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The crystal structure determinations of
 $\text{Cu}_5\text{C}_{110}(\text{C}_3\text{H}_7\text{OH})_2$, $\text{DyC}_{13}\cdot 6\text{H}_2\text{O}$ and
 $\text{Ag}(\text{P}(\text{OCH}_2)_3\text{CCH}_3)_4\text{C}_{10}\text{O}_4$

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THE CRYSTAL STRUCTURE DETERMINATIONS OF
 $\text{Cu Cl}_5 (\text{C}_3 \text{H}_7 \text{OH})_2$, $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ AND
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Iowa State University of Science and Technology, Ph.D., 1967
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THE CRYSTAL STRUCTURE DETERMINATIONS

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AND $\text{Ag}(\text{P}(\text{OCH}_2)_3\text{CCH}_3)_4\text{ClO}_4$

by

Josef Vendal Ugro Jr.

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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Of Science and Technology
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1967

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I. INTRODUCTION TO X-RAY CRYSTALLOGRAPHIC METHODS

A. Introduction

The determination of a crystal structure by x-ray diffraction methods allows the investigator considerable freedom in almost every phase of the solution. For this reason it was felt that the inclusion of a chapter on crystallographic methods would allow for a more concise method of presentation and would supply a guideline for persons who are unfamiliar with crystallographic methods. The emphasis in this chapter will be placed upon those methods which were employed in the solution of the crystal structures which follow.

B. Crystal Selection

Once a crystalline compound has been obtained, one must first select crystals which are suitable for x-ray diffraction measurements. This stage, often marks the difference between obtaining a successful solution to the structure and obtaining no useful results at all. The crystals chosen must be single, untwinned, unfractured, undistorted and if possible, well formed. They should, in general, be approximately 0.2 mm on a side. This latter requirement is, of course, impossible for crystals which normally grow as needles or thin plates. In these cases a compromise must be made. No single dimension can be allowed to exceed 0.65 mm. This limit being imposed

by the maximum dimensions of the x-ray beam at the crystal for a General Electric single crystal orienter, equipped with the largest collimator available at this installation. For smaller collimators the maximum allowable size must be diminished.

The detection of a twinned, distorted, or deformed crystal can generally be accomplished by the use of optical microscopes, polarizing microscopes, or through x-ray photographic methods. Many excellent texts illustrating the use of the polarizing microscope (1) are available, so this subject will not be dealt with here. Various indications of poor crystals can be obtained from x-ray photographs. Photographic methods, however, will not necessarily indicate twinning even if it is present (2). Usually a poor crystal will exhibit either irregular, elongated or multiple spots on one or more x-ray photographs. A crystal whose x-ray photographs exhibit one or more of these features should be immediately rejected and the search for a more suitable crystal continued.

C. Crystal Mounting

When a suitable crystal has been found it is then necessary to mount the crystal so that x-ray measurements can be undertaken. The particular mounting method is strongly dependent on the properties of the crystal (3). For crystals which are stable, it is usual to glue the crystal on the end of a small glass fiber using Duco cement mixed with amyl

acetate, to delay the hardening; clear fingernail polish is also suitable. In mounting crystals by this method a minimum quantity of glue should be used. Also the crystal must be mounted on the very tip of the fiber in such a manner that neither the incident nor diffracted x-ray beam passes through the fiber. It goes without saying that the crystal must not be soluble in the glueing material. For unstable crystals we again have a variety of methods of mounting depending on the type of instability. If the crystal is unstable to water vapor we try to find a substance such as petroleum jelly or Canada balsam which is impervious to H_2O and in which the crystal is insoluble, then mount the crystal inside a Lindemann glass capillary either by wedging or using the adhesive properties of the coating to make the crystal adhere to the side of the capillary. This latter technique is necessary for unstable crystals of dimension less than .2 mm. A modification of this technique must be used with crystals which are unstable with respect to the atmosphere or for which an adequate coating cannot be found. In these cases, the crystal is mounted and sealed in a capillary while in the presence of an inert atmosphere such as N_2 or Ar. In some unusual cases crystals are unstable towards loss of solvent or other component. In these cases where the loss is a function of the loss in vapor pressure of the component over the crystal, this component may be included, in small quantities, in the sealed capillary.

The $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$, $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ crystals were all unstable. The $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$ presumably decomposing to $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ while the $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ structures were deliquescent. In all these cases the crystal was coated with a thin layer of petroleum jelly before sealing in a glass capillary. The $\text{Ag}[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_4\text{ClO}_4$ crystal was glued on the end of a thin glass fiber with clear fingernail polish.

In the use of various coating materials one must exercise great care in the selection of the coating material and the amount used. All of these substances will tend to increase the magnitude of the background radiation, due to amorphous scattering, and if ordered may exhibit various diffraction maxima (3).

D. Space Group Determination

The next phase of the crystal structure determination involves the determination of the space group and of the lattice constants. Many texts are available describing the techniques for the space group determinations (4).

E. Density Measurement

A density measurement is necessary to determine how many molecules or formula units are present in one unit cell. The density measurements are usually performed by the flotation method (3). This method consists of the selection of a single crystal then finding the mixture of two miscible liquids, of known density, for which the crystal will remain suspended. The density of this mixture may now be measured

by the pycnometer method (3). For cases where great accuracy is not required and where the approximation that the partial molar volume of the liquids in the mixture is equal to their original volume is valid, the density of the crystal may be calculated as follows:

$$d_c = \frac{V_1 d_1 + V_2 d_2}{V_1 + V_2}$$

where V_1 , V_2 are the volumes of liquids 1 and 2 in the mixture, d_1 and d_2 are the densities of the liquids, and d_c is the density of the crystal. The number of formula units present in a unit cell can then be calculated from:

$$Z = \frac{d_c \cdot N_o \cdot V_c}{FW}$$

where Z is the number of molecules per unit cell, N_o Avogadro's number, V_c is the volume of the unit cell in cubic centimeters and FW is the formula weight in grams/mole.

Many excellent clues to the position of the atoms and the orientation of the molecules in the unit cell may be obtained from the consideration of the space group, lattice constants and the number of molecules in the unit cell.

F. Collection of Data

Perhaps the most critical stage of the structure determination is the collection and treatment of the intensity data. Using a General Electric XRD-5 x-ray unit equipped with

a single crystal orienter and scintillation counter, three methods of data collection are in general use. These methods are the stationary crystal-stationary counter, the moving crystal-stationary counter (ω scan) and the moving crystal-moving counter (2θ scan) methods (5). An excellent critical comparison of these methods has been given by Alexander and Smith (6).

The easiest way to provide a description of these methods is through a consideration of the motions relative to reciprocal lattice of the crystal and the sphere of reflection (7). With reference to Figure 1, the crystal is turned about the axis Q through an angle ω_0 , chosen such that the desired reciprocal lattice point $P_0(hk\ell)$ on the equatorial net intersects the sphere of reflection. The incident and diffracted beam vectors are \bar{s}_0 and \bar{s} respectively, and the reciprocal lattice vector of the diffracting point $P_0(hk\ell)$ is $\lambda \bar{H}$ with the radius of the reflecting sphere being unity. When the crystal is turned to the position ω_0 and the receiver set at the angle $2\theta_0$, a narrow diffracted x-ray beam enters the receiver. With the stationary crystal-stationary counter method, I_p , the peak intensity can be obtained by recording the number of counts collected in a fixed length of time. If we now off-set the angular position of the crystal by an amount $\delta\omega$, then rotate the crystal with a uniform angular velocity from $\omega_0 - \delta\omega$ to $\omega_0 + \delta\omega$, we have the essence of the moving crystal-stationary counter method. As the crystal

passes through the reflecting angle ω_0 , the point P_0 intersects the sphere of reflection. The number of counts collected during the scan is a measure of the integrated intensity. If the motions of the crystal and receiver are adjusted such that the angular velocity of the receiver is twice that of the crystal, then the receiver scans the reciprocal space along the direction of a central lattice row again passing through the point P_0 . If the receiver collects the counts of a scan, using uniform velocities, with a scan from $2\theta_0 - \delta 2\theta$ and $\omega_0 - \delta\omega$ to $2\theta_0 + \delta 2\theta$ and $\omega_0 + \delta\omega$, we again have a measure of the integrated intensity and have the description of the motion involved in the moving crystal-moving counter method. The integrated intensity is a measure of all x-ray energy which a given crystal can diffract in the direction corresponding to the given reflection.

The stationary crystal-stationary counter method, although in general the least precise, has as its main asset the feature that data can be collected much more rapidly than with any of the other methods. In dealing with structures where large amounts of data must be collected or where an excessive amount of decomposition of the crystal takes place, it is advisable to collect the data using the stationary crystal-stationary counter method. The latter cause was responsible for the decision to collect intensity data on the $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$ structure by this method. Even using this method the crystal decomposed by 27 % before the collection of data was completed.

In the stationary crystal-stationary counter method it is assumed that the peak intensity is proportional to the integrated intensity. This is approximately true (6) for reflections occurring at lower 2θ angles, when a large take off angle and large incident and diffracted beam apertures are used. Generally an empirically derived correction should be determined and applied in order to insure that the resulting intensity is a measure of the integrated intensity (6).

The moving crystal-moving counter method, considered to be the most precise (6), was used in the data collection for the structures $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{HOCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ag}[\text{P}(\text{OCH}_2)_3\text{CCH}_3]_4\text{ClO}_4$.

The calculation of the angle settings for the single crystal orienter for all these structures were performed using a program written by D. E. Williams^{*}.

G. Corrections to Data

The determination of the intensity of the background radiation is usually performed by an omega offset method. When a significant number of background measurements have been accumulated, a plot of average background versus 2θ is prepared. Generally it is advisable to determine whether the background is also a function of the angles χ and

^{*} Willaims, D. E., Iowa State University, Ames, Iowa. SCO-6, a program to calculate angular settings for the General Electric XRD-5 written for the IBM 7074 and 360. Private Communication. 1964.

φ . If this is true then a series of plots must be made to give the background for any angular setting.

A correction to the total count, due to non-linearity of the counting system, must be applied when high counting rates occur. The correction is usually empirically derived. For this installation the relation

$$C_T = \frac{C_T^i}{(1.0 - C_T^i \times 10^{-7})} ,$$

where C_T is the total count after correction and C_T^i the total count before correction was found to be suitable. The correction formula is not applied unless $C_T^i \geq 10^5$ counts/100 seconds.

The intensity data for all the structures presented in this thesis were corrected for absorption. A program which calculated the transmission factor for a given reflection, once the dimensions, shape, orientation and linear absorption coefficient have been specified, was written by Busing and Levy (8). This program was modified for the IBM 7074 by Dr. D. R. Russell and for the IBM 360 by this author.

Lorentz and polarization corrections were applied to all data using the relation:

$$L_P = \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} .$$

When decomposition of the crystal occurs during the collection of intensity data it is necessary that all data be scaled to the same basis. Normally during the data

collection period the intensities of certain selected reflections may be used as a measure of the change that has occurred in the intensity of all reflections. This assumes that all the "standard" reflections exhibit the same rate of decline, on a percentage basis. In cases where this is not even approximately true one must ascertain which reflections are to be treated using which "standard" curve. When the standards are of the same form the intensity of a reflection measured at time, t , is multiplied by the ratio of

$$I_{\text{StD}}(0)/I_{\text{StD}}(t),$$

where $I_{\text{StD}}(0)$ is the intensity of the standard reflection at time zero and $I_{\text{StD}}(t)$ the intensity at time, t . This corrects the intensity of the reflection to that which would, presumably, have been measured at time zero.

The final correction usually applied to the intensity is a correction for streak. Streak is diffracted radiation of wavelength other than that of the characteristic radiation. With the equipment present at this laboratory the radiation is generally of longer wavelength than that of the characteristic radiation. The principal causes of the streak are the presence, in the incident beam, of non-characteristic radiation. Correction for the presence of streak radiation is generally only required for densely packed reciprocal lattice rows.

The method used to calculate the streak contribution for these structures is that of Fitzwater and Benson^{*}, which is similar to that of Rundle and Williams (9).

The streak contribution for a given reflection is given by the relation

$$I_S^{(m)} = \sum_{n > m} \frac{K_2(\lambda_m) |F_m|^2 L_p(\theta_n) \cos(\theta_n)}{\sin(\theta_n)} .$$

Where n refers to the order of the reflection being considered, m is the order of reflections having the same prime indices as the reflection being considered, $|F_m|$ is the structure factor for the m^{th} reflection, $L_p(\theta_n)$ refers to the Lorentz polarization factor calculated at the Bragg angle, θ_n for the n^{th} order reflection and $m = \frac{n}{m} \lambda_0$, where λ_0 is the wavelength of the characteristic radiation. The quantity $K_2(\lambda_m)$ is an experimentally derived quantity and is different both for each crystal and each set of conditions, but is essentially independent of the indices of the reflection. It may be calculated from experimental data taken on a reflection having prime indices using the relation:

$$K_2(\lambda_s) = \frac{I_s \sin(\theta_s) L_p(\theta_o)}{L_p(\theta_s) \cos(\theta_s) I_p} .$$

Where I_p is the intensity measured at the peak angular settings, θ_o is the Bragg angle for the reflection, I_s is the intensity

^{*} Benson, J. and Fitzwater, D., Iowa State University, Ames, Iowa. A formula for streak correction in single crystals. Private communication. 1965.

measured at some angle θ_s with $\theta_s > \theta_0$ and $L_p(\theta_0)$ is again the Lorentz polarization factor calculated at the angle θ_0 .

H. Treatment of Data

By treatment of data is meant the mathematical operations applied to the intensity data to convert to structure factor data and the assignment of the weight or reliability of a given measurement.

Let us represent the total measured counts for the reflection by C_T , the background counts, from a table look-up using the average background versus angular settings, by C_B , and the counts calculated for streak by C_S . Then the intensity, I , of a given reflection is $I = C_T - C_B - C_S$.

The structure factor, on a relative scale, is given by

$$F = \sqrt{\frac{I}{L_p \cdot A}}, \quad (1)$$

where L_p is the Lorentz and polarization correction factor and A is the transmission factor.

A reflection is considered to be "unobserved", (i.e. the number of counts obtained is not large enough that it can be assured that a reflection is actually present at the point of measurement), when $I \leq K\sigma_{\text{stat}}$ where $\sigma_{\text{stat}}^2 = C_T + C_B + C_S$, and K is an arbitrary constant, generally chosen within the range 1.67 to 3. When K is chosen as 3, on a statistical basis one should be 99.9 % certain that the number of counts obtained corresponds to a reflection. Using a value of 1.0 one should be 67 % certain. These

percentages should only be used as a rough guide for this type of work since they include only errors of a random type. In actuality the σ^2_{stat} only represents the variance which may be due to counting errors alone.

An "unobserved" reflection is generally assigned an F of zero and either assigned a very small weight or given zero weight in subsequent least square refinement, although they are used in the determination of a preliminary model for the crystal structure.

"Observed" reflections (i.e. those with $I > K\sigma_{\text{stat}}$) are treated somewhat differently. The relations used can be derived starting with the fundamental equations,

$$F^2 = \frac{I'}{Lp} \text{ where } I' = (C_T - C_B - C_S)/A. \quad (2)$$

It is well known from statistics that the variance σ^2_G in a quantity $G(X_1, X_2, \dots, X_i)$ is given by the relation:

$$\sigma^2_{G(X_1, X_2, \dots, X_i)} = \sum_i \left(\frac{\partial G}{\partial X_i} \right)^2 \sigma^2_{X_i}.$$

Using this relation the variance in I' is given by

$$\sigma^2_{I'} = \frac{1}{A^2} [\sigma^2_{C_T} + \sigma^2_{C_B} + \sigma^2_{C_S} + (I')^2 \sigma^2_A]. \quad (3)$$

The variance for the quantities in the above equations are given by the relations:

$$\begin{aligned} \sigma^2_{C_T} &= C_T + [C_T \cdot F(C_T)]^2 \\ \sigma^2_{C_B} &= [C_B \cdot F(C_B)]^2 \\ \sigma^2_{C_S} &= [C_S \cdot F(C_S)]^2 \\ \sigma^2_A &= [A \cdot F(A)]^2, \end{aligned}$$

where $F(X)$ is the estimated error in the quantity X . Notice that the variances for C_B , C_S and A include only systematic errors since these quantities are all calculated rather than measured individually. Now the variance in F is given by the relation

$$\sigma^2_F = \frac{1}{4} \frac{\sigma^2_{I'}}{I' L_p}. \quad (4)$$

There is a second method of treatment of data which is commonly used at this installation. In this method unless I' is calculated as a negative quantity, equation 2 is used. If I' is negative, F is set to zero. The $\sigma^2_{I'}$ is calculated as before. For this method equation 4 cannot be used since I' equal to zero gives an undefined quantity for σF . Instead the standard deviation for F is calculated from the equation

$$\sigma F = \sqrt{\frac{I' + \sigma I'}{L_p}} - F. \quad (5)$$

This equation is derived starting with equation 2: it is then assumed that small finite changes are made in I' and F , that is

$$\frac{I' + \Delta I'}{L_p} = (F + \Delta F)^2.$$

Solving for ΔF and using the assumptions that $\sigma F = \Delta F$ and $\sigma I' = \Delta I'$ we arrive at equation 5. This method neatly avoids the problem encountered as I' approaches zero, and supplies a consistent method for the calculation of the standard deviation in F throughout the range of I' .

Equation 5 may also be substituted for the equation 4 used in the first method of data treatment. In this case

for "unobserved" reflections $\sigma F = \sqrt{\frac{\sigma I'}{Lp}}$.

The first method of data treatment combined with the modification of the last paragraph was used for all the structures presented in this report. The weight of each reflection is $W = \frac{1}{\sigma^2 F}$.

I. Solution and Refinement

The general methods of the solution and refinement of structures are given in various texts (10, 11). Information pertaining to the solution and refinement of the structures considered in this report can be found under the appropriate sections.

In following sections the term agreement factor will be used extensively. The value for the agreement factor is given by the relation:

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad (6)$$

where the summations are over all reflections included in the refinement.

A weighting scheme analysis is usually performed in the latter stages of the refinement. This test is performed to judge the adequacy of the weighting scheme under the assumption of mostly random errors in the data. Customarily a plot of $W ||F_o| - |F_c||^2$ versus $|F_o|$ or $\frac{\sin \theta}{\lambda}$ is made. If the weighting scheme is correct a horizontal straight line is obtained. If the weighting scheme is not correct a

curved or sloped line will be obtained. This type of error in the weighting scheme will result in a second order error in the standard errors of the parameters. Generally the weighting scheme is corrected such that a horizontal line with the value of $w||F_o| - |F_c||^2 = 1.0$.

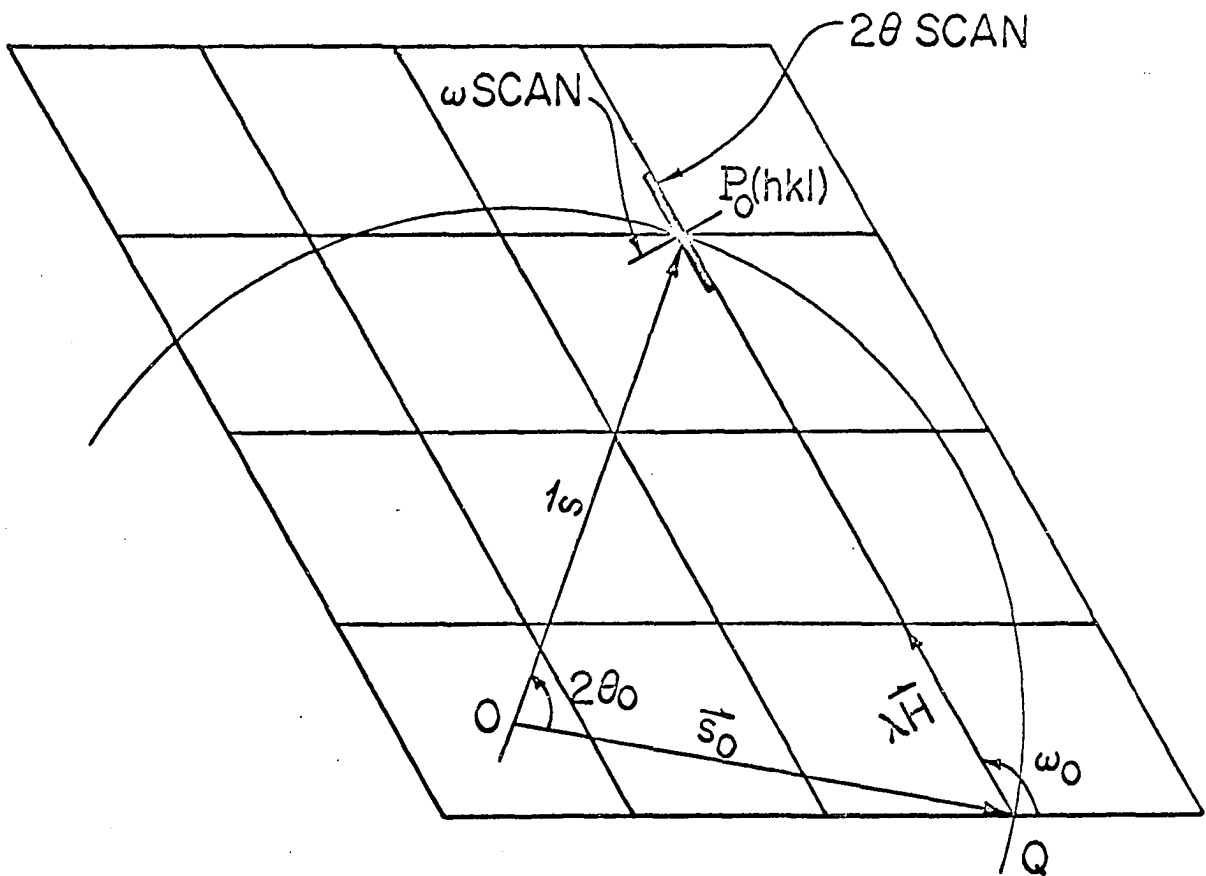


Figure 1. Geometry of various data collection methods

II. THE REDETERMINATION OF THE CRYSTAL STRUCTURE

OF $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$

A. Structure and Properties of Copper (II) Compounds

1. Introduction

A short survey of the structure and properties of copper (II) compounds is presented in this section to aid in the establishment of the location of the compound $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$ in the overall framework of copper (II) compounds. This will be followed by a literature review of the copper (II) chloride complexes.

2. Stereochemistry

Copper (II) has the electronic configuration ($3d^9$). The stereochemistry of copper (II) is greatly influenced by the Jahn-Teller effect (12), i.e. that any nonlinear molecular system which is in a degenerate electronic state is unstable and will undergo a distortion which will remove the degeneracy. In the case of copper (II) in an octahedral environment, the e_g levels $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are degenerate and contain three electrons. A tetragonal distortion will split these levels by decreasing the energy of the $3d_{z^2}$ level while raising the energy of the $3d_{x^2-y^2}$ level. The $3d_{z^2}$ then contains two electrons while the $3d_{x^2-y^2}$ contains only one, resulting in a decrease in the energy of the system. Thus copper (II) is generally found in a tetragonally distorted octahedral

configuration or, in the limit of such distortion, a square planar configuration.

Recently a number of structures have been determined where the copper (II) has a five coordinate environment. Two of these structures have a trigonal bipyramidal (13, 14) configuration, the remainder have a square pyramidal configuration with the copper raised slightly above the base (15). Usually the square pyramidal configuration is favored where there are steric reasons that preclude the formation of a trigonal bipyramid.

3. Magnetic properties

Copper (II) compounds would be expected to have a magnetic moment, in the distorted octahedral configuration, of 1.9B.M, with a spin only moment of 1.73B.M, corresponding to one unpaired electron. In the tetrahedral configuration the expected value is 2.2B.M at room temperature, but this value has not been observed in any compounds.

In actuality compounds of copper (II) can be classified by magnetic properties, into two groups; those having normal magnetic moments and those having subnormal magnetic moments. The first group is of little interest, but the second group has been the object of considerable controversy. The group having subnormal moments may also be broken down into two groups; those having a direct copper to copper interaction and those having a super-exchange type interaction (16) between copper ions.

The first group consists of compounds like the copper (II) salts of carboxylic acids (17) or dioxane addition compounds of some copper alkoxides (18). Many of these compounds have average magnetic moments which are less than the spin only moment (1.73B.M). Compounds of this type are all binuclear, having a copper-copper approach on the order of $2.6\overset{\circ}{\text{Å}}$. The copper to copper approach in copper metal is $2.56\overset{\circ}{\text{Å}}$. The consensus of opinion, for a time, was that some type of bond was formed between the copper (II) ions. The nature of the bond, particularly in $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ was a matter of considerable controversy and still has not been completely elucidated. Figgis (19) and Boudreaux (20) using different approaches reached the conclusion that the bond formed was a δ bond ($3d_{x^2-y^2}$, $3d_{x^2-y^2}$), while Forster and Ballhausen (21) tentatively proposed that a σ bond ($3d_{z^2}$, $3d_{z^2}$) would be favored. More recent calculations by Kokaszka (22) using a hole formalism and Hansen and Ballhausen (23) using as a model two weakly coupled chromophores, have been successful in accounting for the position and polarization of the bands in the spectra as well as the values of the anisotropic g factors, without the inclusion of a copper to copper bond.

Copper (II) compounds which have a super-exchange interaction are characterized by somewhat larger copper-copper distances, on the order of $3.0\overset{\circ}{\text{Å}}$ or greater, and the space between the neighboring copper (II) ions is occupied by one or more diamagnetic atoms. Typical examples of this

type of compound are CuO with a magnetic moment of 0.78B.M, CuS and CuSe which are diamagnetic, halogen or hydroxyl bridged complexes and copper (II) formate tetrahydrate. The phenomenon of super-exchange should be regarded as incipient covalent bonding, and in one model (24) is formally equivalent to a molecular orbital picture. Recent articles by Anderson (25), by Goodenough (26) and by Nesbit (27) give a clear theoretical account of the process. Super-exchange requires not only that overlap between metal orbitals and the carrier orbitals be permitted by symmetry, but that the overlap be significant. Super-exchange pathways for virtually all systems are thought to be π pathways, resulting from overlap of the $3d_{xz}$ or $3d_{yz}$ metal orbitals with the p_z orbitals on the bridge atom or with the π system of the bridging group.

B. Literature Review of the Copper (II)

Chloride Compounds

The red compound CuCl_2 forms an infinite chain of the type $(\text{CuCl}_2)_n$ (28). Each copper atom within the chain is bonded to four chlorine atoms at distances of $2.3\overset{\circ}{\text{A}}$, thus sharing two chlorine atoms with each adjacent copper atom in the chain. In addition each copper atom has two chlorine atoms from adjacent chains at $2.95\overset{\circ}{\text{A}}$, completing a very distorted octahedral configuration. The compound is antiferromagnetic with a $\mu_{\text{eff}}(28.9^\circ\text{K}) = 1.61\text{B.M.}$ (29)

The compound Cs_2CuCl_4 (30) possesses discrete $(\text{CuCl}_4)^=$ ions. The ions have a distorted tetrahedral structure, the tetrahedron being distorted such that the S_4 , but not the C_3

axis, is preserved. The magnetic moments of the $(\text{CuCl}_4)^{2-}$ ion with a number of organic bases have been given (31). They range between 1.8 and 2.0 B.M. These values are considerably below the values predicted for tetrahedrally coordinated copper (II) complexes (2.2 B.M.).

The red compounds KCuCl_3 and NH_4CuCl_3 (32) contain stacks of $(\text{Cu}_2\text{Cl}_6)^{2-}$ ions. Each dimer has approximately D_{2h} symmetry. The two copper atoms in the dimer share two chlorine atoms at 2.32\AA and are each bonded to two other terminal chlorine atoms at 2.25 and 2.27\AA . In addition each copper has, from adjacent $(\text{Cu}_2\text{Cl}_6)^{2-}$ units, chlorine atoms directly above and below it, at 3.11 and 2.94\AA . The chlorine atom at 2.94\AA is of the terminal type and corresponds to the chlorine in the original dimer which has a copper to chlorine distance of 2.27\AA . The other chlorine is of the bridging type. A magnetic investigation of KCuCl_3 has been performed by Maass (33).

The compound CsCuCl_3 (34) consists of infinite helical chains of formula $(\text{CuCl}_3)_n^{n-}$ with each copper atom sharing one chlorine atom with another copper atom in the chain. A relatively short copper to copper approach is observed (3.062\AA); however it is proposed from the results of overlap calculations that no direct interaction occurs. The magnetic moment for this compound is normal down to 80°K (35).

The compound $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ contains stacks of hydrated dimer units of formula $[\text{Cu}_2\text{Cl}_6(\text{H}_2\text{O})_2]^-$ (36). Adjacent copper atoms in the dimer share two chlorine atoms at 2.3\AA .

In addition each copper has a water molecule and a terminal chlorine atom, from an adjacent dimer, in positions corresponding to a distorted octahedral configuration with distances of 2.60 and 2.92 $\overset{\circ}{\text{A}}$ respectively. The compound remains paramagnetic to about 5.9°K, where magnetic ordering, presumably antiferromagnetic, takes place (36).

Recently the structures of $\text{Cu}_2\text{Cl}_4(\text{CH}_3\text{CN})_2$, $\text{Cu}_3\text{Cl}_6(\text{CH}_3\text{CN})_2$ and $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$ have been solved by Willett (37). All these compounds contain stacks composed of units with the above formulae which exist as extended bridge networks and are approximately planar. Each copper has approximately a square planar configuration within the unit. In addition each copper has additional chlorine atoms from adjacent chains in positions corresponding to a distorted octahedral configuration. A comparison of distances in these structures is given in Table 1. To date there has been no magnetic work performed on these compounds.

All of the crystals containing such a bridge system are pleochroic. Maximum absorption occurs when the electric vector of polarized light is approximately parallel to the Cu-Cu vector.

It has been suggested (36) that anhydrous CuCl_2 and other similarly bridged structures (infinite planar chains, symmetrically bridged) should contain ferromagnetically aligned chains. The antiferromagnetism of CuCl_2 would then be attributed to interactions between chains. In asymmetric, weakly bridged halides like $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$, the nearest

neighbor interaction is antiferromagnetic (38).

The crystal structure of $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$ was redetermined to supply a better model for the structure than that given by Willett (37). This will greatly assist in the interpretation of the magnetic data, when it is done. Willett's data were plagued with experimental errors due to poor crystals and a large decomposition problem. For this determination somewhat better crystals were obtained. The crystals were carefully protected from moisture in the atmosphere. The large decomposition was still present, but was minimized by rapid collection of the intensity data.

C. Structure Determination

1. Preparation and properties

Flat red-brown needles of the compounds $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$ were prepared by evaporation of a solution of anhydrous cupric chloride in n-propanol at 50°C. The crystals are hygroscopic and pleochroic. The density of the crystals was determined by the flotation method to be 2.35g/cc.

2. X-ray data

Examination of oscillation, Weissenberg and precession photographs established that the crystal class was monoclinic with Laue symmetry C_{2h} . The systematic extinctions,

$$\begin{aligned} [h0l] & \quad l \neq 2n \\ [0k0] & \quad k \neq 2n \\ [hkl] & \quad \text{none} \end{aligned}$$

implied that the crystals belonged to the space group $p2_1/c$,

with $a = 10.244 \pm .007\text{\AA}$, $b = 6.025 \pm .008\text{\AA}$, $c = 20.41 \pm .015\text{\AA}$, $\beta = 115.48 \pm .03^\circ$ and $z = 2$. The lattice constant data were obtained on a General Electric XRD-5 x-ray unit equipped with a single crystal orienter and scintillation counter. Angular measurements were made on reflections in the back reflection region, using chromium radiation. The lattice constants were then obtained by least squares extrapolation (39) of the data using the Nelson-Riley error formula (40).

Complete three-dimensional x-ray data to $\frac{\sin \theta}{\lambda} = .705$ were taken with zirconium filtered molybdenum K_α radiation using the above mentioned equipment. The stationary crystal-stationary counter technique was employed (5) with a 40 second count at the peak setting. Background counts were determined from a plot of average background versus 2θ .

Corrections to the data were applied as shown in Chapter I, section G. The intensities of the 2.0.0, 3.0.6 and 2.1.5 reflections were followed as standards. Measurement of the intensities of these reflections were made about every four hours during the data collection period. The intensity of each reflection exhibited a near linear decline at a rate of 0.1% per hour and an overall decline of 27%.

3. Structure determination and refinement

The model determined by Willett (37) was tested using a Patterson map. The map indicated that Willett's positions for the three crystallographically independent copper atoms and

four of the chlorine atoms were acceptable. Least squares refinement on the IBM 7074 using Fitzwater's least squares refinement program^{*} was carried out using the 700 strongest reflections and gave an agreement factor of 0.19. A three-dimensional electron density map was calculated using Ledet's MFOUR program (41). This map indicated the positions of the remainder of the atoms. Anisotropic least square refinement and weighting scheme adjustment (Chapter I, section I) on the 1695 "observed" reflections resulted in a final agreement factor of 0.0628. Several reflections were removed because they appeared to have been measured incorrectly. The scattering factors of Hanson *et al.* (42) were used throughout the refinement. Table 1 contains the final positional and thermal parameters along with their standard deviations. Figure 2 gives the observed and calculated structure factors for the "observed" reflections. Tables 3 and 4 contain the interatomic distances and angles, calculated using Busing and Levy's program ORFFE (43).

4. Description of the structure

The structure consists of essentially planar formula units as shown in Figure 3. Deviations from planarity are also indicated in this Figure. Table 5 gives the equations of significant least squares planes in the formula unit and

^{*} Fitzwater, D. R., Iowa State University, Ames, Iowa. A crystallographic full matrix least squares program. Private communication. 1963.

distance, from the plane, of involved atoms, Figure 4 indicates the packing of the formula units in the crystal.

The overall symmetry of a formula unit is C_i , the central copper atom (Cu_1) sitting on the center of symmetry. This copper has a square planar configuration, with bridging type chlorine atoms from other units located in positions corresponding to a tetragonally distorted octahedral configuration at a distance of 3.048\AA . The Cu_2 and Cu_3 atoms must be considered five coordinate with square pyramidal geometry. The copper atoms are slightly out of the basal plane. The copper to apical chlorine distances are 2.680 and 2.691\AA respectively. The apical chlorine atoms are of the terminal type (Cl_5). Bridge type chlorine atoms occupy positions on the side of the basal plane opposite the apical chlorine atom at distances of 3.157 and 3.135\AA respectively.

The n-propanol carbon atoms were found to have large and very anisotropic thermal parameters; for this reason Table 3 also contains the carbon to carbon distances corrected for thermal motion.

5. Discussion of structure

Within one formula unit the bonding is normal for the copper (II) chloride compounds. The copper-chlorine bridge distances average 2.288\AA . The deviations from the average appear to be of borderline significance.

The most significant feature of the structure is the 5 coordination exhibited by the Cu_2 and Cu_3 atoms. The

distorted square pyramidal configuration is not unusual for copper (II) compounds. In this case it appears that the tendency of copper (II) to form square planar compounds and the steric restrictions imposed by packing as well as bridging are sufficient to allow one chlorine to make a close approach to the square planar copper but will not allow two chlorines to approach from opposite sides. The distances of 2.680 and 2.691^oÅ are the closest approach of apical chlorine atoms to distorted square pyramidal copper atoms in any of the copper chloride compounds studied to date.

If the view of Rundle (36) that in the bridged system the unpaired electrons are ferromagnetically aligned and an antiferromagnetic interaction occurs between the chains is correct, then this compounds should exhibit strong antiferromagnetic behavior.

The absence of magnetic data on copper (II) chloride complexes precludes more detailed discussion. Magnetic studies and perhaps neutron diffraction studies on a series of copper (II) chloride complexes may provide very useful information on the nature of the magnetic interaction in copper (II) compounds.

Table 1. Distances in copper chloride complexes

Compound	Chlorine Type ^b	Representative Cu-Cl Distances (Å)
KCuCl ₃	A	2.318
	B	2.267, 2.248
	C	3.11
	D	2.94
NH ₄ CuCl ₃	A	2.32
	B	2.25, 2.26
	C	3.19
	D	2.99
LiCuCl ₃ · 2H ₂ O	A	2.30
	B	2.258, 2.284
	D	2.92
Cu ₂ Cl ₄ (CH ₃ CN) ₂	A	2.30
	B	2.27
	C	3.08
	D	2.79
Cu ₃ Cl ₆ (CH ₃ CN) ₂	A	2.28
	B	2.26
	C	3.19
	D	2.714, 3.006
Cu ₅ Cl ₁₀ (C ₃ H ₇ OH) ₂ ^a	A	2.27
	B	2.287
	C	3.01 - 3.148
	D	2.650, 2.641

^aFrom structure determination of Willett (37).

^bCl-Type A Cl, bridge type, within primary unit
 B Cl, terminal type, within primary unit
 C Cl, bridge type, in adjacent unit
 D Cl, terminal type, in adjacent unit.

Table 2. Parameters for $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2^a$

Atom	X/a	Y/b	Z/c	β_{11}^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu ₁	0.0	0.0	0.0	.00679 (.00028)	.01217 (.00049)	.00120 (.00005)	-.00076 (.00031)	.00069 (.00009)	.00112 (.00012)
Cu ₂	.04948 (.00017)	-.43509 (.00023)	.10652 (.00007)	.00687 (.00019)	.01166 (.00034)	.00120 (.00003)	-.00098 (.00019)	.00084 (.00006)	.00101 (.00008)
Cu ₃	.09784 (.00017)	-.89265 (.00021)	.20476 (.00007)	.00726 (.00019)	.01256 (.00035)	.00125 (.00003)	.00050 (.00023)	.00107 (.00006)	.00095 (.00009)
Cl ₁	-.13248 (.00033)	-.29709 (.00042)	.00305 (.00012)	.00647 (.00037)	.01313 (.00064)	.00131 (.00006)	-.00166 (.00041)	.00075 (.00012)	.00073 (.000170)
Cl ₂	.18943 (.00032)	-.15088 (.00043)	.09782 (.00013)	.00682 (.00036)	.01435 (.00067)	.00133 (.00006)	-.00170 (.00042)	.00068 (.00012)	.00083 (.00016)
Cl ₃	.23871 (.00032)	-.59991 (.00048)	.20055 (.00014)	.00639 (.00036)	.01822 (.00074)	.00165 (.00007)	-.00085 (.00045)	.00080 (.00013)	.00115 (.00019)
Cl ₄	-.08370 (.00031)	-.74041 (.00040)	.10378 (.00013)	.00633 (.00037)	.01277 (.00066)	.00135 (.00046)	-.00112 (.00040)	.00086 (.00012)	.00108 (.00016)
Cl ₅	-.03618 (.00039)	-1.20123 (.00043)	.19276 (.00013)	.01148 (.00044)	.01239 (.00065)	.00135 (.00007)	-.00185 (.00043)	.00257 (.00015)	-.00001 (.00015)
O	.2594 (.0012)	-1.0460 (.0016)	.28205 (.00043)	.0131 (.0015)	.0230 (.0027)	.00188 (.00023)	.0024 (.0017)	.00005 (.00048)	.00205 (.00064)
C ₁	.4067 (.0025)	-.9891 (.0050)	.3268 (.0016)	.0115 (.0031)	.0793 (.0142)	.0116 (.0016)	-.0070 (.0056)	-.0071 (.0081)	.0191 (.0041)
C ₂	.4766 (.0028)	-1.1027 (.0052)	.3920 (.0014)	.0197 (.0044)	.0736 (.0134)	.0080 (.0013)	-.0082 (.0066)	-.0063 (.0018)	.0111 (.0033)
C ₃	.4657 (.0026)	-1.3263 (.0043)	0.4041 (.0013)	.0166 (.0037)	.0543 (.0097)	.0070 (.0010)	.0053 (.0052)	.0014 (.0016)	.0073 (.0027)

^aStandard deviations are enclosed in parentheses.

^bThe temperature factor expression for all atoms is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table 3. Interatomic distances in (Angstroms) for $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Intramolecular Distances			Intermolecular Distances ^a		
Cu ₁	Cl ₁	2.263(0.003)	Cu ₁	Cl ₄ (4)	3.038(0.003)
Cu ₁	Cl ₂	2.289(0.003)	Cu ₁	Cl ₄ (2)	3.038(0.003)
Cu ₁	Cu ₂	3.302(0.003)	Cu ₂	Cl ₁ (4)	3.157(0.004)
Cu ₂	Cl ₁	2.288(0.003)	Cu ₂	Cl ₅ (2)	2.680(0.003)
Cu ₂	Cl ₂	2.289(0.004)	Cu ₃	Cl ₅ (1)	2.691(0.003)
Cu ₂	Cl ₃	2.285(0.003)	Cu ₃	Cl ₂ (3)	3.135(0.004)
Cu ₂	Cl ₄	2.276(0.004)	Cl ₁	Cu ₂ (4)	3.157(0.004)
Cu ₂	Cu ₃	3.318(0.004)	Cl ₂	Cu ₃ (2)	3.135(0.004)
Cu ₃	Cl ₃	2.304(0.004)	Cl ₄	Cu ₁ (3)	3.038(0.003)
Cu ₃	Cl ₄	2.290(0.003)	Cl ₅	Cu ₃ (5)	2.691(0.003)
Cu ₃	Cl ₅	2.261(0.004)	Cl ₅	Cu ₂ (3)	2.680(0.003)
Cu ₃	O	1.957(0.009)	Distances Corrected for Thermal Motion		
O	C ₁	1.43(0.02)	First Atom Riding on Second Atom		
C ₁	C ₂	1.39(0.03)	O	C ₁	1.56(0.03)
C ₂	C ₃	1.38(0.04)	Cl ₁	C ₂	1.37(0.04)
Cl ₁	Cl ₂	3.146(0.004)	C ₂	C ₃	1.34(0.04)
Cl ₁	Cl ₄	3.275(0.005)			

Table 3 continued

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Intramolecular Distances			Independent Atom Assumption		
Cl ₄	Cl ₃	3.147(0.005)	O	C ₁	1.63(0.03)
Cl ₄	Cl ₅	3.237(0.005)	Cl ₁	C ₂	1.69(0.03)
Cl ₂	Cl ₃	3.325(0.005)	C ₂	C ₃	1.60(0.03)
Cl ₃	O	3.12(0.01)			
Cl ₅	O	2.92(0.01)			

^aNumber in parentheses refer to those related to the given atom by

(1) $-x, 1/2 + y, 1/2 - z$
(2) $x, 1 + y, z$
(3) $x, y - 1, z$
(4) $-x, -y - 1, -z$
(5) $-x, y - 1/2, 1/2 - z.$

Table 4. Interatomic Angles^a (in degrees) for $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Cu ₁	Cl ₁	Cu ₂	93.0(0.1)	Cl ₄ (2)	Cu ₁	Cl ₂	89.1(0.1)
Cu ₁	Cl ₂	Cu ₂	92.3(0.1)	Cl ₁ (4)	Cu ₂	Cl ₁	83.9(0.1)
Cl ₁	Cu ₁	Cl ₂	87.4(0.1)	Cl ₁ (4)	Cu ₂	Cl ₂	87.6(0.1)
Cl ₁	Cu ₂	Cl ₂	86.9(0.1)	Cl ₁ (4)	Cu ₂	Cl ₃	89.0(0.1)
Cl ₁	Cu ₂	Cl ₄	91.7(0.1)	Cl ₁ (4)	Cu ₂	Cl ₄	84.9(0.1)
Cl ₂	Cu ₂	Cl ₃	93.3(0.1)	Cl ₅ (2)	Cu ₂	Cl ₅ (2)	176.5(0.1)
Cl ₃	Cu ₂	Cl ₄	87.3(.01)	Cl ₅ (2)	Cu ₂	Cl ₁	92.7(0.1)
Cu ₂	Cl ₃	Cu ₃	92.6(0.1)	Cl ₅ (2)	Cu ₂	Cl ₂	92.9(0.1)
Cu ₂	Cl ₄	Cu ₃	93.2(0.1)	Cl ₅ (2)	Cu ₂	Cl ₃	94.4(0.1)
Cl ₃	Cu ₃	Cl ₄	86.5(0.1)	Cl ₅ (2)	Cu ₂	Cl ₄	94.5(0.1)
Cl ₃	Cu ₃	0	93.8(0.3)	Cl ₅ (1)	Cu ₃	Cl ₃	93.5(0.1)
0	Cu ₃	Cl ₅	87.8(0.3)	Cl ₅ (1)	Cu ₃	Cl ₄	99.0(0.1)
Cl ₄	Cu ₃	Cl ₅	90.7(.01)	Cl ₅ (1)	Cu ₃	Cl ₅	95.84(0.09)
Cu ₃	0	C ₁	134.(1.)	Cl ₅ (1)	Cu ₃	0	88.6(0.3)
0	C ₁	C ₂	117.(2.)	Cl ₅ (1)	Cu ₃	Cl ₂ (3)	174.0(0.1)
C ₁	C ₂	C ₃	127.(3.)	Cl ₂ (3)	Cu ₃	Cl ₃	88.5(0.1)
Cu ₁	Cu ₂	Cu ₃	176.32(0.06)	Cl ₂ (3)	Cu ₃	Cl ₄	86.7(0.1)
Cl ₄ (4)	Cu ₁	Cl ₁	87.9(0.1)	Cl ₂ (3)	Cu ₃	Cl ₅	82.3(0.1)
Cl ₄ (4)	Cu ₁	Cl ₂	90.9(0.1)	Cl ₂ (3)	Cu ₃	0	85.6(0.3)
Cl ₄ (2)	Cu ₁	Cl ₁	92.0(0.1)				

^aAtom designations are as in the interatomic distance table

Table 5. Significant least squares plane in $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2^a$

1. Plane of copper and chlorine atoms

$$0.61240X - 0.51052Y - 0.60361Z - 2.4739 \times 10^{-8} = 0$$

Atom	Distance from plane (Å)	Atom	Distance from plane (Å)
Cu ₁	0.0	Cl ₄	0.0401
Cu ₂	-0.1087	Cl ₅ [*]	0.2875
Cu ₃	-0.0188	O [*]	0.1913
Cl ₁	0.0324	C ₁ [*]	0.2020
Cl ₂	0.0386	C ₂ [*]	-0.0858
Cl ₃	0.0340	C ₃ [*]	0.3340

2. $0.6122X - 0.5101Y - .6042Z - 3.41 \times 10^{-2} = 0$

Cl ₁	-0.0031	Cl ₃	-0.0031
Cl ₂	0.0031	Cl ₄	0.0031
Cl ₃		Cu ₂ [*]	-0.1444

3. $0.6316X - 0.4543Y - 0.6283Z - 0.3005 = 0$

Cu ₃	-0.1289	Cl ₅	0.0541
Cl ₃	0.0533	O	0.0128
Cl ₄	0.0088		

4. $0.6128X - 0.4937Y - 0.6170Z = 0$

Cu ₁	0.0	Cl ₂	0.0
Cl ₁	0.0		

^a The orthogonalized coordinate system is composed of the a, b and c^{*} vectors.

^{*} Atoms not included in the least squares plane calculation.

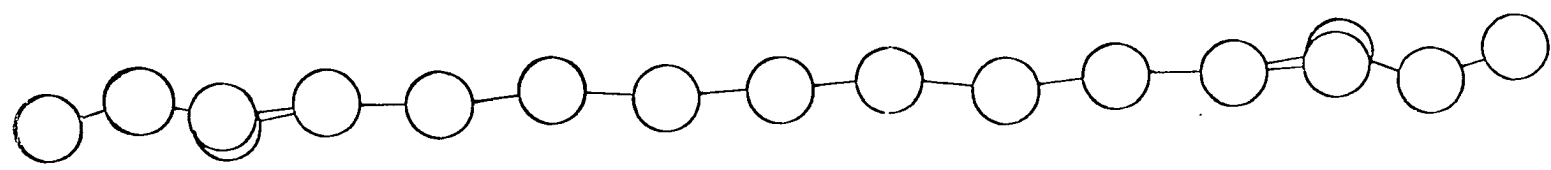
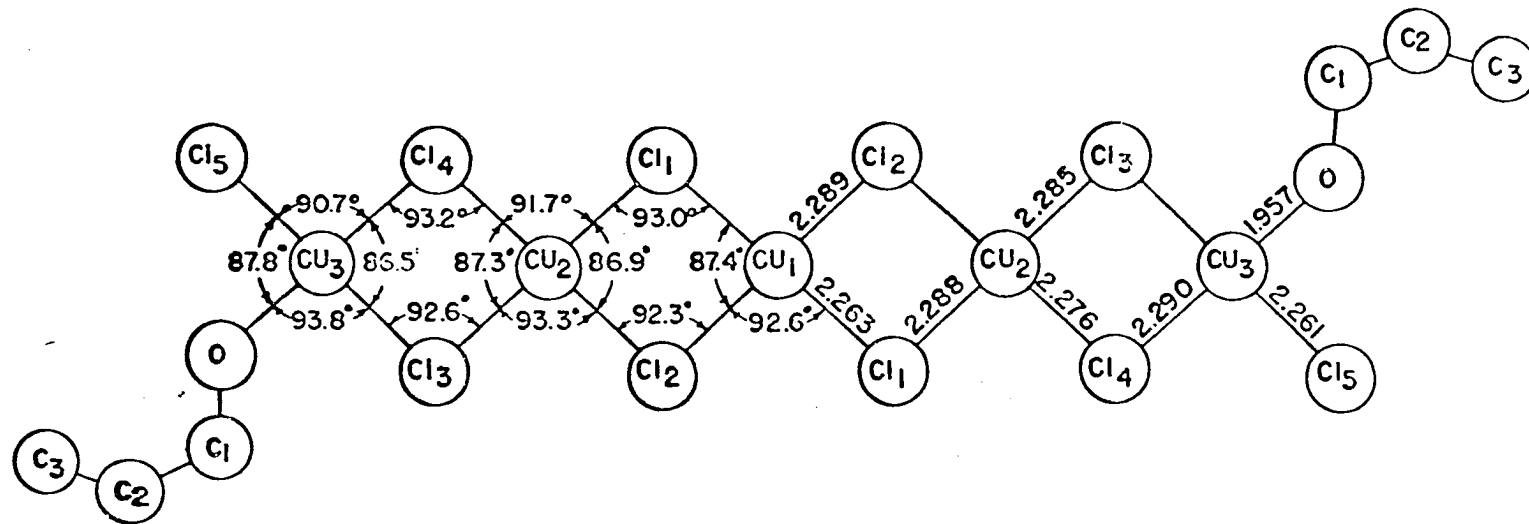


Figure 3. Structure of $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$

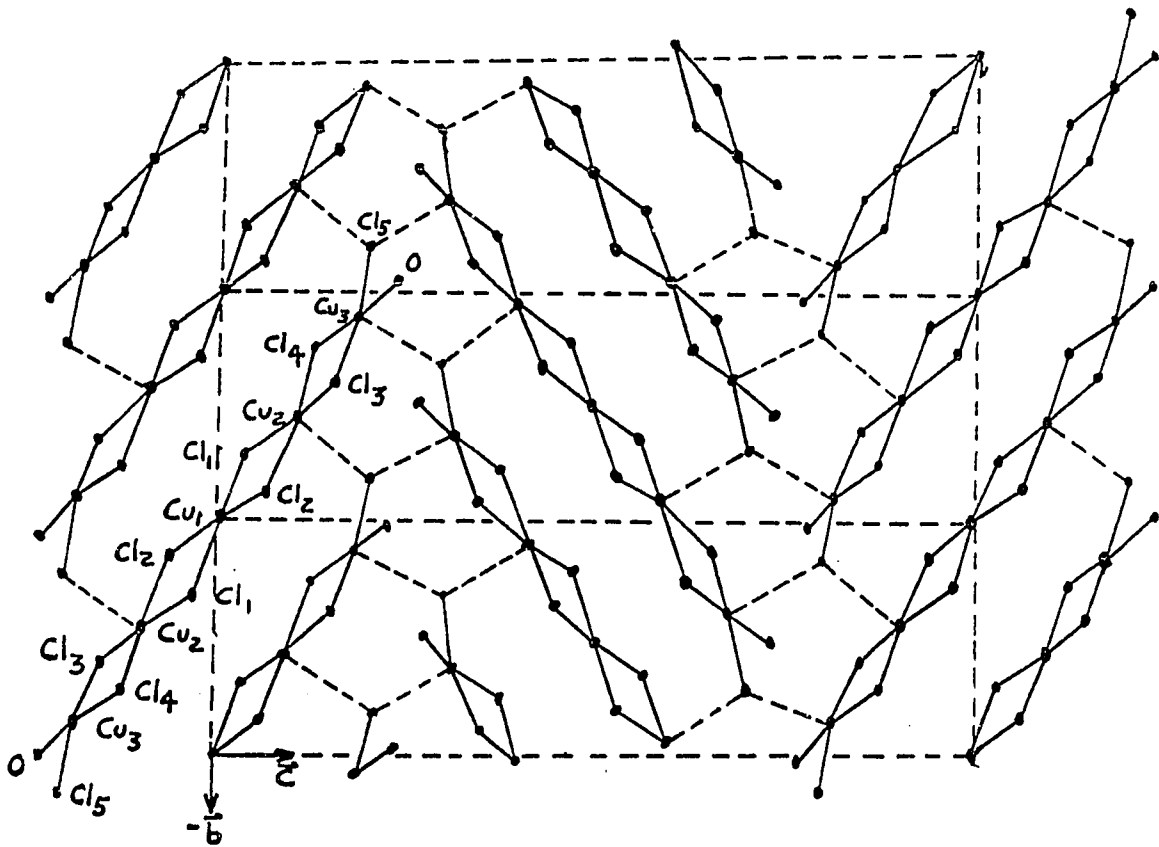


Figure 4. Packing of $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$

III. THE CRYSTAL STRUCTURES OF



A. Introduction and Literature Review

1. Introduction

These structural investigations were undertaken to ascertain what changes in structure, if any, occur within a series of rare earth chloride hexahydrates. A second goal was to determine what type of hydrogen bonding is found in the type of hydrates represented by these compounds. The second goal was not met, since this installation is not at present equipped for a neutron diffraction investigation. A neutron diffraction investigation on these compounds is, however, planned in the near future. This report presents the results of x-ray diffraction studies on the compounds $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ and compares their structure to the structures of other compounds of similar nature.

2. Literature review

The crystalline rare earth chloride hexahydrates are known to form an isostructural series. Space groups and lattice constants have been reported for the neodymium, samarium, erbium and plutonium hydrates (44, 45). The crystal structure of $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (46) was reported in 1960 and the structure of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ in 1965 (47). The latter structure was rather poorly done giving an agreement factor of

approximately .15 for two zero level zones of data (456 reflections).

B. Structure Determination of $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$

1. Preparation and properties

Single crystals of this compound were prepared by H. Weber of Iowa State University by evaporation of a water solution of DyCl_3 using $\text{Mg}(\text{ClO}_4)_2$ as a dessicant. The clear yellowish crystals tend to grow as rectangular parrallelepiped and are very hygroscopic. The density of the crystals was determined to be $2.53 \pm 0.03 \text{ g/cm}^3$ by a rough flotation method. The calculated density assuming 2 molecules/unit cell is 2.56 g/cm^3 .

2. X-ray data

Crystals of this compound were lightly coated with white petroleum jelly and mounted in 0.2 mm Lindemann glass capillaries. Examination of oscillation, Weissenberg and precession photographs established that the crystal class was monoclinic with Laue symmetry C_{2h} . The systematic extinctions,

$[\text{h}0\ell]$	$h+\ell \neq 2n$
$[0k0]$	none
$[\text{h}k\ell]$	none

indicate that the crystals belong to one of the space groups Pn or $P2/n$, with $a = 7.868 \pm 0.003 \text{ \AA}$, $b = 6.491 \pm 0.003 \text{ \AA}$, $c = 9.596 \pm 0.004 \text{ \AA}$ and $\beta = 93.69 \pm 0.02^\circ$. The lattice constant data were obtained on a General Electric xRD-5 x-ray unit equipped with a single crystal orienter and scintillation counter. Angular measurements were made on reflections in the back reflection

region, using chromium radiation. The lattice constants were then obtained by a least squares extrapolation (39) on 19 reflections using the Nelson-Riley error formula (40).

Complete three-dimensional x-ray data to $\frac{\sin \theta}{\lambda} = .705$ were taken with zirconium-filtered molybdenum K_{α} radiation using the above mentioned equipment. The moving crystal-moving counter method (5) was used with a 100 second scan through the peak setting. The background was determined from a plot of average background versus 2θ .

Corrections to the data were applied as shown in Chapter I, section G. No decomposition correction was necessary, the maximum fluctuation in the intensity of the standard reflections being 1^o/o. A correction for absorption was made using Busing and Levy's polyhedral absorption correction program (8).

3. Structure solution and refinement

A statistical plot was made after the data were taken using the method of Howells, Phillips and Rogers (48). Results of this plot indicated that the crystals belong to a centric space group. The space group P2/n was thus indicated. The requirement of two molecules/unit cell requires that the Dy and one Cl sit on positions having C_2 symmetry. A Patterson map was prepared, from which the Dy position was located. Least squares refinement of the Dy position and scale factor using the Busing and Levy (49) program modified for the IBM 360 system and all data, resulted in an agreement

factor of .31. In all of the least squares refinement the scattering factors of Hanson, et al. (42) were used. The scattering factor of the Dy atom was corrected for the real part of the anomalous dispersion effect (3). A three-dimensional electron density map indicated probable positions for the remaining Cl and O atoms. Isotropic least squares refinement of all atomic and thermal parameters using all data resulted in an agreement factor of .08. A difference electron density map indicated that all atoms were at least slightly anisotropic. Anisotropic least squares refinement, using all data, gave an agreement factor of .05 and for observed data only, an agreement factor of .034. Examination of the very strong reflections indicated that they were probably affected by secondary extinction, therefore the 20 strongest reflections were removed. Least squares refinement then resulted in an agreement factor of .029 for the 1295 "observed" reflections and .044 for the 1444 reflections of all types except those where secondary extinction was suspected. The maximum shift in the positional parameters was on the order of 1/100 of a standard deviation. Subsequent attempts to determine the hydrogen atoms positions using difference Fourier methods were unsuccessful. The final positional parameters are given in Table 6, the final thermal parameters along with their standard deviation are given in Table 7. A comparison of the magnitudes of the observed and calculated structure factors for the "observed" reflections is given in Figure 5.

Significant interatomic distances and angles and their standard deviations are given in Tables 8 and 9, respectively. Figure 6 indicates the positions of the atoms within one unit cell.

C. Structure of $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$

The compound $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ is isomorphous with $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ with $a = 7.852 \pm 0.004 \text{ \AA}$, $b = 6.480 \pm \text{\AA}$, $c = 9.581 \pm 0.005 \text{ \AA}$ and $\beta = 93.675 \pm 0.015^\circ$. Lattice constant data were obtained on a General Electric XRD-5 x-ray unit equipped with a single crystal orienter and scintillation counter. Angular measurements were made on reflections in the back reflection region, using chromium radiation. The lattice constants were then obtained by a least squares extrapolation (39) on 18 reflections using the Nelson-Riley error formula (40).

Intensity data collection and the majority of the solution and refinement of the structure were performed by James E. Truelove. Final refinement, weighting scheme analysis and alteration, as well as precision lattice constant determination were performed by this author. The forty strongest reflections were removed since it appeared that they were affected by secondary extinction. A final agreement factor of .043 based on 1776 "observed" reflections was obtained. The final positional parameters are given in Table 6 and the final thermal parameters and their standard deviations are given in Table 10.

D. Description of the Structures

The formulae of these compounds should be written as $[M(H_2O)_6Cl_2]^+Cl^-$, the metal ion exhibiting eight coordination. The geometry of the metal coordination sphere may best be described by the consideration of the distortion which would occur if two chlorine atoms were to approach a regular octahedron of oxygen atoms surrounding a metal ion. Assuming initially a regular octahedron of oxygen atoms about the metal ion, then allowing the chlorine atoms to approach along the three-fold axes which are perpendicular to the planes defined by one O_3 atom and two O_1 atoms, the distortions indicated in Figure 9 occur. The final geometry, shown in Figure 6, may be called a distorted dodecahedron with triangular faces (i.e similar to the B_8Cl_8 configuration).

The geometry about the ionic chlorine atoms is shown in Figure 7. This corresponds to a distorted octahedral configuration.

The geometry about the Cl_2 type atoms is shown in Figure 8, each chlorine having seven nearest neighbors.

E. Comparison of the Structures

The rare earth trichloride hexahydrates form an isostructural series. A comparison of the available lattice constants is shown in Table 11. A near linear decline in all the lattice vectors is observed, with the β angle remaining approximately constant. From Table 8 it is apparent that there is a near linear contraction in the coordination sphere

of the metal ion as the atomic number of the metal is increased. The metal ion to ionic chlorine atom distance also decreases almost linearly. Virtually all of the significant oxygen to chlorine distances either remain constant or show a slight but statistically non-significant alternation. The one exception to this is marked with an asterisk in Table 8. This distance shows a near linear decrease.

F. Speculation on Hydrogen Bonding

In these structures it was not possible to locate the hydrogen atom positions using x-ray diffraction techniques. The probable hydrogen bonding configurations presented in this report are thus based primarily on interatomic distances and angles. The factors involved in deducing the hydrogen bonding configurations are discussed in detail below.

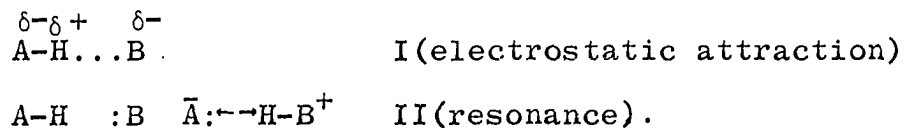
The van der Waals distance for the species O...Cl and O...O are said to be 3.20 and 2.80^oÅ respectively (50). The extent to which the environment of the atoms influence these distances is, at this time, unknown.

The normal H-O-H angle in water is 104.5°, however in dealing with hydrogen bonded systems, nonlinearity of the hydrogen bond may result in A...O...B angles of 83-120° in hydrates (50).

A factor which greatly complicates the prediction of the hydrogen bonding is the lack of reliable data on the relative strengths of hydrogen bonds for the species O-H...Cl⁻, O-H...Cl (covalently bonded) and O-H...O as a function of

interatomic distance. In an attempt to surmount this problem a somewhat arbitrary criterion on relative strengths was developed. The quantity Δ was defined as $\Delta = R_a - R_v$, where R_v is the sum of the van der Waals radii for the two atoms and R_a is the observed separation of the two atoms in the structure. A negative Δ is taken to indicate that the observed separation of the atoms is less than the van der Waals distance. The van der Waals distance is assumed to represent the closest non-bonded approach of the atoms, the influence of packing was therefore completely neglected. With the assumption that the quantity Δ is an indication of the extent to which there is an attractive interaction between the atoms, it was then necessary to decide which of the possible combinations of atoms, with equal values of Δ , was most likely to correspond to the formation of a hydrogen bond.

The hydrogen bond may be considered to be a combination of two canonical structures (50)



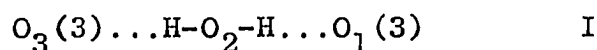
The form represented by I appears to be the main contributor, that of II only contributing to an extent of less than 10⁰%. Considering only the canonical structure I, the following order of preference for hydrogen bonding might be expected: Cl⁻, Cl (covalently bonded), and H₂O (in the coordination sphere). The contribution of the second form would be expected

to alter the magnitude of the difference in ability to hydrogen bond but the effect should not be great enough to alter the order.

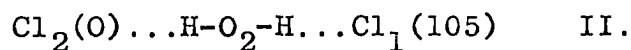
The values of Δ for each of the nearest neighbors, to each of the crystallographic independent oxygen atoms, are given in Table 12. The interatomic distances for these atoms are given in Table 8 and the significant A...O...B angles are given in Table 9. The angles represent the final factor considered in the speculation about the hydrogen bonding present in these structures.

The configuration about the O_2 atom appears to be the simplest and thus represents a logical starting place. The atom designations used below are defined in Table 8. It appears that there are two possible configurations both of which show good contractions and have reasonable angles.

These are



and



Although other combinations involving $Cl_2(0)$ appear to be possible, they all result in very acute angles.

If we start with configuration I above, there appear to be two reasonable configurations about the O_1 atom. Either we have the configuration $Cl_2(203) \dots H-O_1-H \dots Cl_2(2)$ or else one hydrogen is not involved in hydrogen bond formation. Notice that the O_1 to $Cl_2(203)$ distance is larger than the sum of

the van der Waals radii. This may mean that no hydrogen bond is present or that the sum of the van der Waals radii is too small, either because of the neglect of the contribution to the radius due to the presence of a hydrogen atom between the atoms, or due to errors present in the values of the van der Waals radii of the individual atoms.

The best possibility about the O_3 atom is the configuration $Cl_2(102)\dots H-O_3-H\dots Cl_1(0)$, although the configurations $Cl_1(0)\dots H-O_3-H\dots Cl_2$ and $Cl_2(102)\dots H-O_3-H\dots Cl_2(203)$ are also possible.

If we begin with configuration II about the O_2 atom, the same configurations are possible about the O_1 atom, since the $O_2\dots H-O_1-H\dots Cl_2$ angle is less than 78° . The same configurations occur about the O_3 atoms, with the addition of the configurations $Cl_1(0)\dots H-O_3-H\dots O_2(3)$ and $O_2(3)\dots O_3\dots Cl_2(203)$.

In summary there are a number of possible configurations which can occur in these structures, the most likely one appears to be $O_3\dots H-O_2-H\dots O_1$, $Cl_2(2)\dots H-O_1-H\dots Cl_2(203)$ and $Cl_1(0)\dots H-O_3-H\dots Cl_2(102)$. It will remain for neutron diffraction investigations to finally resolve the question.

Table 6. Comparison of atomic positions in rare earth chloride hexahydrates

Atom Type	Position	Compound			
		$\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$	$\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$	$\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$	$\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$
M	x	0.25000	0.25000(0)	0.25000(0)	0.25000(0)
	y	0.1512	0.1521(2)	0.15391(5)	0.15483(4)
	z	0.25000	0.25000(0)	0.25000(0)	0.25000(0)
Cl_{I}	x	0.25000	0.25000(0)	0.25000(0)	0.25000(0)
	y	0.373	0.3769(4)	0.3749(3)	0.25000(0)
	z	0.75000	0.75000(0)	0.75000(0)	0.75000(0)
Cl_{II}	x	0.259	0.2601(4)	0.26015(17)	0.26009(21)
	y	0.84	0.8370(8)	0.83865(23)	0.83972(20)
	z	0.057	0.587(4)	0.05999(13)	0.06023(15)
O_{I}	x	0.552	0.5432(12)	0.5419(5)	0.5401(5)
	y	0.040	0.0471(19)	0.0519(7)	0.0515(8)
	z	0.281	0.2813(12)	0.2823(4)	0.2815(5)
O_{II}	x	0.088	0.0888(12)	0.0890(5)	0.0896(6)
	y	0.427	0.4254(20)	0.4254(7)	0.4235(7)
	z	0.152	0.1423(12)	0.1460(4)	0.1456(5)
O_{III}	x	0.110	0.1058(12)	0.1063(5)	0.1064(6)
	y	0.297	0.2988(20)	0.2999(7)	0.3002(8)
	z	0.440	0.4406(12)	0.4382(4)	0.4363(5)

Table 7. Thermal parameters for $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}^{\text{a}}$

Atom	β_{11}^{b}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Dy	0.00456(5)	0.00679(7)	0.00308(3)	0.0	0.00085(2)	0.0
Cl ₁	0.0082(3)	0.0149(5)	0.0062(2)	0.0	0.0010(2)	0.0
Cl ₂	0.0096(2)	0.0108(3)	0.0049(1)	-0.0006(2)	0.0013(1)	-0.0018(2)
O ₁	0.0068(5)	0.0159(9)	0.0074(4)	0.0018(6)	0.0005(4)	-0.0017(5)
O ₂	0.0082(6)	0.0017(9)	0.0075(4)	0.0016(6)	0.0013(4)	0.0030(5)
O ₃	0.0104(6)	0.016(1)	0.0053(3)	-0.0006(6)	0.0026(4)	-0.0016(5)

^aStandard deviations given in parentheses.

^bThe temperature factor expression for all atoms is
 $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + \beta_{23}kl)]$.

Table 8. Interatomic distances in rare earth chloride hexahydrates

Atom 1 ^a	Atom 2	Distance (in Å)			
		EuCl ₃ ·6H ₂ O	GdCl ₃ ·6H ₂ O	DyCl ₃ ·6H ₂ O	HoCl ₃ ·6H ₂ O
M(0)	Cl ₁ (5)		5.044	4.983(2)	4.968(2)
M(0)	Cl ₁ (3)		5.014	5.008(2)	4.999(2)
M(0)	Cl ₂ (0)	2.76(1)	2.768(8)	2.745(2)	2.739(2)
M(0)	Ox ₁ (0)	2.52(3)	2.42(2)	2.391(4)	2.375(4)
M(0)	Ox ₂ (0)	2.37(3)	2.39(2)	2.354(4)	2.336(4)
M(0)	Ox ₃ (0)	2.42(3)	2.42(2)	2.387(4)	2.368(4)
Ox ₁ (0)	Ox ₂ (3)	2.86(4)	2.80(3)	2.739(6)	2.725(7)
Ox ₁ (0)	Ox ₃ (3)	2.94(4)	2.89(3)	2.848(6)	2.823(7)
Ox ₁ (0)	Cl ₁ (4)	3.15(3)	3.24(2)	3.243(5)	3.244(5)
Ox ₁ (0)	Cl ₂ (2)	3.12(3)	3.18(2)	3.157(4)	3.166(5)
^x Ox ₁ (0)	Cl ₂ (203)	3.33(3)	3.24(2)	3.212(5)	3.193(5)
Ox ₂ (0)	Cl ₁ (105)	3.21(3)	3.21(2)	3.183(3)	3.186(5)
Ox ₂ (0)	Cl ₂ (0)	3.20(3)	3.14(2)	3.136(5)	3.143(5)
Ox ₂ (0)	Ox ₃ (3)	2.78(4)	2.72	2.704(6)	2.682(6)
Ox ₃ (0)	Cl ₁ (0)	3.18(3)	3.17(2)	3.167(4)	3.179(5)
Ox ₃ (0)	Cl ₂ (102)	3.16(3)	3.16(2)	3.163(5)	3.168(5)
Ox ₃ (0)	Cl ₂ (203)	3.23(3)	3.19(2)	3.172(5)	3.162(6)

^a(2) 1/2+x, 1-y, 1/2+z (102) -1/2+x, 1-y, 1/2+z
(3) 1/2-x, y, 1/2-z (105) -1/2-x, y, 1/2-z
(4) 1-x, -y, 1-z (203) 1-x, -1-y, 1-z
(5) 1-x, 1-y, 1-z

Table 9. Interatomic angles for $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$

Atom 1 ^a	Atom 2	Atom 3	Angle (in degrees)	
			$\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$	$\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$
$\text{O}_2(3)$	$\text{O}_1(0)$	$\text{O}_3(3)$	62.9(2)	62.8(2)
$\text{O}_2(3)$	$\text{O}_1(0)$	$\text{Cl}_2(2)$	77.4(2)	77.3(2)
$\text{Cl}_2(203)$	$\text{O}_1(0)$	$\text{Cl}_2(2)$	94.5(1)	94.3(1)
$\text{Cl}_2(0)$	$\text{O}_2(0)$	$\text{Cl}_1(105)$	96.7(1)	96.3(1)
$\text{Cl}_1(105)$	$\text{O}_2(0)$	$\text{O}_1(3)$	86.9(1)	87.0(2)
$\text{O}_3(3)$	$\text{O}_2(0)$	$\text{O}_1(3)$	99.4(2)	99.5(2)
$\text{Cl}_1(0)$	$\text{O}_3(0)$	$\text{O}_2(3)$	88.1(1)	87.9(2)
$\text{Cl}_2(102)$	$\text{O}_3(0)$	$\text{Cl}_1(0)$	87.6(1)	87.2(1)
$\text{Cl}_1(0)$	$\text{O}_3(0)$	$\text{Cl}_2(203)$	92.4(1)	92.2(1)
$\text{O}_2(3)$	$\text{O}_3(0)$	$\text{Cl}_2(203)$	89.2(2)	89.0(2)
$\text{Cl}_2(102)$	$\text{O}_3(0)$	$\text{Cl}_2(203)$	91.3(1)	91.0(1)

^aAtom designations are defined in Table 8.

Table 10. Thermal parameters for $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}^a$

Atom	β_{11}^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ho	0.00444(5)	0.00711(7)	0.00265(3)	0.0	0.00044(2)	0.0
Cl ₁	0.0083(2)	0.0147(4)	0.0058(2)	0.0	0.0007(1)	0.0
Cl ₂	0.0098(2)	0.0118(3)	0.0052(1)	-0.0008(2)	0.0010(1)	-0.0020(1)
O ₁	0.0068(5)	0.0153(9)	0.0073(4)	0.0014(6)	-0.003(3)	-0.0015(5)
O ₂	0.0087(6)	0.0122(9)	0.0078(4)	0.0018(5)	0.0017(4)	0.0028(5)
O ₃	0.0092(6)	0.0158(9)	0.0054(4)	-0.0005(6)	0.0024(4)	-0.0019(5)

^aStandard deviations are in parentheses.

^bThe temperature factor expression is
 $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table 11. Lattice constants of the rare earth chloride hexahydrates

Lattice Constant	$\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$	$\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$	$\text{TbCl}_3 \cdot 6\text{H}_2\text{O}^{\text{a}}$	$\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$	$\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$	$\text{ErCl}_3 \cdot 6\text{H}_2\text{O}^{\text{a}}$
$a(\text{\AA})$	7.99(2)	7.923(1)	7.88(3)	7.868(3)	7.852(4)	7.83(3)
$b(\text{\AA})$	6.52(1)	6.525(1)	6.52(3)	6.491(3)	6.480(4)	6.47(3)
$c(\text{\AA})$	9.67(3)	9.651(1)	9.62(3)	9.596(4)	9.581(5)	9.57(3)
$\beta(\text{degrees})$	94.6(5)	93.65(2)	93.66(12)	93.69(2)	93.68(2)	93.75(12)

^aLattice constants determined by the author using precession photographs.

Table 12. Nearest neighbors and values of Δ for $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$

Oxygen Atom	Neighboring Atom ^a	$\Delta = R_a - R_v$	
		$\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$	$\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$
O_1	$O_2(3)$	-.061	-.075
	$\text{Cl}_2(2)$	-.043	-.034
	$\text{Cl}_2(203)$	+.013	-.007
	$\text{Cl}_1(4)$	+.043	+.044
O_2	$O_3(3)$	-.096	-.118
	$O_1(3)$	-.061	-.075
	$\text{Cl}_2(0)$	-.064	-.057
	$\text{Cl}_1(105)$	-.017	-.014
O_3	$O_2(3)$	-.096	-.118
	$\text{Cl}_1(0)$	-.033	-.021
	$\text{Cl}_2(102)$	-.037	-.032
	$\text{Cl}_2(203)$	-.028	-.038

^aAtom designations are defined in Table 8.

Figure 5. Comparison of the observed and calculated structure factors for $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ -
 $F(0.0.0) = 1496.7$

Table with multiple columns of numbers and text labels (e.g., H K, H K, H K) interspersed throughout the data.

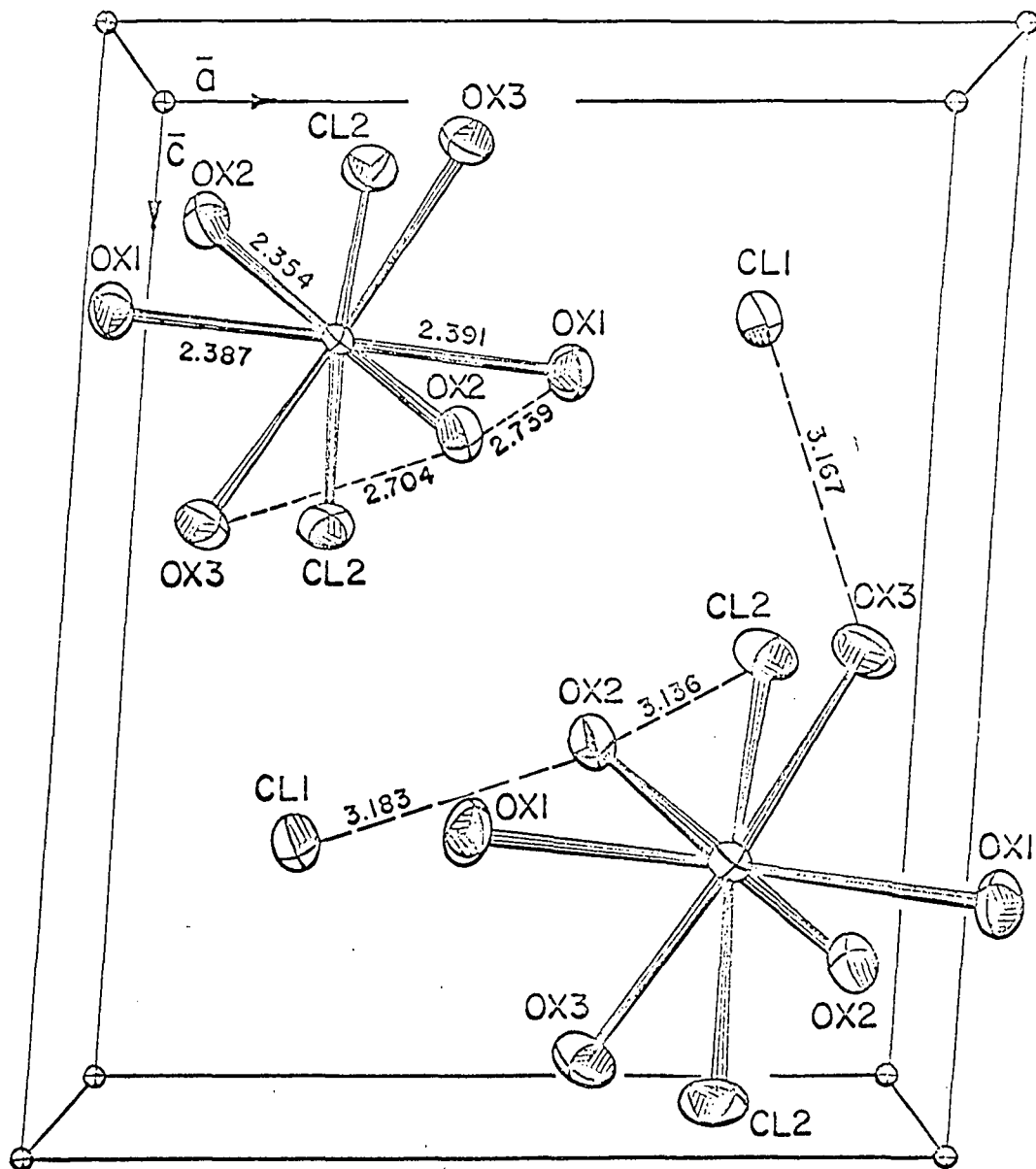


Figure 6. Unit cell for $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$

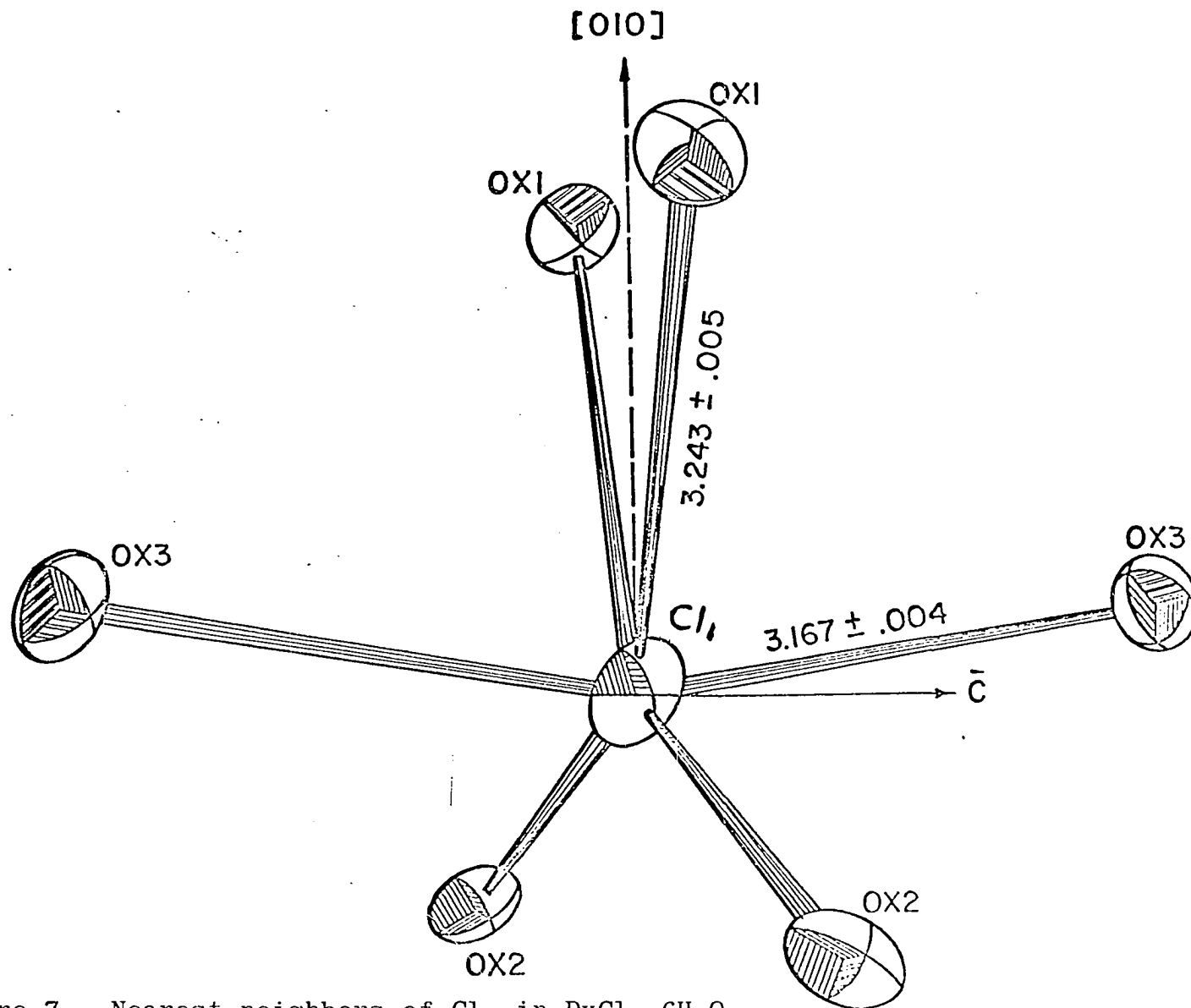


Figure 7. Nearest neighbors of Cl_1 in $DyCl_3 \cdot 6H_2O$

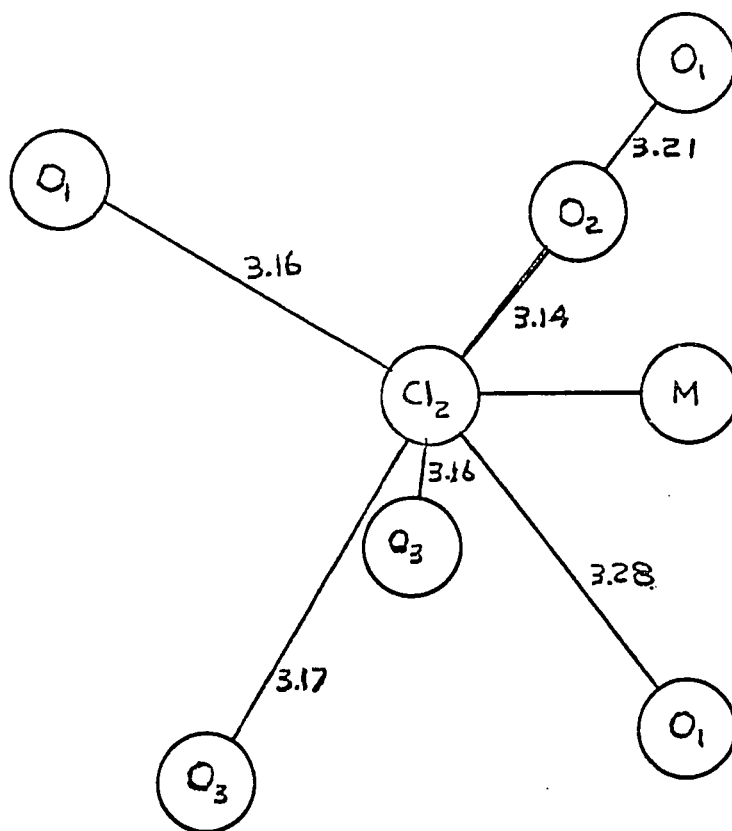


Figure 8. Nearest neighbors of Cl_2 in $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$

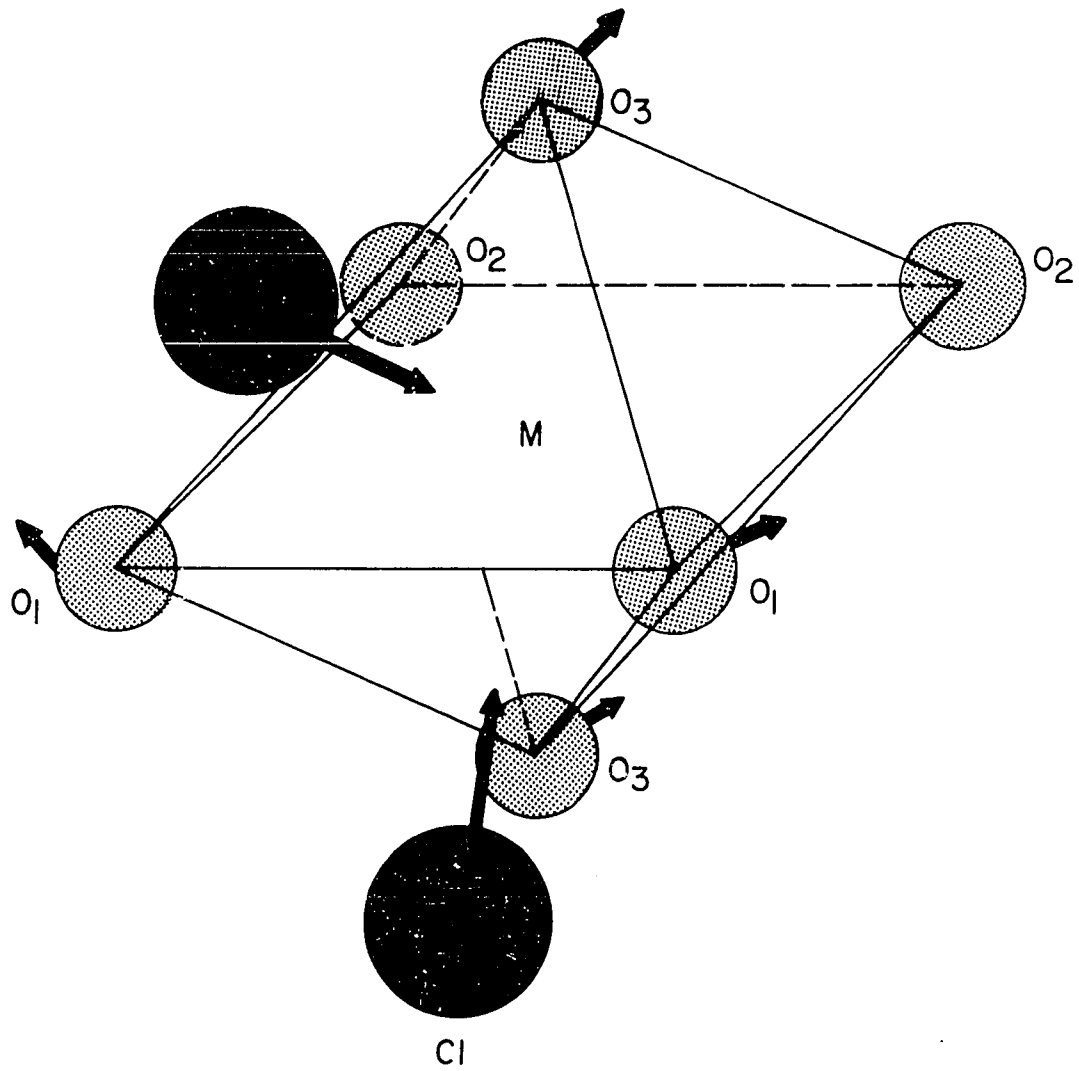
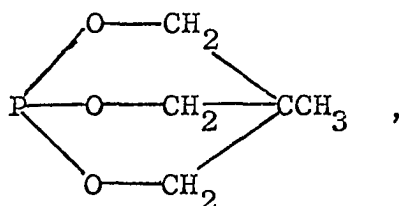


Figure 9. Distortion in $MCl_3 \cdot 6H_2O$ compounds

IV. THE CRYSTAL STRUCTURE OF $\text{Ag}(\text{P}(\text{OCH}_2)_3\text{CCH}_3)_4\text{ClO}_4$

A. Literature Review

A large variety of types of compounds containing phosphorus are known. Recently a new type of phosphorus containing compound, called a triane, has been prepared (51). An example of this type of compound is $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, (4 methyl 2,6,7, trioxa 1-phospha bicyclo (2.2.2) octane). The structure of this complex is thought to be



the phosphorus having a tetrahedral (sp^3) configuration, with a lone pair of electrons occupying one of the tetrahedral positions. The reactions and physical properties of this compound have been investigated by Verkade and his associates (52, 53, 54). The crystal structure of a derivative of this compound, with the formula $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$, has recently been determined by Nimrod^x, and confirms the above structure.

With a ligand such as $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, appreciable shortening of the M-P distance relative to the sum of the metal and phosphorus covalent radii might be expected because of the possibility of "back donation" of d electrons from

^xNimrod, Dale., Iowa State University, Ames, Iowa. Structure determination of $\text{OP}(\text{OCH}_2)_3\text{CCH}_3$. Private Communication. 1967.

the metal to the fairly low energy, empty d orbitals on phosphorus. The structure of $\text{Ag}(\text{P}(\text{OCH}_2)_3\text{CCH}_3)_4\text{ClO}_4$ was undertaken to determine the magnitude of this shortening, if any, and to confirm the configuration of the ligand. The structure of only one other complex containing silver and phosphorus has been determined (55, 56), namely $\text{AgSCNP}(\text{n-C}_3\text{H}_7)_3$.

B. Structure Determination

1. Preparation and properties

Crystals of this compound were kindly prepared by Dr. J. G. Verkade of Iowa State University. The colorless crystals grow as tetragonally distorted octahedra. No indications of twinning have been found in any crystals of this compound. The density of the crystals was determined by a rough flotation method to be 1.60 ± 0.05 g/cc. The crystals tend to blacken appreciably on exposure to light.

2. X-ray data

Examination of Weissenberg and precession photographs established that the crystal class was tetragonal with Laue symmetry C_{4h} . The systematic extinctions

$$\begin{aligned} [\text{hk}\ell] &, \quad h+k+\ell \neq 2n \\ [\text{hk}0] &, \quad h, (k) \neq 2n \\ [\text{o}\ell] &, \quad \ell \neq 4n, \end{aligned}$$

imply that the crystals belong to the space group $I4_1/a$, with $a = b = 11.757 \pm 0.003 \text{ \AA}$, $c = 23.624 \pm 0.006 \text{ \AA}$ and $z = 4$.

The lattice constant data were obtained on a General Electric

XRD-5 x-ray unit equipped with a single crystal orienter and scintillation counter. Angular measurements were made on reflections in the back reflection region, using chromium radiation. The lattice constants were then obtained by least squares extrapolation (39) on nine reflections using the Nelson-Riley error formula (40).

Complete three-dimensional x-ray data to $\sin \theta/\lambda = 0.705$ were taken with zirconium-filtered molybdenum K_{α} radiation using the above mentioned equipment. The moving-crystal moving-counter technique was employed (5), with a 100 second scan through the peak setting. Background counts were determined from a plot of average background versus 2θ .

Corrections to the data were applied as shown in Chapter I, section G. The intensities of the 4.4.0, 0.8.0 and 0.0.12 reflections were followed as standards. Measurement of the intensities of these reflections were made about every four hours during the data collection period. The intensity of each reflection showed a near linear decline at a rate of 0.04 % per hour and an overall decline of 14 %.

3. Structure determination and refinement

The fact that there are four molecules per unit cell requires that the silver and chlorine atoms be placed at a precisely defined special positions having S_4 symmetry. The remaining atoms are in general positions, which mean that once the positions of the atoms in one ligand and the position of one of the perchlorate oxygen atoms are determined, the

remaining atoms in the cell are generated by the space group symmetry.

A Fortran program was written to calculate a three-dimensional Patterson map. From this map and the knowledge of the Ag and Cl positions, the position of the phosphorus atom was determined. Least squares refinement on the scale factor and the positional parameters of the phosphorus atom using the 600 strongest reflections gave an agreement factor of 0.29.

A Fortran space group specific Fourier summation program was written and an electron density map was calculated with it. Peaks of reasonable height and position were found which corresponded to the positions of the O_1 , O_2 , O_3 , C_1 , C_2 , and C_3 atoms. Isotropic least squares refinement (49) using the 600 strongest reflections resulted in an agreement factor of 0.15. A difference electron density map was then calculated, which revealed the positions of the C_4 and C_5 atoms. No resolvable peaks which correspond, either in height or in position, to the perchlorate oxygen atoms were found on any of the electron density maps. On the maps a smear of electron density is observed in the vicinity of the chlorine atom (i.e within $1.5\overset{\circ}{\text{Å}}$ of the chlorine atom). A peak corresponding in area to one-half of an oxygen atom appeared on the map approximately $2.5\overset{\circ}{\text{Å}}$ from the chlorine position, but a negative peak of equal area occurs at approximately the same radial distance from the chlorine position. Placing one-half of an oxygen atom at this position

produces an insignificant refinement and is not chemically reasonable. This peak and the related valley must be considered as spurious peaks due either to poor data or to the inability to consider the effect of the apparently randomly disordered perchlorate groups. The latter cause appears more reasonable, at this time.

Anisotropic least squares refinement (49) using all the "observed" data resulted in a final agreement factor of 0.146. No significant secondary extinction effects are apparent in the data.

Final positional parameters are given in Table 13 and the final thermal parameters in Table 14. The significant interatomic distances and angles are given in Tables 15 and 16, respectively. Figure 10 shows a comparison of the observed and calculated structure factors.

C. Discussion

Figure 11 shows the configuration of the ligand and the position of the Ag ion with respect to it. As expected the geometry about the Ag(I) atom is almost exactly tetrahedral, with P-Ag-P angles of 108.98° and 109.53° . The Ag-P distances of 2.436\AA are significantly shorter than the sum of the silver and phosphorus covalent radii (2.63\AA), and are shorter than any Ag-P distances which have been previously determined. This indicates that there is considerable "back donation" of electrons from the filled d orbitals on the silver atom to the empty d orbitals on the phosphorus

atoms. The fact that the Ag-P distance in this structure is less than that found in the $\text{AgSCNP}(\text{n-C}_3\text{H}_7)_3$ structure (i.e. 2.48\AA) is not too surprising when it is considered that the presence of the electronegative oxygen atoms attached to the phosphorus atom should reduce the electron density about the phosphorus atom, thus reducing the σ character of the Ag to P bond slightly while markedly increasing the acceptor character of the phosphorus 3d orbitals.

The nearest neighbors of the phosphorus atom are arranged in a distorted tetrahedral configuration, with O-P-O angles on the order of 100° , compared to the ideal value of 109.47° for a regular tetrahedral configuration. The compression in these angles is probably the result of the closure of the cage. The P-O-C angles are approximately 120° and the O-C-C₄ angles are roughly tetrahedral. Two of the C-C₄-C₅ angles are approximately tetrahedral while the third is roughly 119° , probably due to packing effects. The intra-cage C-C₄-C angles are roughly tetrahedral.

Two of the O-C distances are approximately the same as those observed in paraffinic alcohols, but the O₁-C₁ distance of $1.54 \pm 0.03\text{\AA}$ differs from the O-C distance in alcohols (1.43\AA) by slightly more than three standard deviations. There does not appear to be any rational explanation for this difference in length. The C-C distances in the cage are slightly longer than that of a normal C-C single bond

(1.54Å), while the C₄-C₅ distance is the same as that for a normal C-C single bond.

Table 13. Positional parameters for $\text{Ag}(\text{P}(\text{OCH}_2)_3\text{CCH}_3)_4\text{ClO}_4$

Atom	X	Y	Z
Ag	0.5000(0)	0.7500(0)	0.125(0)
Cl	0.0(0)	0.2500(0)	0.125(0)
P	0.3804(4)	0.6289(4)	0.18380(18)
O ₁	0.3919(12)	0.4974(12)	0.1755(6)
O ₂	0.2435(10)	0.6386(12)	0.1788(7)
O ₃	0.3958(16)	0.6386(12)	0.2494(6)
C ₁	0.3219(16)	0.4118(24)	0.2097(12)
C ₂	0.1695(20)	0.5731(18)	0.2095(11)
C ₃	0.3281(18)	0.5660(21)	0.2849(8)
C ₄	0.2423(15)	0.4887(14)	0.2471(8)
C ₅	0.1815(27)	0.4084(22)	0.2885(9)

Table 14. Thermal parameters for $\text{Ag}(\text{P}(\text{OCH}_2)_3\text{CCH}_3)_4\text{ClO}_4$

Atom	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag	0.00521(24)	0.00521(24)	0.00116(4)	0.0	0.0	0.0
Cl	0.0096(11)	0.0096(11)	0.0034(3)	0.0	0.0	0.0
P	0.0071(4)	0.0067(4)	0.00174(8)	-0.0005(3)	0.00017(15)	0.00018(15)
O ₁	0.0117(14)	0.0110(14)	0.0029(4)	0.0006(11)	0.0023(6)	-0.0008(6)
O ₂	0.0058(10)	0.0119(4)	0.0039(4)	0.0003(10)	-0.0008(5)	0.0016(6)
O ₃	0.0183(20)	0.0122(15)	0.0022(3)	-0.0079(14)	-0.0001(6)	-0.0011(6)
C ₁	0.0043(14)	0.018(3)	0.0048(8)	0.0005(17)	0.0023(9)	-0.0039(13)
C ₂	0.0121(23)	0.0087(19)	0.0043(7)	-0.0071(17)	-0.0001(10)	0.0000(9)
C ₃	0.0088(18)	0.0150(25)	0.0022(4)	-0.0070(7)	0.0011(7)	-0.0012(8)
C ₄	0.0060(14)	0.0065(14)	0.0019(3)	-0.0019(13)	-0.0003(5)	0.0011(6)
C ₅	0.024(4)	0.0123(23)	0.0019(4)	-0.0049(25)	0.0033(11)	0.0002(8)

^aThe temperature factor expression for all atoms is
 $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

Table 15. Interatomic distances for $\text{Ag}(\text{P}(\text{OCH}_2)_3\text{CCH}_3)_4\text{ClO}_4$

Atom (1)	Atom (2)	
Ag	P	2.436(4)
P	O ₁	1.565(15)
P	O ₂	1.559(13)
P	O ₃	1.564(14)
O ₁	C ₁	1.54(3)
O ₂	C ₂	1.41(2)
O ₃	C ₃	1.43(2)
C ₁	C ₄	1.58(3)
C ₂	C ₄	1.58(3)
C ₃	C ₄	1.63(3)
C ₄	C ₅	1.54(2)
O ₁	O ₂	2.37(2)
O ₁	O ₃	2.41(2)
O ₂	O ₃	2.40(2)
O ₂	O ₃	2.40

Table 16. Interatomic angles for $\text{Ag}(\text{P}(\text{OCH}_2)_3\text{CCH}_3)_4\text{ClO}_4$

Atom 1	Atom 2 ^a	Atom 3	Angle
P	Ag	P(1)	108.98(.10)
P	Ag	P	109.53(.10)
Ag	P	O ₁	117.2(6)
Ag	P	O ₂	119.2(6)
Ag	P	O ₃	117.2(6)
P	O ₁	C ₁	122.8(1.2)
P	O ₂	C ₂	124.9(1.5)
P	O ₃	C ₃	118.4(1.2)
O ₁	C ₁	C ₄	103.1(1.8)
O ₂	C ₂	C ₄	106.4(1.7)
O ₃	C ₃	C ₄	110.6(1.5)
C ₁	C ₄	C ₅	106.0(1.7)
C ₂	C ₄	C ₅	119.4(1.9)
C ₃	C ₄	C ₅	106.6(1.6)
O ₁	P	O ₂	98.5(8)
O ₂	P	O ₃	100.5(1.0)
O ₁	P	O ₃	100.8(9)
C ₁	C ₄	C ₂	111.5(1.8)
C ₁	C ₄	C ₃	105.5(1.6)
C ₂	C ₄	C ₃	107.0(1.5)

^aAtom 2 is vertex atom

Figure 10. Comparison of the observed and calculated structure factors for $\text{Ag}(\text{P}(\text{OCH}_2)_3\text{CCH}_3)_4\text{ClO}_4 - \text{F}(0.0.0) = 3054.3$

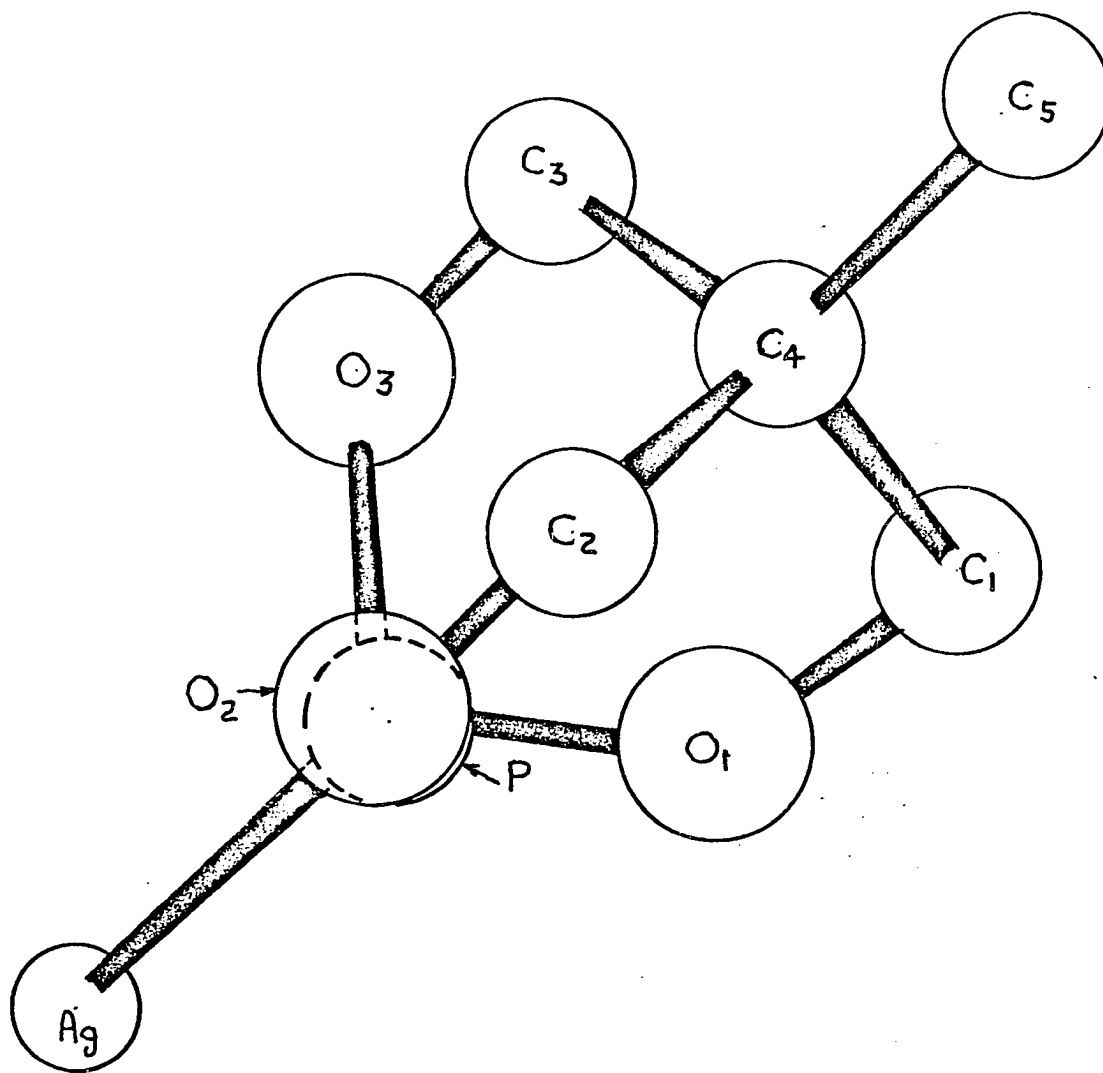


Figure 11. Ligand configuration in $\text{Ag}(\text{P}(\text{OCH}_2)_3\text{CCH}_3)_4\text{ClO}_4$

V. RESEARCH PROPOSALS

The following ideas might make interesting future research projects. At this time these ideas have not been researched in any depth.

The view of Rundle (36) that in the CuCl_2 complexes the spins on the copper atoms are aligned in parallel within one planar network, but arranged antiparallel with respect to adjacent units has not been verified. Magnetic neutron diffraction studies could be undertaken to test this view.

Another interesting series of experiments on the CuCl_2 complexes might be to investigate the relationship between the Néel point of these compounds and the length and number of the "long" copper to chlorine distance observed in these complexes. With this data it may be possible to obtain valuable information on the inter-chain magnetic interaction as function of chain separation.

A followup neutron diffraction investigation on $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ should be done to establish the hydrogen atom positions. The hydrogen bonding in the rare earth trichloride hexahydrates may then be established and the direction of the water dipole with respect to the metal to oxygen calculated.

An interesting series of compounds has recently been investigated using IR and Raman spectra, they are the carbodiimides with formula R-N=C=N-R . The compounds have some

very interesting properties. For example they have dipole moments on the order of two Debyes, yet the N-C-N system is apparently linear. The spectral investigations were unable to determine the angle the R groups make with respect to the N-C-N system, nor the configuration, other than that they are approximately cis. A three-dimensional x-ray diffraction investigation would supply this information.

VI. SUMMARY

The results of single crystal x-ray diffraction studies on $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$, $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ag}(\text{P}(\text{OCH}_2)_3\text{CCH}_3)_4\text{ClO}_4$ were reported.

The compound $\text{Cu}_5\text{Cl}_{10}(\text{C}_3\text{H}_7\text{OH})_2$ crystallizes in the monoclinic system with space group $\text{P}2_1/c$, lattice constants $a = 10.244 \pm 0.007 \text{ \AA}$, $b = 6.025 \pm 0.008 \text{ \AA}$, $c = 20.41 \pm 0.015 \text{ \AA}$, $\beta = 115.48 \pm 0.03^\circ$ and $z = 2$. The crystals consist of an interlacing of essentially planar copper-chlorine bridge networks, each of which have the above formula. The n-propanol groups are attached to the terminal copper atoms and are located trans with respect to each other. The planar networks are held together by long copper to chlorine bonds of 2.68 and 2.69 \AA . The central copper in each unit has a square planar configuration, while the remaining coppers are five coordinate with a square pyramidal configuration.

The compound $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ crystallizes in the monoclinic system with space group $\text{P}2_1/n$, lattice constants $a = 7.868 \pm 0.003 \text{ \AA}$, $b = 6.491 \pm 0.003 \text{ \AA}$, $c = 9.596 \pm 0.004 \text{ \AA}$, $\beta = 93.69 \pm 0.02^\circ$ and $z = 2$. The formula for this compound should be written $[\text{Dy}(\text{H}_2\text{O})_6\text{Cl}_2]^+\text{Cl}^-$, the metal ion having an eight membered coordination sphere. The atoms in this coordination sphere are arranged in a distorted dodecahedron with triangular faces. There appears to be a strong possibility that hydrogen bonding occurs between water oxygens within the coordination

sphere. The result of a joint structure determination on $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ was presented for completeness. A comparison of the structures of the isostructural compounds $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ was given.

The compound $\text{Ag}(\text{P}(\text{OCH}_2)_3\text{CCH}_3)_4\text{ClO}_4$ crystallizes in the tetragonal system with space group $I4_1/a$, lattice constants $a = b = 11.757 \pm 0.003 \text{ \AA}$, $c = 23.624 \pm 0.006 \text{ \AA}$ and $z = 4$. The ligands are arranged in a regular tetrahedron about the silver ion, with a Ag-P distance of 2.436 \AA indicating strong $d\pi-d\pi$ back bonding. The ligand has a cage structure of the triane type.

Several proposals for future research were given.

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