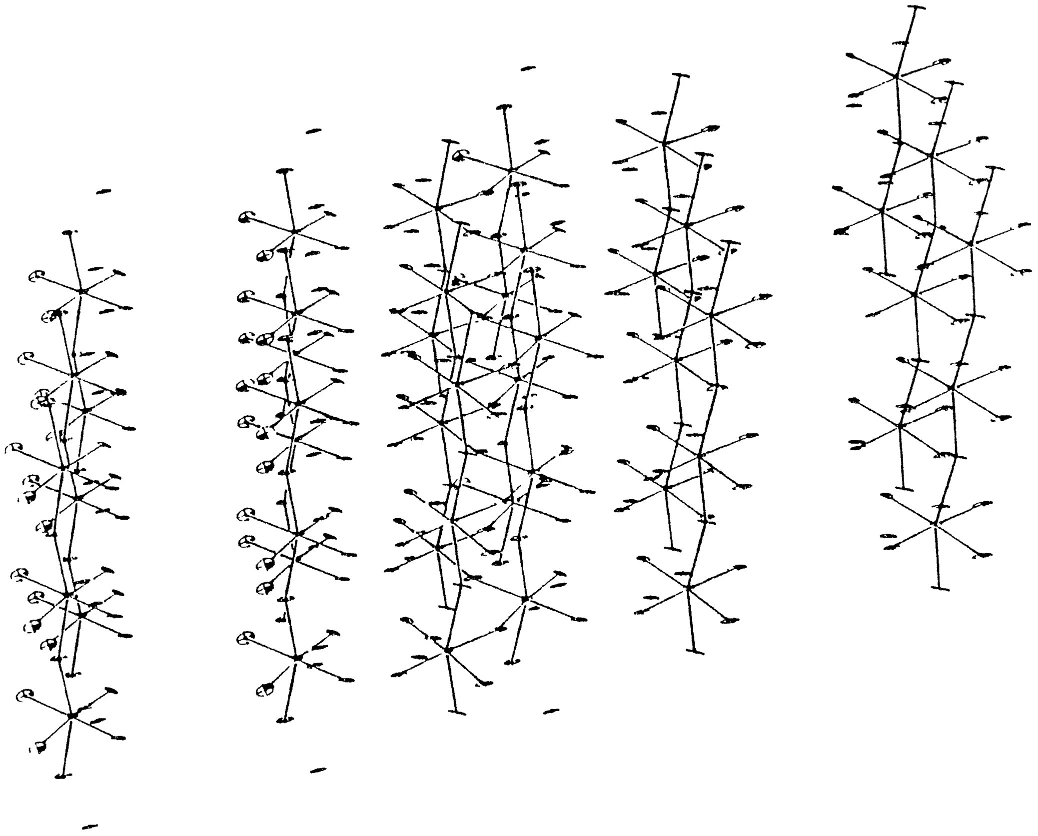


Figure 49. Packing Diagram of Barium Catenatetrafluorocuprate.

TABLE 77

CRYSTAL DATA FOR BARIUM (CATENA-TETRAFLUOROCUPRATE)

Formula	$BaCuF_4$
MWT	276.9 g $mole^{-1}$
a	4.485 (1) Å
b	5.549 (2)
c	7.346 (4)
a	90.0°
b	197.97 (3)
g	90.0
V	173.91 $Å^3$
F(000)	121
$mMoK_a$	86.63 cm^{-1}
$lMok_a$	0.71069 Å
D_{calc}	2.643 g cm^{-3}
Z	1
obs. refl.	506
R	10.9
R_w	10.4
Space group	P_21 (Monoclinic)
Octants meas.	±h, +k, +l

TABLE 78

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

Cu1-F1	1.95(4)	F1-Cu1-F2	92.(2)
C1-F2	1.91(4)	F1-Cu1-F3	83.(1)
Cu1-F3	2.23(3)	F1-Cu1-F4	177.(2)
Cu1-F4	1.87(4)	F1-Cu1-F1^{1}	94.(2)
Cu1-F1^{1}	1.92(4)	F1-Cu1-F3^{2}	82.(1)
Cu1-F3^{2}	2.31(3)	F2-Cu1-F3	97.(2)
		F2-Cu1-F4	91.(2)
		F2-Cu1-F1^{1}	174.(1)
		F2-Cu1-F3^{2}	94.(2)
		F3-Cu1-F4	96.(2)
		F3-Cu1-F1^{1}	85.(1)
		F3-Cu1-F3^{2}	162.(1)
		F4-Cu1-F1^{1}	83.(2)
		F4-Cu1-F3^{2}	99.(2)
		F1^{1}-Cu1-F3^{2}	86.(1)
		Cu1-F1-Cu1^{3}	156.(2)
		Cu1-F3-Cu1^{4}	162.(1)

TABLE 78 (Continued)

---

1 = symmetry operation -x, y-0.5, 2.0-z
2 = symmetry operation x-1, y, z
3 = symmetry operation x, y+0.5, 2.0-z
4 = symmetry operation 1+x, y, z

TABLE 79

POSITIONAL PARAMERTERS FOR BARIUM (CATENATETRAFLUOROCUPRATE)

ATOM	X(SIG(X))	Y(SIG(Y))	Z(SIG(Z))
Ba1	0.3630 (5)	0.0639	0.7257 (4)
Cu1	-0.0924 (12)	-0.4603 (13)	0.8156 (7)
F1	0.0286 (75)	-0.2567 (73)	1.0428 (47)
F2	-0.1859 (95)	-0.1857 (62)	0.6516 (57)
F3	0.4237 (60)	-0.4590 (79)	0.8663 (42)
F4	-0.1877 (92)	-0.6664 (72)	0.6042 (61)

TABLE 80

THERMAL PARAMETERS FOR BARIUM (CATENATETRAFLUOROCUPRATE)

ATOM	U11	U22	U33	U12	U13	U23
Ba1	1.(1)	1.(1)	24.(1)	0.(1)	4.(1)	-5.(1)
Cu1	4.(2)	0.(3)	12.(2)	0.(2)	1.(1)	-1.(2)
F1	9.(12)	5.(16)	31.(19)	6.(15)	3.(13)	-3.(15)
F2	6.(17)	5.(17)	16.(18)	0.(11)	10.(13)	2.(12)
F3	4.(10)	4.(17)	29.(14)	-2.(12)	10.(10)	-9.(14)
F4	1.(159	4.(14)	24.(18)	0.(12)	5.(13)	3.(13)

Anisotropic parameters are in the form:

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

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

CHAPTER VII

CONCLUSIONS

The research completed in this thesis encompasses the synthesis of 15 new compounds which contain anionic copper (I) halide complexes of formula $Cu_4X_6^{=}$ and $Cu_2X_4^{=}$, X=I, Br, in which copper is tricoordinate, or of formula CuX_2^{-}, X= Br, Cl in which copper is dicoordinate. The emission spectra of these materials confirm the basic premise that copper atoms in equivalent environments give rise to similar emission behavior. The substitution of more electronegative halides for less electronegative ones leads to emission at longer wavelengths. This presumably arises from a lowering of energy levels of the emitting state although emission from halide based excited states cannot be ruled out.

The prescence of a crystallographic symmetry element at copper leads to a change in the emission wavelength. This may arise from a change in available vibration states of the excited state.

Exploration of the possibilities of existance of mixed copper (II) copper (III) systems which might display solid state emission resulted in the synthesis of four previously unknown anionic cupric fluoride systems. These materials displayed complex patterns of halide linkage and patterns of successive Jahn-Teller distortion which may presage interesting magnetic phenomena.

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