STUDIES IN X-RAY CRYSTALLOGRAPHY

I. CALCIUM CHLORIDE HEXAHYDRATE

II. HEXAMETHYLENE TETRAMINE COMPLEXES WITH METAL HALIDES

Thesis by

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Abstracts

Abstract of Section I

The crystal structure of calcium chloride hexahydrate has been determined by means of Patterson syntheses and stereochemical consideration of the atomic positions allowed by possible space groups. The parameters were determined from peaks in the Patterson syntheses, which were well resolved.

This determination confirms the conclusions of Jensen (7,8), who used a method of successive Fourier syntheses to arrive at the structure of the alkaline earth hexahydrates and to obtain approximate parameters for strontium chloride hexahydrate, but did not refine these parameters.

The results of this investigation were as follows:

Space group: D_3^2—C321
Unit cell: a = 7.80 Å., c = 3.95 Å.; contains one molecule $CaCl_2 \cdot 6H_2O$.
Atomic positions: Ca at 1(a) 0 0 0;
Cl at 2(d) $\frac{1}{3}\,\frac{2}{3}\,z,\ \frac{2}{3}\,\frac{1}{3}\,\bar{z}$, z = 0.576
O_I at 3(e) $x\,0\,0,\ 0\,x\,0,\ \bar{x}\,\bar{x}\,0$, x = 0.313
O_{II} at 3(f) $x\,0\,\frac{1}{2},\ 0\,x\,\frac{1}{2},\ \bar{x}\,\bar{x}\,\frac{1}{2}$, x = − 0.218.

The bonding within the crystal is discussed in the light of the observed interatomic distances.

Abstract of Section II

The structures of certain complexes of metal halides with hexamethylene tetramine, $C_6H_{12}N_4$, have been investigated.

The compound $SnCl_4 \cdot 4C_6H_{12}N_4$ and the isomorphous $TiCl_4 \cdot 4C_6H_{12}N_4$ have space group C_{3v}^5–R3m. The triply primitive hexagonal unit cell has $a = c = 8.95$ Å. It contains three hexamethylene tetramine molecules and three chlorine atoms. The centers of the hexamethylene tetramines and of the chlorines form two interpenetrating rhombohedral lattices, separated by half the rhombohedral body diagonal. The tin atoms are probably distributed randomly among the gaps between the larger atoms.

The compounds $MnCl_2 \cdot 2C_6H_{12}N_4$ and $MnBr_2 \cdot 2C_6H_{12}N_4$ give powder photographs considerably different from each other. The former has Laue symmetry D_{2h}, $a = 11.86$ Å., $b = 21.92$ Å., $c = 7.23$ Å. The lattice is primitive. There is no glide plane normal to *a*, but possibly an *n* glide normal to *b* and probably a *b* glide normal to *c*.

A complex of hexamethylene tetramine with $SnCl_2$ gave the same powder pattern as $SnCl_4 \cdot 4C_6H_{12}N_4$. A compound with $SbCl_3$ gave the same pattern with a few additional lines. The formulas of the complexes are reported (7) to be $SnCl_2 \cdot 2C_6H_{12}N_4$ and $SbCl_3 \cdot 3C_6H_{12}N_4$.

The main factors determining the structures of these compounds seem to be packing of the anions with hexamethylene tetramine molecules and interactions among the latter as in crystals of the pure compound.

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I. Calcium Chloride Hexahydrate

Introduction

The crystal structure of calcium chloride hexahydrate and the other alkaline earth halide hexahydrates was first investigated by Z. Herrmann (5). The structure chosen by him contained very flat octahedral $Ca(H_2O)_6$ groupings, almost plane hexagons, in which the water molecules are only 1.8 to 2.0 Å. apart. The description in the Strukturbericht (4) terms this structure sehr unwahrscheinlich.

It was decided to undertake a determination of the structure of calcium chloride hexahydrate, since this contains the lightest ions of the isomorphous series of calcium, strontium, and barium chlorides, bromides, and iodides. Other things equal, the positions of the weakly scattering water molecules should permit of most accurate determination when the other atoms present are the weakest scatterers possible.

Only after this work had been in progress for some time was another investigation of the structure discovered in the literature. Jensen (7) investigated strontium chloride hexahydrate, using a method of successive Fourier projections to determine the space group and approximate parameters. He used the heavy-atom method to establish the signs of F in a few reflections from which he calculated preliminary Fourier projections. Choosing likely peaks for atomic positions, he calculated the signs of more F's, used them in another Fourier projection, and repeated the process until all the F's had been used.

Jensen's intensity data were obtained from crude assignments to six grades of intensity from "strong" to "very weak." He made charts, from data given by Yü and Beevers (13) for zinc bromate hexahydrate, showing $|F|$ as a function of $\sin\theta$ for each of these grades. Assuming that corrections for absorption, Lorentz and polarization factors, and temperature factors would be the same as for zinc bromate hexahydrate, he used these curves to find $|F|$ values for his investigation.

The structure arrived at by Jensen has a hexagonal unit cell containing one molecule $SrCl_2 \cdot 6H_2O$. The axes are $a = 7.940$ Å., $c = 4.108$ Å. The space group[1] is D_3^2–C321 with atomic positions as follows:

Sr in 1(a) 0 0 0;

2 Cl in (d) $\frac{1}{3}\,\frac{2}{3}\,z$, $\frac{2}{3}\,\frac{1}{3}\,z$, $z = 0.42$;

O_I in 3(e) $x\,0\,0$, $0\,x\,0$, $\bar{x}\,\bar{x}\,0$, $x = 0.33$;

O_{II} in 3(f) $x\,0\,\frac{1}{2}$, $0\,x\,\frac{1}{2}$, $\bar{x}\,\bar{x}\,\frac{1}{2}$, $x = -0.24$.

In this structure each Sr^{++} ion is surrounded by nine water molecules, a rather unusual configuration. In view of the novelty of the structure it was thought desirable to continue my investigation in order to obtain independent confirmation by methods as different as possible from those used by Jensen. In addition, as Jensen says (8, pp. 71, 90), it was desirable that his parameter determinations be considerably refined so that conclusions might be drawn as to the nature of bonding in the crystal.

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[1] All symbols for space groups and special positions correspond to the descriptions in the Internationale Tabellen (6).

Preparation of Samples

Samples of calcium chloride hexahydrate were prepared by evaporation of water from a solution in a desiccator, but the method was inconveniently slow and tended to give a crust of solid on the surface rather than separated single crystals. It was found more convenient to cool a solution having slightly more than the stoichiometric ratio $H_2O : CaCl_2 = 6 : 1$. Such a solution frequently remained supercooled for a long time in a bottle or sealed test tube in the refrigerator, but seed crystals could be formed by touching the container to a piece of solid carbon dioxide. The best crystals were obtained if the container, with a seed crystal in the liquid, was placed inside a Dewar vessel in the refrigerator's freezing compertment.

The difficulty in obtaining large single crystals of pure material was strikingly different from that experienced in the Biology Department, where a technical grade calcium chloride solution in a battery jar with stirrer was used for humidity control. There the difficulty was that crystals formed immediately whenever the temperature of the bath fell below the melting point of the hexahydrate. They were regular hexagonal prisms, often the length of a lead pencil and up to twice that diameter. It is unfortunate that the material was not sufficiently pure for use in this investigation.

Because of the hygroscopic nature of calcium chloride hexahydrate, any sample to be used for long X-ray exposures must be well protected from the atmosphere. Thin-walled Pyrex glass capillaries were used for this purpose. It was very difficult to insert single crystals and seal the capillaries without access of moisture, especially if a particular orientation of the crystal was desired. This difficulty was eventually overcome by a technique of recrystallization within the sealed capillary.

In the method finally used for preparing single-crystal X-ray specimens, a sample of the solid compound was prepared by slow cooling in the refrigerator. The crystals were filtered by suction in an apparatus which covers the solid with dry air at all times. Then a few fragments were inserted in a capillary and it was sealed by means of a microburner as quickly as possible. Any adhering liquid was centrifuged to the other end of the rather long capillary, and the section containing the solid was sealed off.

The material now sealed in the capillary was recrystallized under a binocular microscope. Very gentle warming from one end by means of the finger, a seven-watt lamp, or (preferably) a "hot wire" tool with enough current passing to make the wire just noticeably warm to the fingers, was sufficient to melt the solid slowly. Melting was continued until almost all of the material, occupying perhaps 4 mm. in a 1/2 – mm. capillary, was liquid. Then removal of the heat source allowed the few remaining small crystals to grow and fill the tube.

Remelting several times from opposite ends caused all but a single crystal to disappear. This crystal could be observed as it grew, so that the approximate orientation could be determined.

There was considerable tendency for new crystals to form whenever a growing needle struck the capillary wall, especially if the room temperature was lower than about 24° C.[1] With the binocular microscope, however, it was easy to make sure that only one crystal was finally present. This single crystal was cylindrical, since it completely filled the capillary. To correct X-ray intensities for absorption it is frequently desirable to make a cylindrical crystal in order to simplify the calculations; this capillary technique is very useful for the purpose.

The needles of calcium chloride hexahydrate grew about ten times as rapidly along the needle axis as they did perpendicular to it. This fact made it a simple matter to prepare a crystal with the needle axis along the capillary tube, but very difficult to grow a needle perpendicular to the axis of the capillary. Attempts were made to crystallize a droplet at a sharp right-angle bend in the capillary, but the needle axis tended to "bend" and follow the tube because new crystallization was initiated whenever a needle struck the capillary wall obliquely. Eventually after many trials a crystal was prepared with the needle axis almost perpendicular to the capillary by mounting the tube vertically, melting away all but one small needle shorter than the diameter of the tube, and shaking this crystal into the desired position before it grew too large.

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[1] The tendency of calcium choride hexahydrate to initiate new crystallization when a growing crystal strikes the capillary wall is similar to the tendency for ice crystals to form in different directions when one growing crystal strikes the surface or the container wall (see Reference (3)).

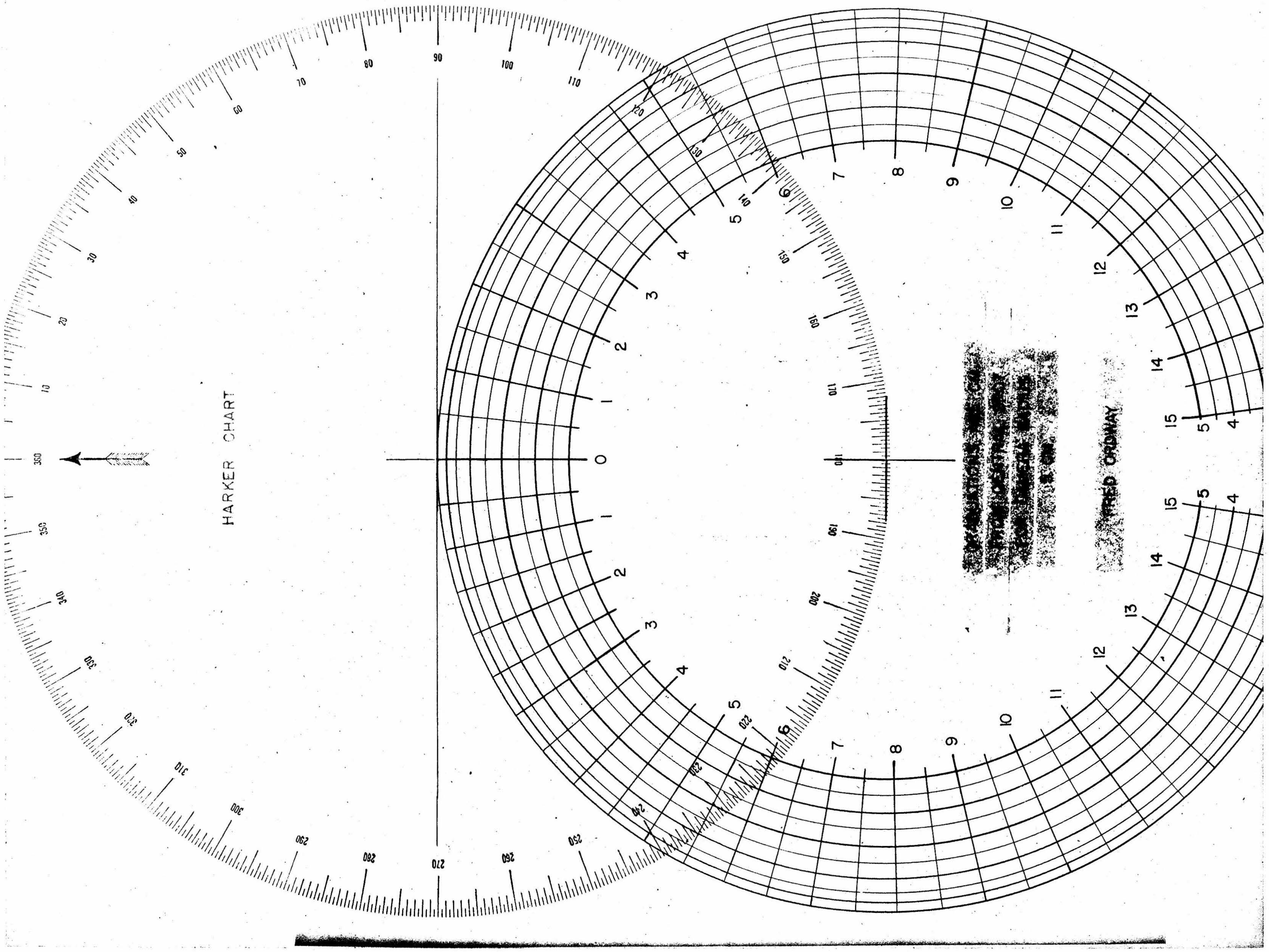
Preparation of X-Ray Photographs

The crystals of calcium chloride hexahydrate sealed in thin-walled Pyrex capillaries were kept in a refrigerator except during X-ray exposures. While photographs were being taken, the crystal was kept cool by a stream of chilled dry air. Compressed air from the laboratory line, after passing through a filter and pressure reducer which regulated the pressure at 1/2 to 1 pound per square inch, was led through three 24-inch glass drying towers containing technical potassium hydroxide flakes and one such tower containing indicating Drierite. The air, dried in this way to prevent clogging of the cold chamber, passed through a U-tube cooled with solid carbon dioxide and then by means of a vacuum-jacketed tube was led into the X-ray camera directly above the crystal.

The difference between room temperature and the temperature of the crystal was indicated continuously by a copper-constantan thermocouple, whose junction was about 1 cm. above the crystal, connected to a microammeter. The crystal temperature varied over a range of about 5°–15° C.

Crystals were oriented for oscillation and rotation photographs by means of Laue photographs.

The oscillation photographs were indexed by means of a reciprocal lattice diagram and a Harker chart showing actual film coordinates in centimeters (Figure 1). It was found most convenient to use the Harker chart as a transparency made from Ozalid sensitized foil, with a separate black-line print of the reciprocal lattice diagram for each layer line.



[redacted]

Figure 1. Harker chart for indexing rotation and oscillation photographs. Reciprocal lattice scale is 1/ = 10 cm. Camera radius is 5 cm.

The values of the lattice constants were determined from oscillation photographs made with CuKα radiation. Measurements of the films were made on a viewing box equipped with a glass cursor sliding on a brass scale, read with a vernier to 0.1 mm.

For intensity estimations MoKα oscillation photographs were prepared by the multiple-film technique. The three films were interleaved with 0.001-inch copper sheets to increase the ratio between densities of corresponding spots on successive films. In comparing spots on different films of a set, the film factor (9, p. 42) was taken to be 4.0.

The estimates of intensity were made for one set of films by assigning an arbitrary value to one strong spot on the first film and corresponding values to corresponding spots on the succeeding films. This provided a geometric series of intensities which was extended by comparison of the first and last films. Eventually a scale of intensities covering the whole range was established. The remaining spots were estimated by comparison with this scale. The scales for different sets of films were correlated by using as standards those spots which were equivalent, because of symmetry or overlapping ranges of oscillation, to reflections previously estimated on another set of films.

The observed intensities were corrected for the "velocity factor" by use of a transparent chart reproduced from the publication of Cox and Shaw (2). The remaining portion of the reciprocal Lorentz-polarization factor, dependent only on the Bragg angle θ, is the expression $(\sin 2\theta) / (1 + \cos^2 2\theta)$. The value of this function for each reflection

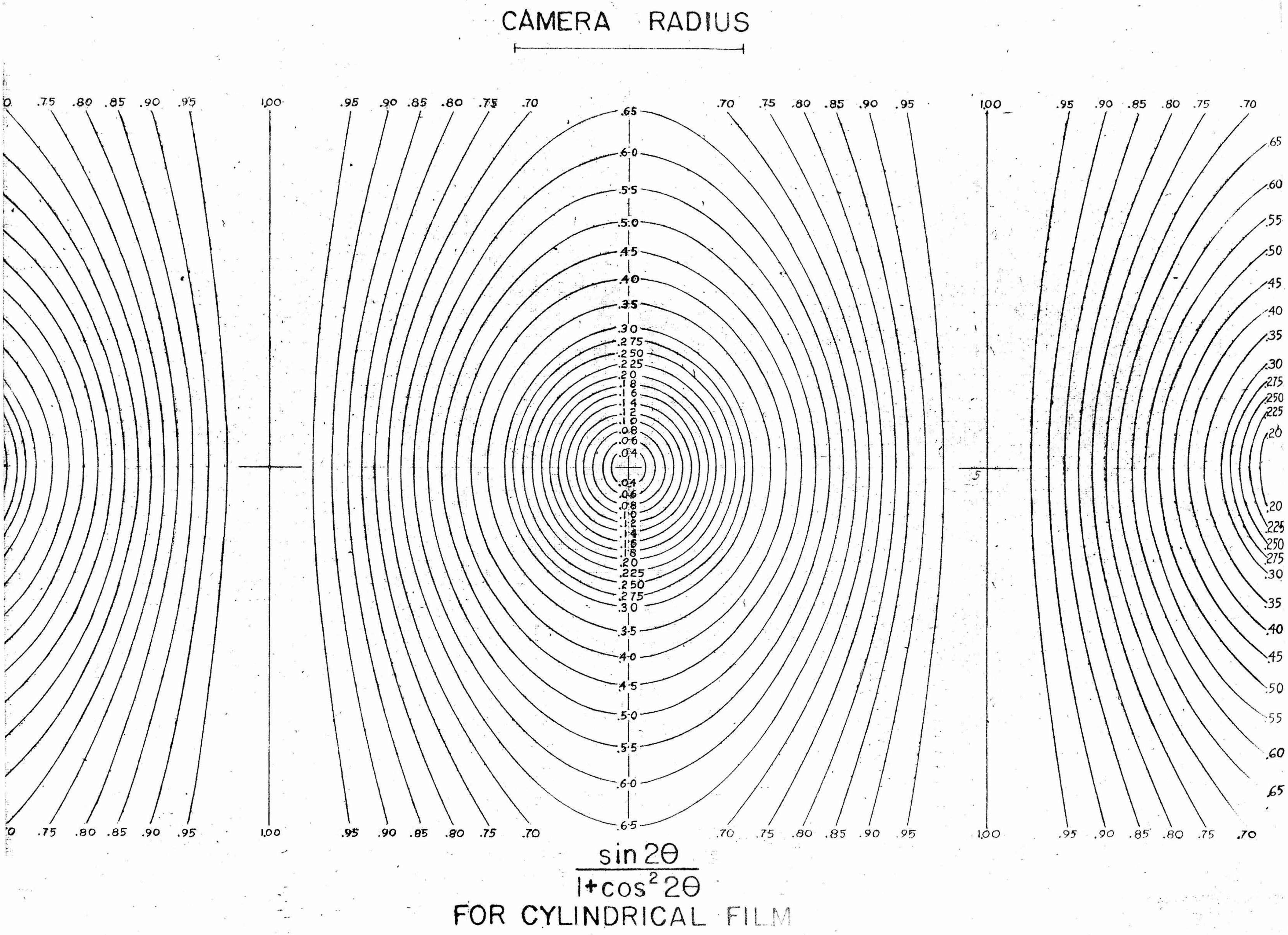


Figure 2. Chart for determination of $(\sin 2\theta)/(1 + \cos^2 2\theta)$ from rotation and oscillation photographs. Camera radius is 5 cm.

Unit Cell and Space Group

The Laue symmetry of calcium chloride hexahydrate was found to be $D_{3d}-\bar{3}m$. A rotation photograph about the three-fold axis with CuKα radiation gave the length of the $\underset{\sim}{c}$ axis as 3.9 Å. The rotation photograph was indexed on a hexagonal lattice, with a = 7.8 Å.

There were two possible choices for the direction of the $\underset{\sim}{a}$ axis, lying at an angle of 30° from each other. The proper choice was made by taking a rotation photograph of a crystal grown with the needle axis perpendicular to the capillary tube, with one of the mirror planes vertical and the three-fold axis horizontal. The layer-line spacing corresponded to a vertical unit translation of 13.5 Å., which is $7.8\sqrt{3}$. Therefore the shortest $\underset{\sim}{a}$ axis is 7.8 Å. and lies normal to the mirror plane and parallel to the two-fold axis. A well-exposed Laue photograph taken along the three-fold axis with a minimum wavelength of 0.24 Å. was indexed on this lattice and found to contain spots corresponding to wavelengths as low as 0.28 Å. but none below the minimum.

The best values of the lattice parameter, obtained from reflections at high angles, are

$$a = 7.80 \pm 0.02 \text{ Å.}$$

$$c = 3.95 \pm 0.01 \text{ Å.}$$

The density reported in "International Critical Tables" (Vol. 3, p. 43) is 1.72; this corresponds to 0.98 molecules $CaCl_2 \cdot 6H_2O$ in the unit cell. Thus the number may be taken as unity.

The Laue symmetry D_{3d} requires that the true point group be C_{3v}, D_3, or D_{3d}. Since there is only one calcium atom per unit cell, no space group need be considered which has no one-fold special positions. This restriction eliminates all but six space groups: C_{3v}^1–C3m1, D_3^2–C321, D_{3d}^3–C$\overline{3}$m1, C_{3v}^2–C31m, D_3^1–C312, D_{3d}^1–C$\overline{3}$1m. These are in pairs corresponding to the alternative choices of the $\underset{\sim}{a}$ axis. The axes already chosen therefore allow only the first three space groups.

Atomic Positions

In all cases, the calcium ion may be placed at the origin without loss of generality. The special positions suitable for the chloride ions are listed in Table 1.

Table 1

Possible Positions of Chlorine in $CaCl_2 \cdot 6H_2O$

Space Group	Positions
C^1_{3v}–C3m1	1(a) $0\ 0\ z$ 1(b) $\frac{1}{3}\ \frac{2}{3}\ z$ 1(c) $\frac{2}{3}\ \frac{1}{3}\ z$
D^2_3–C321	2(c) $0\ 0\ z;\ 0\ 0\ \bar{z}$ 2(d) $\frac{1}{3}\ \frac{2}{3}\ z;\ \frac{2}{3}\ \frac{1}{3}\ \bar{z}$
D^3_{3d}–C$\bar{3}$m1	2(c) $0\ 0\ z;\ 0\ 0\ \bar{z}$ 2(d) $\frac{1}{3}\ \frac{2}{3}\ z;\ \frac{2}{3}\ \frac{1}{3}\ \bar{z}$

The ionic radii of Ca^{++} and Cl^- are 0.99 Å. and 1.81 Å. respectively (12, p. 346). One chloride ion therefore will fit within the height of the unit cell, 3.95 Å.; but it cannot be placed at the same x and y coordinates as the calcium ion or the other chloride ion. This consideration rules out the three sets of positions involving 0 0 z. The chloride ions then must have x y coordinates $\frac{1}{3}\ \frac{2}{3}$ and $\frac{2}{3}\ \frac{1}{3}$ respectively. The z coordinates may be independent if the space group is C^1_{3v}–C3m1, or equal and opposite if the space group is one of the other two.

The fact that there is insufficient space for another atom to fit directly above or below the chloride ions or the calcium ion means that the only interatomic vectors with components $\frac{1}{3}\ \frac{2}{3}\ z$ are Ca—Cl and Cl—Cl, and O—O vectors whose effect should be negligible. Therefore it was possible to determine the chloride positions, except for possible ambiguity due to lack of a center of symmetry, by calculating a Patterson synthesis (10) along the line $\frac{1}{3}\ \frac{2}{3}\ z$. Such a three-dimensional summation requires values of $|F|^2$ for all observable reflections. Accordingly, multiple-film MoKα oscillation photographs were made with the crystal which had been oriented to rotate about an axis perpendicular to both $\underset{\sim}{a}$ and $\underset{\sim}{c}$. Having the three-fold symmetry axis horizontal made it possible to cover the reciprocal lattice efficiently in all directions by means of a single series of oscillations.

All spots up to and including the eleventh layer line were indexed. Their intensities were estimated and $|F|^2$ values calculated. No correction was made for absorption because the absorption coefficient of calcium chloride hexahydrate is only 14.2. For a sample of this nature with a diameter of 0.8 mm. the absorption correction is at most only a few percent (6, Vol. 2, p. 584).

The relative $|F|^2$ values on an arbitrary scale for the 229 forms observed are listed in Appendix 1. From these data the function

$$P(\tfrac{1}{3}\ \tfrac{2}{3}\ z) = \sum_{H}\sum_{K}\sum_{L} |F_{HKL}|^2 \cos 2\pi\left(\frac{H}{3} + \frac{2K}{3} + Lz\right)$$

was calculated, by means of punched cards prepared from Lipson—Beevers strips, at intervals of 1/60 in z. The resulting curve is shown in Figure 3. Similar calculations for the lines x 0 0 and x 0 $\frac{1}{2}$ were also made, with the results shown in Figure 4.

The interatomic vectors represented by the synthesis along $\frac{1}{3}$ $\frac{2}{3}$ z are two Ca—Cl and one Cl—Cl interaction. In this case the two types are indistinguishable because Ca^{++} and Cl^{-} have the same number of electrons; a repetition of the procedure for $SrCl_2 \cdot 6H_2O$ would clearly distinguish between them.

There are two peaks in the function: one at z= 0.853 and another almost exactly twice as high at z = 0.578. This accurate 2:1 ratio in height indicates that the larger peak is due to very close coincidence of two of the three vectors.

The smaller peak may be due to a Ca—Cl interaction or a Cl—Cl interaction. The three choices of chlorine positions which may be made corresponding to the observed Patterson function are shown in Figure 5.

The first two arrangements correspond to space group C_{3v}^{1}—C3ml and one is an inversion, through the origin, of the other. This type of arrangement places one chlorine approximately in the horizontal plane of the calcium ions and the other approximately half—way between such planes.

If the space group is C_{3v}^{1}—C3ml there are two possible arrangements for the six water molecules: two sets 3(d) $x\ \bar{x}\ z;\ x\ 2x\ z;\ 2\bar{x}\ \bar{x}\ z;$ or one set 6(e) $x\ y\ z;\ \bar{y},\ x{-}y,\ z;\ y{-}x,\ \bar{x},\ z;\ \bar{y}\ \bar{x}\ z;\ x,\ x{-}y,\ z;\ y{-}x,\ y,\ z.$

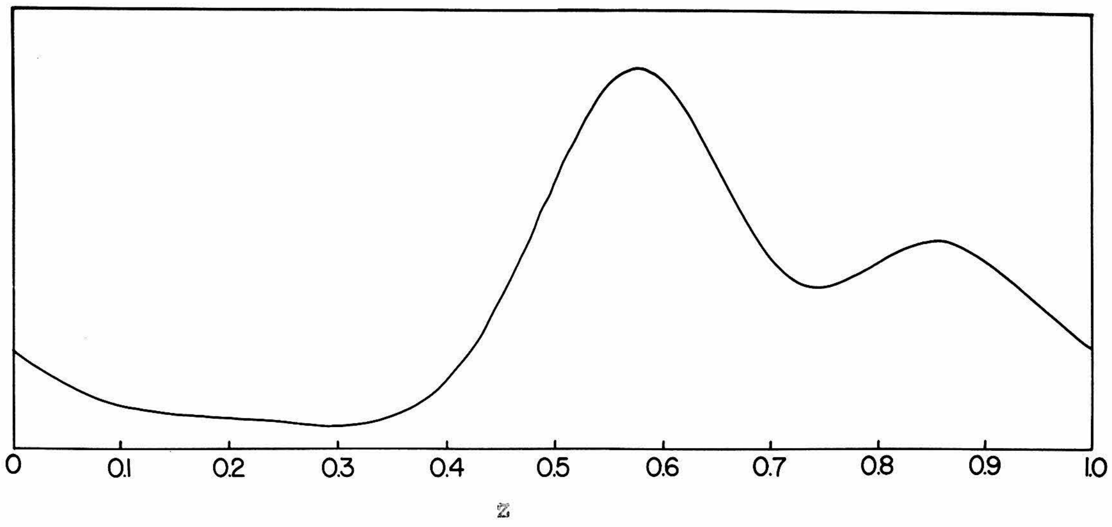


Figure 3. Patterson synthesis $P(\frac{1}{3}\ \frac{2}{3}\ z)$ for calcium chloride hexahydrate.

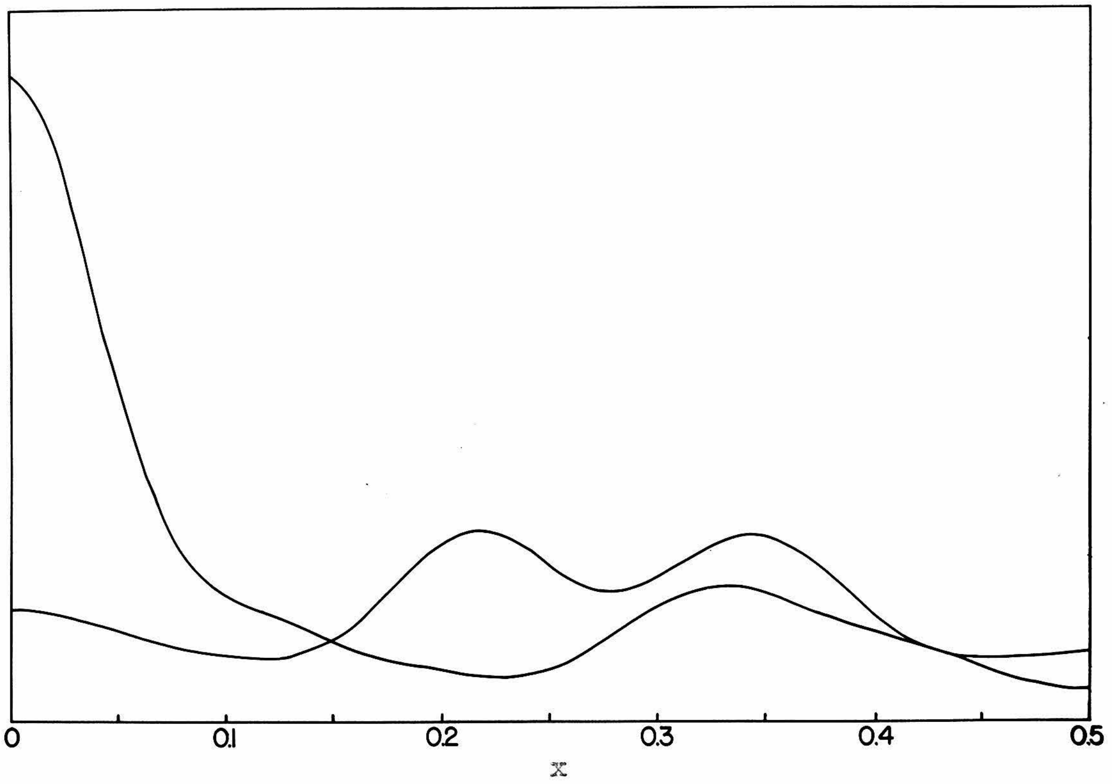


Figure 4. Patterson syntheses $P(x\ 0\ 0)$ (with high peak at the origin) and $P(x\ 0\ \frac{1}{2})$ for calcium chloride hexahydrate.

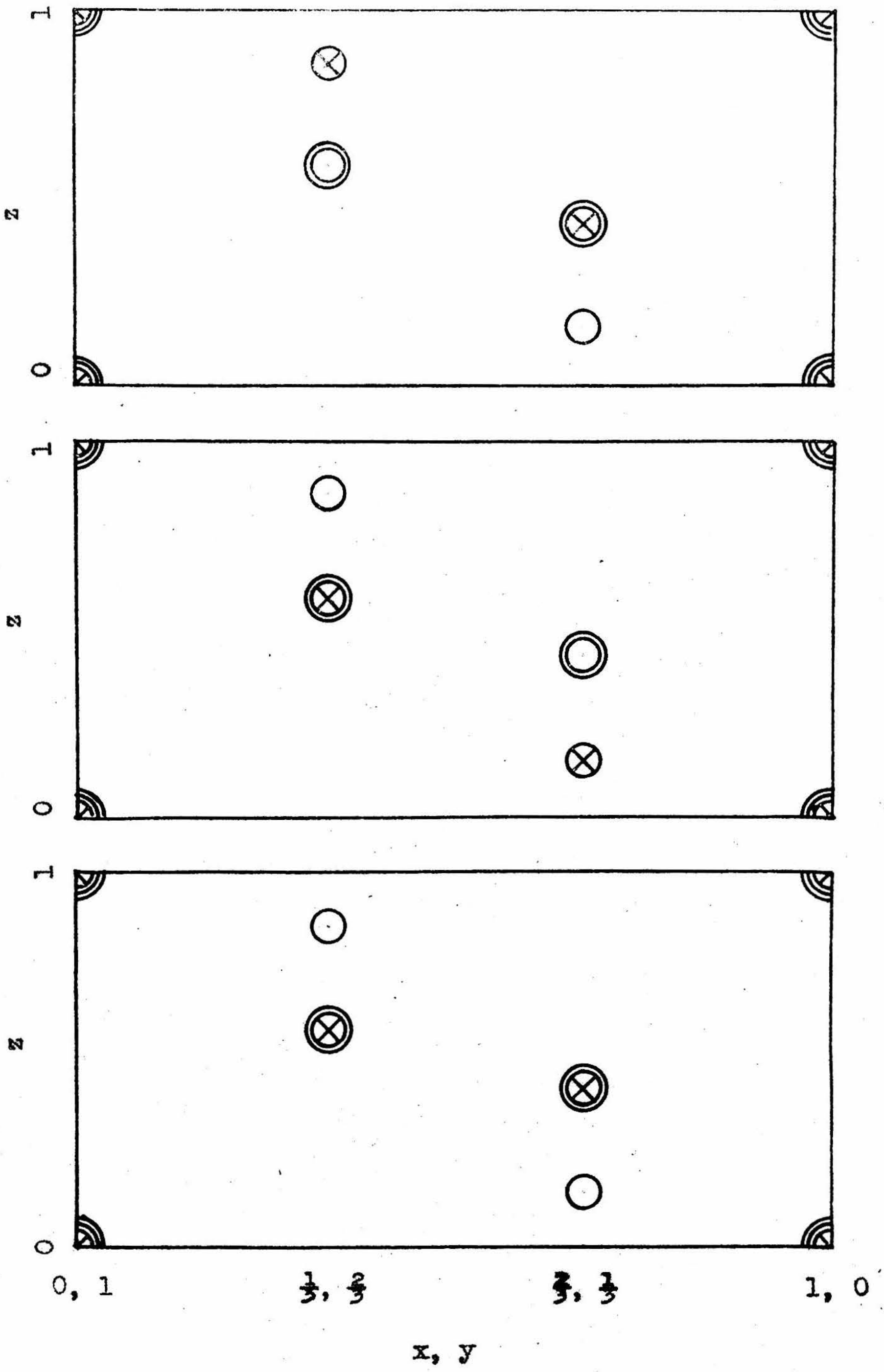


Figure 5. Positions of calcium and chloride ions and corresponding Patterson peaks. Each X represents the position of an atom; each circle, an interatomic vector. The height of a peak is proportional to the number of circles at that point.

The six-fold position places all the oxygen atoms at the same z, in a fairly regular hexagon. But there is no level at which such a grouping can fit if we assume van der Waals radii of 1.0 Å. for calcium, 1.8 Å. for chlorine, and 1.3 Å. for water. Therefore this six-fold position may be discarded.

The three-fold position allows two triangular groupings at different levels. One member of each triangle must be in a position $x \bar{x} z$ and thus in the plane containing the calcium and the two chlorine atoms corresponding to the diagrams in Figure 5. The radius of the water molecule defines the minimum size of the triangle and requires that x be positive or negative by at least 0.11. One suitable position in this plane corresponds to $x = 0.11$, z about $\frac{1}{2}$, in the first diagram of Figure 5; but the corresponding position at $x = -0.11$, z about $\frac{1}{2}$ is much too near the second chlorine atom. No other suitable position can be found, and therefore this arrangement of the water molecules is impossible.

Thus, because of stereochemical considerations, the asymmetric chlorine arrangement must be abandoned.

The alternative arrangement puts both chlorines at z about $\frac{1}{2}$. Stereochemical considerations rule out position 3(d) in space group C_{3v}^{1}–C3ml as before. Position 6(e), forming a plane group of six water molecules, is also impossible because of insufficient space.

The special positions possible in the remaining space groups are as follows:

D_3^2–C321: 3(e) $x\ 0\ 0;\ 0\ x\ 0;\ \bar{x}\ \bar{x}\ 0;$

3(f) $x\ 0\ \tfrac{1}{2};\ \bar{x}\ \bar{x}\ \tfrac{1}{2};$

6(g) $x\ y\ z;\ \bar{y},\ x{-}y,\ z;\ y{-}x,\ \bar{x},\ z;$
$y\ x\ \bar{z};\ \bar{x},\ y{-}x,\ \bar{z};\ x{-}y,\ \bar{y},\ \bar{z}.$

D_{3d}^3–$C\bar{3}$m1: 3(e) $\tfrac{1}{2}\ 0\ 0;\ 0\ \tfrac{1}{2}\ 0;\ \tfrac{1}{2}\ \tfrac{1}{2}\ 0;$

3(f) $\tfrac{1}{2}\ 0\ \tfrac{1}{2};\ 0\ \tfrac{1}{2}\ \tfrac{1}{2};\ \tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2};\ 0\ x\ \tfrac{1}{2}$

6(g) $x\ 0\ 0;\ 0\ x\ 0;\ \bar{x}\ \bar{x}\ 0;\ \bar{x}\ 0\ 0;\ 0\ \bar{x}\ 0;\ x\ x\ 0;$

6(h) $x\ 0\ \tfrac{1}{2};\ 0\ x\ \tfrac{1}{2};\ \bar{x}\ \bar{x}\ \tfrac{1}{2};\ \bar{x}\ 0\ \tfrac{1}{2};\ 0\ \bar{x}\ \tfrac{1}{2};\ x\ x\ \tfrac{1}{2};$

6(i) $x\ \bar{x}\ z;\ x\ 2x\ z;\ 2\bar{x}\ \bar{x}\ z;\ \bar{x}\ x\ z;\ \bar{x}\ 2\bar{x}\ \bar{z};\ 2x\ x\ \bar{z}.$

To obtain more information as to the positions of the water molecules a Patterson projection was calculated from $|F|^2$ values of the reflections in the zone [120] perpendicular to the plane (010). The modification function $1/(\bar{f})^2$ suggested by Patterson (10) was applied in order to sharpen the peaks. A plot of this projection is shown in Figure 6. As expected, it contains the Ca and Cl peaks at $x = 0$ and $\tfrac{1}{2}$, with less prominent Ca–O or Cl–O peaks in between. Apparently the oxygens, like the calcium and chlorine atoms, have z approximately zero or one-half.

The fact that this projection shows no maxima at $x = \tfrac{1}{4}$ rules out positions 3(e) and 3(f) in space group D_{3d}^3–$C\bar{3}$m1. Positions 6(g) and 6(h) are impossible because they form hexagons of water molecules all with the same z.

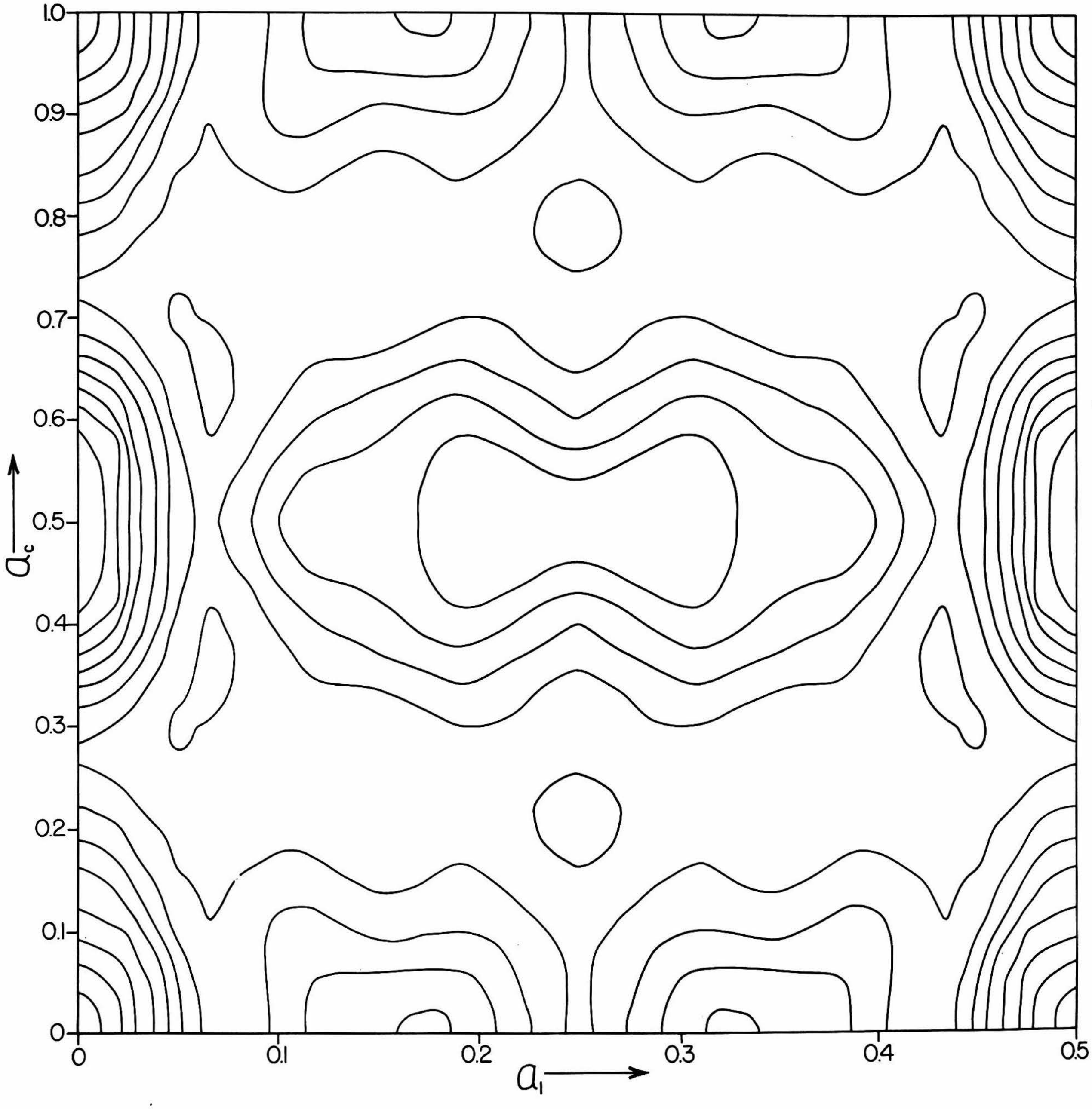


Figure 6. Patterson projection perpendicular to the plane (0 1 0) with modification function $1/(\bar{f})^2$.

Values of the contour lines on an arbitrary scale: −100, −50, 0, 50, 100, 200, 300, 400, 500.

Two Harker sections were calculated, giving the values of the Patterson function in planes x 0 z and x y 0. These are shown in Figures 7 and 8. There are three peaks in the function P(x 0 z) corresponding to calcium—oxygen or chlorine—oxygen distances: a peak at (0.34, 0, $\frac{1}{2}$) which is elongated in the z direction: a symmetrical peak at (0.218, 0, $\frac{1}{2}$); and another symmetrical peak at (0.313, 0, 0). The plot of P(x y 0) shows no calcium- or chlorine-oxygen peaks other than the one at (0.313, 0, 0).

The remaining position 6(i) of space group D_{3d}^{3}—$C\bar{3}m1$ would require that oxygen atoms be in vertical planes containing a calcium and its chlorine neighbors. The coordinate z would have to be about $\frac{1}{2}$ to fit in one water molecule in such a position, but this would put the six molecules at corners of an impossibly small hexagon. Thus D_{3}^{2}—C321 must be the true space group.

In D_{3}^{2}—C321, position 6(g) with z about 0 or $\frac{1}{2}$ would again form a plane hexagon of oxygens and must therefore be discarded. Positions 3(e) and 3(f), however, are permitted by stereochemistry and are not in conflict with the observed Patterson peaks.

All the peaks in the functions P(x 0 z) and P(x y 0) are explained by this choice of oxygen positions. In particular, the symmetrical oxygen peaks in the x 0 z section (Figure 7) at z = 0 and $\frac{1}{2}$ are assigned to Ca—O vectors. In the x y 0 section (Figure 8) the peaks at x = 0.313 correspond to Ca—O. The remaining maxima, vertically elongated in Figure 7 and correspondingly less intense in Figure 8, are Cl—O peaks.

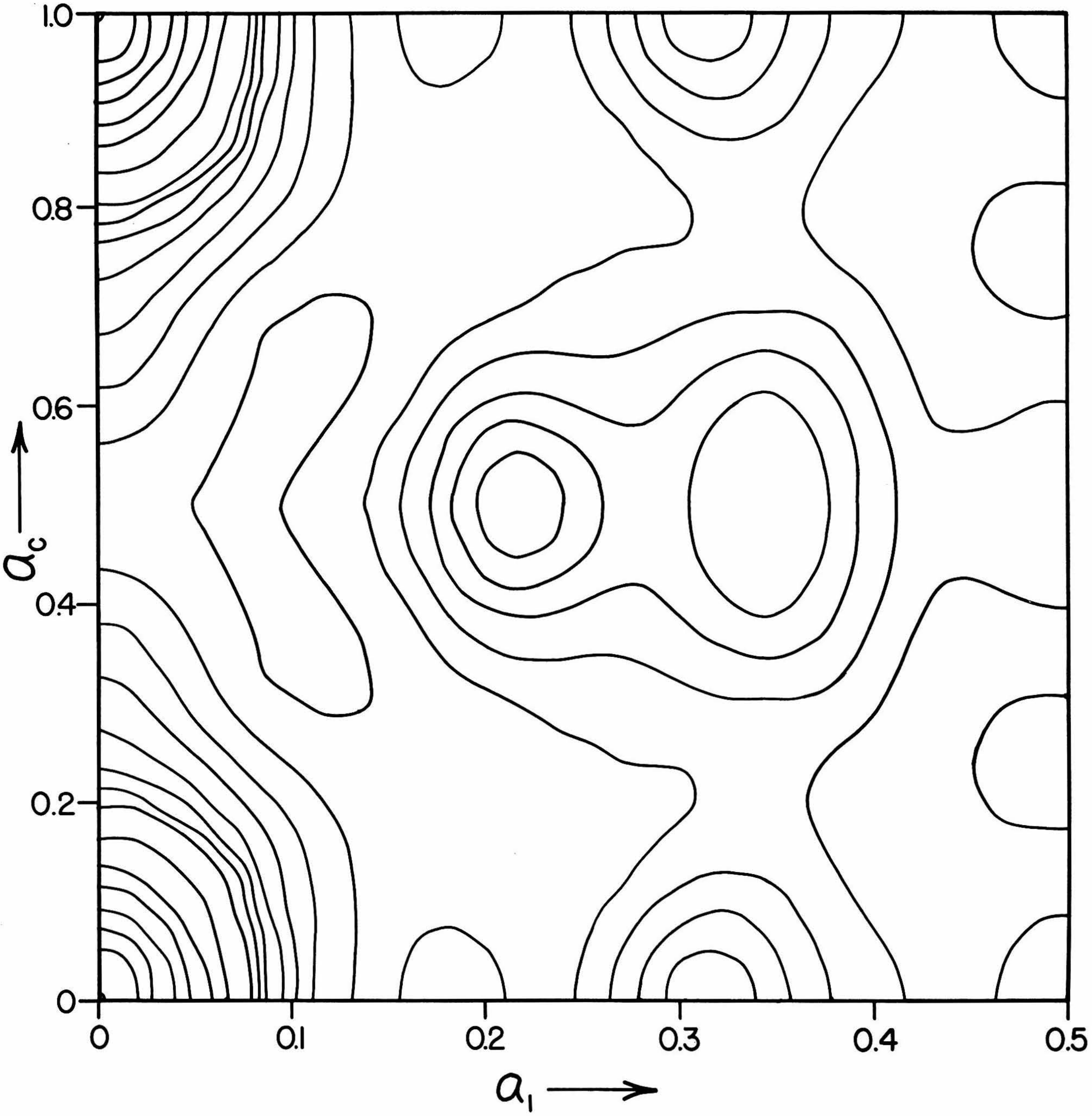


Figure 7. Harker section P(x 0 z) for calcium chloride hexahydrate.

Values of the contour lines on an arbitrary scale: -100, 0, 100, 200, 300, 400, 500, 600, 1000, 1500, 2000, 2500, 3000, 3500, 4000.

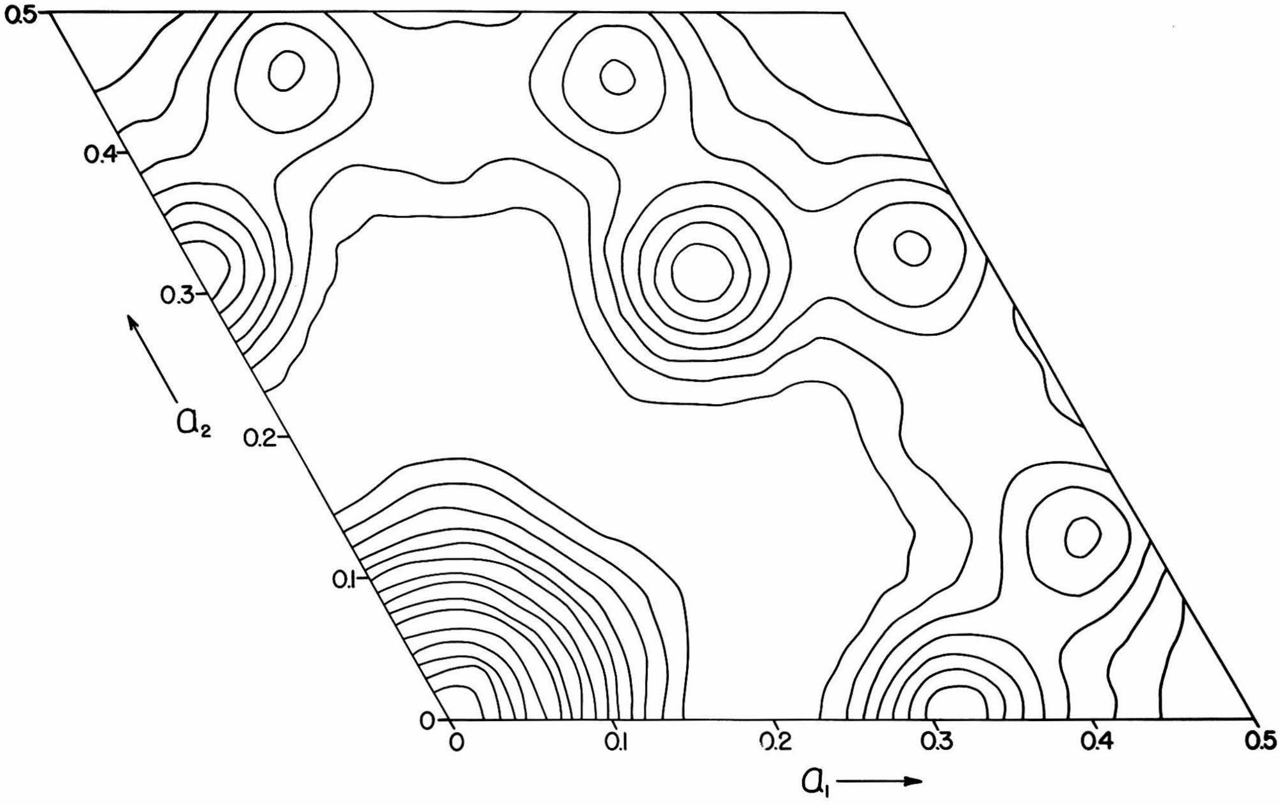


Figure 8. Harker section P(x y 0) for calcium chloride hexahydrate.

Values of the contour lines on an arbitrary scale: -25, 0, 25, 50, 75, 100, 125, 150, 200, 400, 600, 800, 1000, 1200, 1400, 1600.

The parameters for chlorine and oxygen may be determined from the maxima in the Patterson function plotted in Figures 3 and 4. The maxima in Figure 3, corresponding to z and (1–2z) for chlorine, are at 0.578 and 0.853. The two values of z are 0.578 and 0.574. This difference is undoubtedly due to the slight effect of the "tail" of each peak in displacing the maximum of the other. The best value for z was taken to be 0.576.

The two x parameters for the different types of oxygen atoms were taken at the maxima: 0.218 and 0.313. In order to fit the two triangular groups of water molecules between calcium and chloride ions it is necessary that one of these parameters be negative. Here again the choice is immaterial because the resulting structures differ only by inversion through the origin.

The structure of calcium chloride hexahydrate may be summarized as follows:

Space group: D_3^2–C321

Unit cell: a = 7.80 Å., c = 3.95, contains one molecule $CaCl_2 \cdot 6H_2O$.

Atomic positions: Ca at 1(a) 0 0 0;
Cl at 2(d) $\frac{1}{3}\ \frac{2}{3}\ z,\ \frac{2}{3}\ \frac{1}{3}\ \bar{z},\ z = 0.576$
O_I at 3(e) $x\ 0\ 0,\ 0\ x\ 0,\ \bar{x}\ \bar{x}\ 0,$
$x = 0.313$
O_{II} at 3(f) $x\ 0\ \frac{1}{2},\ 0\ x\ \frac{1}{2},\ \bar{x}\ \bar{x}\ \frac{1}{2},$
$x = -0.218$

This is, in principle, the same structure as arrived at by Jensen's process of successive Fourier projections. The larger number of data used and the greater precision with which the $|F|^2$'s were calculated make it probable that the parameters listed here are much more accurate than Jensen's, which were given only to two significant figures.

Further refinement of the parameters would require use of least squares or Fourier syntheses of electron density. It is not believed that the additional labor of such calculations for this non-centrosymmetric structure would be justified, since the problem is so ideally suited to the use of Patterson syntheses. Greater accuracy in estimating the parameters may be obtained from Fourier syntheses of electron density in which all maxima are well resolved than from Patterson syntheses with overlapping maxima. In this case, however, the structure is simple and the few Patterson peaks happen to be well separated. The error caused by overlapping of peaks is probably not more than about $\pm$ 0.002 in z or $\pm$ 0.001 in x. The corresponding errors in interatomic distances are less than $\pm$ 0.01 Å., which is as low as can be expected from any treatment of the data.

Figure 9. Stereoscopic drawing of the structure of calcium chloride hexahydrate. The large circles represent chlorine; the small circles, calcium. Lines are drawn outlining the unit cell and joining two of the calcium ions to the water molecules they share.

Table 3

Distance	Method of Computation	Calculated Value	Observed Distance
D(O–H–Cl)	= $D(O\text{–}H\text{–}O)$[1] – $R(O^{--})$ + $R(Cl^{-})$		
	= 2.76 – 1.40 + 1.81	= 3.17 Å.	3.16 Å.
			3.16
			3.52
D(Ca–O)	= $R(Ca^{++})$ + $R(O^{--})$		
	= 0.99 + 1.40	= 2.39 Å.	2.44 Å
			2.61

[1] Observed in ice; Reference (12), p. 301.

The six oxygens at 3.16 Å. from each chlorine are joined to it by hydrogen bonds comparable to those in ice. The other three oxygens, 0.36 Å. farther away, are hydrogen-bonded to the chlorine atom directly above or below in an adjacent unit cell.

The three oxygens in the basal plane with each calcium are closely packed around it, while the six oxygens shared with another calcium ion are 0.17 Å. farther away. This difference agrees well with that calculated (11) from the relation

$$\triangle D = -0.60\left(\log_{10}\frac{v}{N'} - \log_{10}\frac{v}{N}\right) = 0.60 \log_{10} 2 = 0.18\ \text{Å}.$$

where v is the valence and N is the number of positions among which the bonding electrons resonate.

Jensen (8) considered the isomorphous structure of strontium chloride hexahydrate from the viewpoint of electrostatic bonding and noted that the bond strengths might be divided among the water molecules in many ways, all of which satisfy the rule of electrical neutrality.

Since my determination of the parameters in calcium chloride hexahydrate indicates that each chlorine has six nearest oxygen neighbors, it seems best to assign each water molecule −1/6 charge from each of its two chlorines, or −1/3 in all. Then each calcium should supply + 1/3 to each of three water molecules and + 1/6 to each of six. The total is +2, equal to the charge of the calcium ion.

The charge which we might actually expect to be transferred from calcium to oxygen may be calculated from the percentage of ionic character in a Ca^{++} −O bond. Making the usual correction for the formal charge +2 gives the electronegativity (12, pp. 64–70) of Ca^{++} as 1.4. That of oxygen is 3.5; the difference is 2.1, corresponding to 67°/₀ ionic character. Thus a consideration of the partial ionic character of the Ca^{++} −O bond leads to exactly the same result as the simple idea of electrostatic bonding: Each calcium ion is essentially neutralized by the contribution of 1/3 electron from its three nearest oxygen neighbors and 1/6 electron from its six next nearest neighbors.

As Jensen has noted (7, p. 26), the two types of water molecules in this structure differ in that one has a tetrahedral environment of two positive and two negative ions while the other is near the center of a triangle of one positive and two negative ions. The angle Cl–O–Cl for the water molecules with tetrahedral coordination is 91.7°; that for the water molecules with triangular coordination is 125.1°. In the free water molecule the angle H–O–H is 104½°. The fact that this is larger than 90°, the angle which would be expected for the most stable p bonds

(12, p. 78), is attributed to mutual repulsion of the hydrogens by their slight positive charges. In the crystal of calcium chloride hexahydrate the presence of chloride ions might be expected to neutralize this positive charge and allow the H—O—H angle to approach 90° more nearly. It might also be expected, however, that the 1/6 covalent bond with each of two calcium ions would cause some tendency toward a tetrahedral s—p hybrid configuration with H—O—H angle 109° 28'.

It might be expected, furthermore, that the water molecules forming a 33% covalent bond with calcium would have considerable tendency to use triangular s—p hybrid orbitals giving an angle H—O—H equal to 120°.

The experimental results do not provide a good test of these predictions, since only the Cl—O—Cl angles have been determined. The chloride ions are rather large, and it seems probable that the O—H—Cl bond need not be exactly linear but may form an angle of five or ten degrees.

The pronounced basal cleavage of calcium chloride hexahydrate is in accord with the layer-like structure with bonds in a horizontal direction generally stronger than those directed more nearly parallel to the c axis. The Cl—O_{II} hydrogen bonds are very nearly horizontal. The hydrogen bonds between Cl and O_I go down from one unit cell to the next, up to the third, down again to the fourth, and so on—always oscillating about a horizontal plane. The horizontal bonds from O_I to Ca are twice as strong as the O_{II}—Ca bonds inclined more toward the vertical direction.

The bonding within a single unit cell is shown in the stereoscopic drawings of Figure 10.

Since the vertical bonds are in general considerably weaker than the horizontal, it might be expected that thermal vibrations would tend to have larger amplitudes in the vertical direction. The peaks at the origin in the Patterson function (Figures 6 and 7) are noticeably elongated in a vertical direction as would be expected for anisotropic thermal vibrations.

Figure 10. Stereoscopic drawing of bonds in the unit cell of calcium chloride hexahydrate.

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Appendix 1

Observed $|F|^2$ Values for $CaCl_2 \cdot 6H_2O$ on an Arbitrary Scale

HKL	$\|F\|^2$	HKL	$\|F\|^2$	HKL	$\|F\|^2$
001	2.9	081	3.7	160	0.4
002	120	083	1.8	161	16.1
003	0.6	090	10.3	162	0.5
004	3.4	092	3.3	163	4.8
005	1.2	094	0.4	170	6.6
010	21.7	0.10.0	0.4	171	0.2
011	3.0	0.10.1	0.7	172	1.4
012	26.8	0.10.2	0.8	173	0.7
014	8.6			181	0.6
020	3.6	101	49.9	182	1.2
021	86.5	103	12.2	184	0.6
022	4.2	105	0.5	191	1.6
023	14.2	110	71.4	193	0.6
025	0.5	111	48.5	1.10.0	1.3
030	166	112	9.3	1.10.2	1.5
031	3.6	113	2.6	1.11.1	0.4
032	32.5	114	0.1		
033	4.7	115	1.6	201	16.9
035	2.1	120	9.1	202	7.8
040	9.7	121	27.1	204	4.5
041	1.7	122	8.0	206	0.5
042	22.8	123	0.8	211	92.5
044	6.2	124	3.9	212	5.1
050	3.1	126	0.4	213	16.0
051	4.7	130	5.1	215	0.9
053	3.4	131	38.0	220	49.5
054	0.4	133	13.4	221	1.6
056	0.2	135	0.6	222	9.7
060	44.7	140	63.1	223	0.5
062	11.3	141	8.3	224	0.3
063	1.0	142	13.4	225	1.0
071	4.6	144	0.1	231	5.6
072	3.2	145	0.5	232	4.6
074	1.9	151	1.0	234	3.2
080	5.0	152	7.2	240	1.8

HKL	$\|F\|^2$	HKL	$\|F\|^2$	HKL	$\|F\|^2$
241	23.7	351	7.6	503	0.7
242	0.8	353	4.7	504	5.3
243	10.7	360	12.2	511	10.0
250	13.4	362	4.6	513	4.4
252	4.1	363	0.5	521	0.1
260	0.9	371	1.5	522	3.8
261	1.7	372	1.8	531	1.1
262	1.7	374	0.7	532	2.5
264	0.6	381	2.4	534	1.4
271	10.2	383	1.6	541	3.2
273	1.8			543	1.1
280	3.6	401	21.4	550	10.8
282	0.7	402	0.1	551	0.2
		403	9.2	552	4.5
301	3.4	411	6.9	571	0.6
302	32.3	412	11.3		
303	2.9	414	0.2	602	12.5
304	0.7	415	0.7	603	0.7
305	2.4	421	4.2	611	4.4
311	7.9	422	6.5	612	4.5
312	12.8	424	3.5	614	3.0
314	6.4	431	26.2	621	9.8
321	26.6	433	13.5	622	2.2
322	2.3	440	14.1	623	4.7
323	15.8	441	0.8	632	4.1
330	43.2	442	5.7	641	0.3
331	3.8	450	1.0	642	2.9
332	13.7	452	4.4	644	1.4
333	3.8	454	2.6	651	2.3
335	2.6	461	4.2	653	0.5
341	7.6	463	1.8	660	1.2
342	5.0	470	2.7	662	0.2
344	3.2	472	0.4		
344	3.2			701	16.5
350	0.2	502	11.4	703	6.1

HKL	$\lvert F\rvert^2$	HKL	$\lvert F\rvert^2$	HKL	$\lvert F\rvert^2$
711	0.2	802	1.2	914	0.6
712	2.1	804	0.7	921	1.1
713	0.5	811	2.0	931	1.5
721	1.9	813	1.2	941	0.6
722	2.0	822	1.4		
724	1.2	841	0.8	10.0.1	1.2
731	6.8			10.0.3	0.4
733	3.9	902	4.0		
742	0.4	912	1.3	11.1.1	0.2
761	0.4	913	0.7		

II. Hexamethylene Tetramine Complexes with Metal Halides

Introduction

It has long been known that hexamethylene tetramine readily forms molecular compounds. A long list of these is given in Beilstein (3, pp. 308-17). There are crystalline compounds with inorganic and organic acids, with inorganic salts both anhydrous and hydrated, with many organic compounds, and with the halogens. The molecular proportions are often complicated, particularly in the compounds with hydrated salts.

One might expect that the molecule would have some tendency to form complex cations rather like those formed by ammonia, using one of its four equivalent, tetrahedrally oriented tertiary amino groups. Such complexes are in fact produced; the reaction with silver ion, for instance, has been thoroughly investigated (11, 12).

Several investigators (18, 20, 21) have recognized, however, that the Werner coordination theory does not provide a general correlation for these hexamethylene tetramine complexes as it does for the ammoniates. It would seem likely that the properties of any hexamethylene tetramine compound analogous to one of ammonia should be considerably affected by the presence of the other three nitrogen atoms, and that steric hindrance would prevent coordination of more than two molecules around one metal atom. These effects are evident in the great tendency of hexamethylene tetramine to form solid complexes. The voluminous microcrystalline precipitates it produces in solutions of many salts are often used in qualitative microchemical analysis.

It was believed that a determination of the crystal structure of one of the hexamethylene tetramine complexes would give valuable information about their nature and reasons for their stability. Even though the unit cell of one of these complexes might contain many atoms it was thought that the previous work on hexamethylene tetramine itself should be of great assistance; the structure of the molecule has been thoroughly investigated both in the vapor (9, 24) and in the crystal (4, 6, 8, 25, 29).

The large number of known complexes made the choice for a structure determination rather difficult. It was felt desirable that the structure investigated be as simple as possible, so as to facilitate the determination, and be characteristic of the interactions between salts and hexamethylene tetramine molecules rather than of the thoroughly investigated interactions between salts and water of hydration.

The latter requirement dictated the choice of unhydrated hexamethylene tetramine complexes with salts. The requirement of a structure which would facilitate X-ray crystallography indicated that the salts should contain simple ions and combine with hexamethylene tetramine in simple proportions. Preferably, too, the complex should permit isomorphous substitution of ions with widely different atomic numbers.

The substances chosen for investigation on the basis of these considerations were complexes with metallic halides. Those with the tetrachlorides of tin and titanium were most intensively investigated; those with manganous chloride and bromide, stannous chloride, and antimonous chloride were investigated in a preliminary fashion.

Literature

Compounds of hexamethylene tetramine with tetrahalides of tin and titanium have been described by Scagliarini (19, 20) and by Duff and Bills (7). The compounds prepared by Scagliarini were precipitated from solutions in chloroform and bromoform, and all of his formulas for these precipitates contain one or more molecules of the solvent.

Duff and Bills prepared their anhydrous complexes by precipitation from solutions in absolute alcohol. Their analyses of the precipitates were in good agreement with the formulas

$SnCl_4 \cdot 4C_6H_{12}N_4$
$SnCl_2 \cdot 2C_6H_{12}N_4$
$SbCl_3 \cdot 3C_6H_{12}N_4$
$SbCl_5 \cdot 6C_6H_{12}N_4$
$ZnCl_2 \cdot 2C_6H_{12}N_4$
$BiCl_3 \cdot C_6H_{12}N_4$

They stated that the first four compounds "have the same crystalline structure."

This list includes all the halides used in the present investigation except those of titanium and manganese.

It seemed probable that the titanium tetrachloride complex would be analogous to that of stannic chloride; but no prediction could be made for manganous halides.

Manganous compounds of the following formulas have been reported by Barbieri and Calzolari (1, 2):

$MnX_2 \cdot 2C_6H_{12}N_4 \cdot 10H_2O$ (X = a halogen)
$Mn(SCN)_2 \cdot 2C_6H_{12}N_4 \cdot 4H_2O$
$Mn(NO_3)_2 \cdot 2C_6H_{12}N_4 \cdot 10H_2O$
$Mn(ClO_4)_2 \cdot 2C_6H_{12}N_4 \cdot 8H_2O$

They found (2) that the analogous complexes of iron, cobalt, and nickel thiocyanates lost one molecule of hexamethylene tetramine when recrystallized from water, but the manganous thiocyanate complex did not. Some related anhydrous compounds were reported by Scagliarini and Tartarini (21, 22) as being precipitated from solutions in 95°/₀ alcohol:

$CoCl_2 \cdot C_6H_{12}N_4$
$NiCl_2 \cdot C_6H_{12}N_4$
$CoBr_2 \cdot C_6H_{12}N_4$
$M(SCN)_2 \cdot 2C_6H_{12}N_4$ (M = Fe, Mn, Co, Ni)

These data made it appear that the molecular ratio in a complex between manganous halide and hexamethylene tetramine might be 1:1 or 1:2; but a definite prediction was impossible.

Experimental Methods

(A) Preparation of Samples

The hexamethylene tetramine used in this investigation was Eastman White Label grade.

The metal halides were all commercial c.p. anhydrous compounds except for stannous chloride, which was the c.p. dihydrate, and manganous bromide. The latter was prepared from c.p. manganous carbonate and diluted c.p. hydrobromic acid; the solution, containing a slight excess of acid, was evaporated on a hot plate to yield the tetrahydrate and this was dried for about a week in an oven at 100° C.

The complexes were prepared by precipitation from absolute ethanol or from acetone. In general a small amount of a dilute solution of the halide was added to a solution of hexamethylene tetramine whose concentration was 50°/₀ or more of the saturation value. This produced a momentary white precipitate which could be redissolved by swirling the container. Additions were continued until a slight cloudiness persisted, and the solution was allowed to stand. Usually within a few minutes fine needle-like crystals began to form. Occasionally standing overnight or for several days was necessary. The appearance of these phenomena and of the resulting crystals were the same with absolute alcohol and acetone.

The crystals produced with $SnCl_4$ and $TiCl_4$ were identical in appearance, but this appearance varied markedly with the concentration and therefore with the rate of crystallization. The first instantaneous precipitate consisted of microscopic platelets, rhombic in shape, with an obtuse angle of about 120°. Crystals which grew a little more slowly were microscopic needles. Those which formed more slowly still—in a few minutes to a few hours—were large needles up to a few tenths of a millimeter by ten millimeters. After standing for a few days the mixtures gave crystals which were rhombohedra, not greatly elongated in any direction, with a maximum size of perhaps one-half millimeter.

As an example the following typical precipitation is described: One milliliter of absolute alcohol containing 0.03 ml. of stannic chloride was poured into 5 ml. of absolute alcohol almost saturated with hexamethylene tetramine. A fine white precipitate formed immediately, giving the appearance of milk. Five more milliliters of the hexamethylene tetramine solution were added and the precipitate redissolved. After two or three minutes a voluminous colorless precipitate formed, consisting of needles and rosettes visible as such to the naked eye.

Considerably larger crystals were produced by the method of slow diffusion. The dilute stannic chloride solution was carefully floated on top of the almost saturated hexamethylene tetramine solution in a cylindrical separatory funnel 15 cm. high and 15 mm. in diameter. When precipitation at the interface had ceased the crystals were separated off.

An interesting phenomenon observed in the experiments with stannic chloride was the formation of a yellow to dark brown color within a few minutes after a fairly strong solution in acetone was prepared. The behavior with acetone is similar to that described by Whittaker (27, p. 60) for vanadium tetrachloride except for a difference in color. These halides probably form addition products with acetone and alcohol related to the complexes which Pfeiffer (17) found to be formed with various benzoyl compounds. The effect I observed was readily reversible; when the brown solution came in contact with the solution of hexamethylene tetramine its color disappeared and the hexamethylene tetramine complex precipitated instantaneously.

The precipitation of the other complexes was carried out in a similar manner to that described for stannic chloride. The only other ones for which conditions were varied in an attempt to obtain large single crystals were the manganous halide compounds. Varying the conditions greatly affected the size of the crystals but did not particularly alter the shape. It was found possible to grow well-developed crystals of suitable size by recrystallization from acetone.

The apparatus used was a small Erlenmeyer flask sealed into a circuit, roughly square in shape, made of glass tubing the same diameter as the neck of the flask. The apparatus was filled with solvent, the powder was added, and a small electric heater placed under the flask. Convection carried the liquid from the powder layer up the neck of the flask, over in the horizontal side arm, down the third side of the square where seed crystals adhered to the walls and the tube was water jacketed, and back over into the side of the flask at the bottom. The cooling effect of the water jacket and absence of constrictions in the circuit made the flow very rapid.

In this apparatus microscopic seed crystals of the manganous bromide complex grew large enough for use as X-ray samples in one day. The stannic chloride complex could not be recrystallized at a satisfactory rate, probably because of its much lower solubility.

Samples of the compounds for preparation of powder photographs were ground in an agate mortar and sealed in thin-walled Pyrex capillaries about 0.5 mm. in diameter.

The first single crystal used for X-ray photography, a long, thin needle of the stannic chloride complex, was inserted in a Pyrex capillary which was then pushed into a small lump of wax to seal out moisture. It was found, however, that although the compounds were readily soluble in water their crystals showed no tendency to become sticky and no change in diffraction pattern after long exposure to the atmosphere. Thereafter the crystals were simply mounted on glass fibers in the usual way with Aquanite clear lacquer. This delicate manipulation was done under a binocular microscope.

Two details of the mounting technique will be described fully because they greatly facilitated orientation of the crystal.

The first is the flexible goniometer pin, which permitted the crystal to be tilted considerably with respect to the goniometer head if the arc motions of the latter otherwise were too limited to give the desired orientation.

This type of goniometer pin was similar to the "Christmas tree" pin already in use, but was designed for adjustment in tilt only and not in translation. The tilt adjustment requires that the goniometer pin be cut down enough for flexibility at only one point rather than two, and therefore it requires much less overall length. The decrease in distance required between the top of the goniometer head and the crystal is important for some of the apparatus, in which the range of height adjustment is short.

The flexible goniometer pins were made of brass rod 1/8 inch in diameter and 5/8 inch long. Two holes were drilled 1/16 inch from the end, at right angles to the axis of the rod and to each other, with a number 55 drill. Beginning at 1/8 inch from the same end a notch about 1/8 inch wide with tapering sides was cut on the lathe, leaving a cylindrical neck 0.04 inch in diameter and almost 1/8 inch long. The taper was to prevent the undue stress concentration which would occur at a sharp shoulder when this neck was bent. The pins were annealed and provided with a four-inch length of hardened number 55 drill rod as a handle.

The second detail of technique is the use of "artificial signals" for reorientation of crystals. It happened that some of the single crystals used in this investigation could be oriented optically but others gave no reflections from the faces because they were covered by a glass capillary or a layer of vaseline, or because the crystal had become etched. It was found extremely convenient in such cases to mount on the glass fiber, just below the crystal, two one-millimeter squares cut from a microscope cover slip. These two reflectors, at right angles, give brilliant signals in the optical goniometer. If the angular readings of the artificial signals are noted after a crystal has been oriented by means of Laue photographs, then the goniometer pin can be removed from the goniometer head at any time and set aside with the assurance that the crystal can be returned to its orientation in a few minutes whenever desired. In fact, even when the character of the crystal faces permits optical orientation it is more convenient to use the artificial signals for reorientation because they are bright enough to be clearly distinguished even without darkening the room.

(B) X-Ray Photographs

All Laue photographs were taken with a crystal-to-film distance of five centimeters and with radiation whose minimum wavelength was 0.24 Å. Photographs for orientation were made with intensifying screens. Long exposures for gnomonic projections were made on Eastman No-Screen film. The projections were constructed by means of the gnomonic ruler first proposed by Huggins (see Reference (28), p. 130). They were indexed and tested for conflicts with the lower wavelength limit by the graphical method originated by Murdock (14).

The oscillation, rotation, and powder photographs were taken on No-Screen film in a camera of radius five centimeters with well-filtered CuKα or MoKα radiation. Oscillation and rotation photographs were indexed with the aid of a Harker chart (Section I, Figure 1). Measurements of film coordinates were made with a brass scale equipped with a transparent cursor and vernier reading to 0.1 mm., mounted on an illuminated viewer. The wavelengths used in translating film distances to lattice spacings were

$CuK\alpha_1 = 1.5405$ Å.
$CuK\alpha_2 = 1.5443$ Å.
$CuK\alpha(\text{average}) = 1.5418$ Å.

Photographs of the $SnCl_4$ complex intended for quantitative intensity estimates were prepared by the multiple-film method (5) with MoKα radiation; the three films were interleaved with 0.001-inch copper foil. The film factor for this combination (13, p. 42) was taken as 4.0.

The reciprocal lattice could be covered efficiently with only six oscillation photographs because the axis of rotation was normal to the three-fold axis of the crystal. These six exposures will be referred to by their arbitrarily assigned film numbers n running from 1 to 6.

The intensities were estimated on each of the six sets of three successive films with an independent scale. No correction was necessary for absorption (10, p. 584), since the longest dimension of the crystal was 0.3 mm. and its absorption coefficient was only 12.4. The corrections for Lorentz-polarization factor were determined from two charts as described in Section I. When these had been applied, the intensity estimates were converted to values of $C_n |F|^2$, still with a different scale factor C_n for each of the six sets of films. Then punched cards were prepared, about 600 in number. Each card contained a $C_n |F|^2$ value together with its film number n and the indices of the form (*i.e.* the symmetry-equivalent HKL which has all indices positive).

The cards were sorted by film number and these six groups were paired in the 15 possible ways. Each pair of groups was sorted by form number HKL and tabulated in that order. Thus for that pair of exposures all cards for the same HKL were tabulated together. In this way all possible comparisons of $C_n |F|^2$ values for the same HKL in different exposures were assembled. For each of the pairs of film numbers n_1, n_2 $(n_2 > n_1)$ an average ratio of the scale factors C_{n_1}/C_{n_2} was computed. From these fifteen ratios a set of five independent ratios $C_1/C_n (n > 1)$ was obtained by averaging the fifteen, with weights proportional to the number of comparisons each represented.

These ratios were used to obtain the values of $C_1 |F|^2$ from all the estimated intensities. All of the $C_1 |F|^2$ values for each form were then listed together and averaged to yield the values of $|F_{obs}|^2$ for 137 independent reflections, on an arbitrary scale. The $|F_{obs}|$ figures were corrected to an approximate absolute scale by comparison with the first few sets of calculated structure factors.

Structure factors were always calculated for the primitive rhombohedral cell, since these differ from those for the hexagonal cell only by a factor of three. The atomic scattering factors used were those tabulated in the "Internationale Tabellen" (10, Vol. 2, p. 571). For the nitrogen atoms the neutral N factors were used, and for the methylene groups the scattering factors were taken equal to those for carbon plus the difference between the factors for the oxide ion and for neutral oxygen.

Before the scattering factors were used in any calculations they were multiplied by the isotropic temperature factor found by Shaffer (25) for the hexamethylene tetramine crystal, $\exp[-B(\sin^2\theta)/\lambda^2]$ with $B = 2.4\ \text{Å}^2$. In a few cases an additional temperature factor was also used.

The calculations of Fourier syntheses were made by means of the punched card analog of Lipson-Beevers strips (23).

The final adjustments of temperature factor and scale factor were carried out by the method of least squares in such a way as to minimize the residuals $|F_{obs}| - |F_{calc}|$. The formation of normal equations was done by the punched-card method described by Shaffer, et al. (26, p. 657).

Although no International Business Machines plugboard was available at the time for least squares calculations, it was found convenient to use the "S—C—E" board since all the coefficients of the observational equations were positive.

(C) Other Experiments

Pyroelectric tests were attempted by heating the crystals, cooling them on a glass plate, and then sprinkling a mixture of powdered sulfur and red lead on them through a silk screen or placing a jar of magnesium oxide smoke over them. No positive test could be obtained by either of these methods, even with a crystal of tourmaline 4 mm. in diameter and 13 mm. long.

The only method tried which gave any definite results was the liquid air test. A crystal was tied at the end of a fine silk thread obtained by unraveling ordinary silk thread and using only one to three fibers at a time. Dangling at the end of this thread, the crystal was dipped under the surface of liquid air in a Dewar flask. When cooled to the temperature of the liquid air, it was slowly lifted above the surface, with the fiber supported at a point on the axis of the Dewar flask. Pyroelectric crystals showed a noticeable tendency to leap to the walls of the vessel and stick there, both just after immersion and after withdrawal from the liquid. The tourmaline crystal, in addition to exhibiting this behavior, collected a thick hairy coat of ice crystals at its ends, resembling iron filings around a bar magnet. Crystals of potassium iodide and sodium chloride gave no effect.

Determinations of density were made by either the pycnometer method or the flotation method. In the former procedure the liquid used to fill the 1-ml. pycnometer was benzene or toluene. The liquid used in the flotation method was a mixture of high-boiling ligroin or carbon tetrachloride and ethylene dibromide. The final tests for equilibrium were speeded by a few turns in a hand centrifuge.

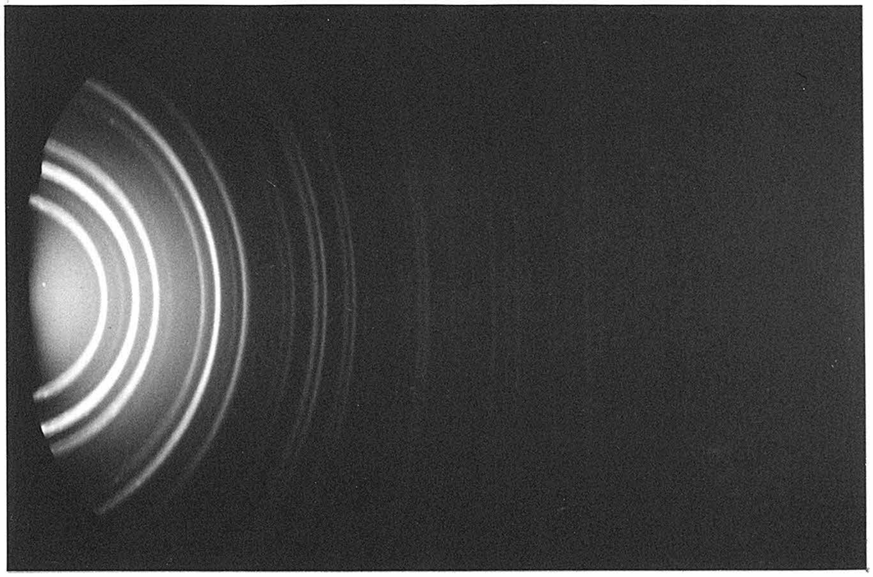
Results and Discussion

(A) $SnCl_4$ and $TiCl_4$ Complexes

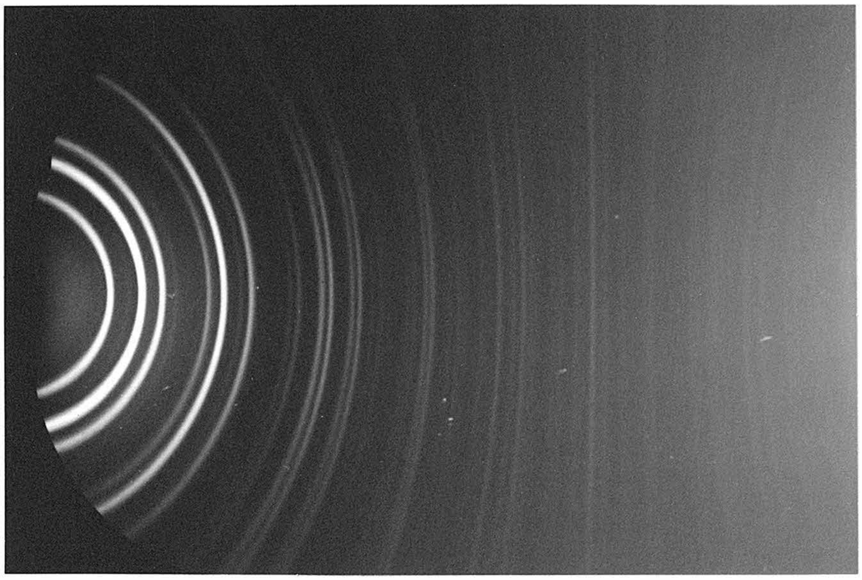
It was found that the crystals of varying shapes formed by different solutions of the tetrahalide and hexamethylene tetramine gave the same powder pattern and identical Laue photographs. Furthermore, it was found that the powder photographs (Figure 1), Laue photographs, and rotation photographs about the needle axis (Figure 2) obtained from the complexes of both tetrahalides were also identical. Thereafter only the structure of the stannic chloride complex was studied in detail, in confidence that the two compounds were isomorphous; and crystals of the various shapes were used interchangeably.

As a check on the formula $SnCl_4 \cdot 4C_6H_{12}N_4$ given by Duff and Bills (7), analyses were obtained from the Smith–Emery Company on a batch of the stannic chloride compound precipitated from acetone and air-dried. Their results were Sn = 13.09°/₀, Cl = 15.60°/₀, N = 23.30°/₀. The values calculated for the molecular ratio 1:4 are Sn = 14.45°/₀, Cl = 17.27°/₀, N = 27.29°/₀. The analyses give just the theoretical ratio Sn:Cl and a slightly higher ratio Sn:N than the theory. The results are nearly those which would be expected for a preparation of $SnCl_4 \cdot 4C_6H_{12}N_4$ containing 9.6°/₀ inert material such as water or acetone. The results were accepted as agreeing with Duff and Bills' formula.

A sample of the titanium tetrachloride complex was submitted to the microchemical laboratory of this Institute for carbon and hydrogen determinations. The results were C = 41.3°/₀, H = 7.6°/₀, compared with

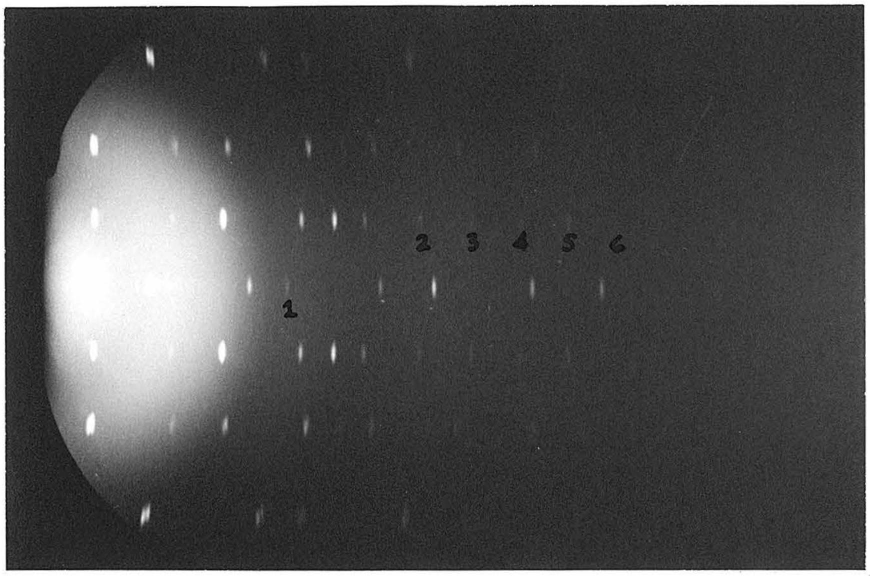


(A)

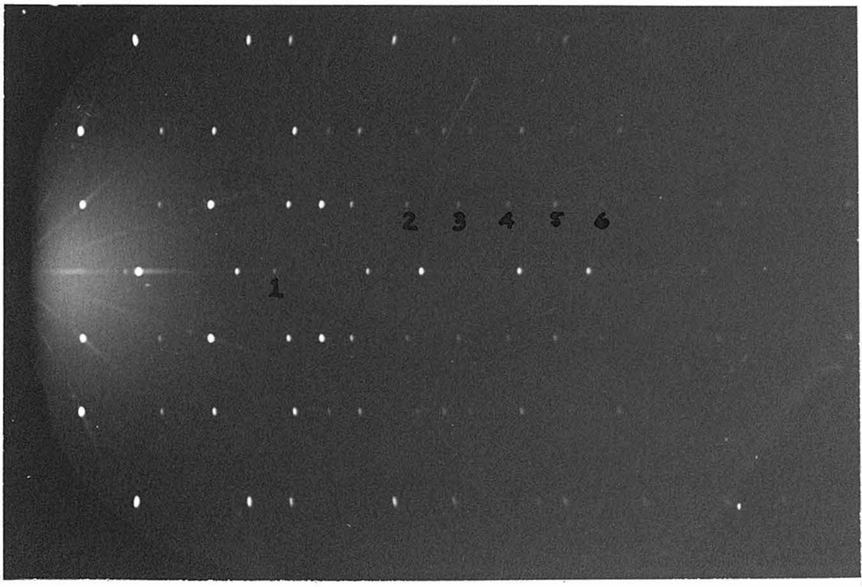


(B)

Figure 1. Powder photographs of complexes $MCl_4 \cdot 4C_6H_{12}N_4$ taken with CuKα radiation. (A) $SnCl_4 \cdot 4C_6H_{12}N_4$; (B) $TiCl_4 \cdot 4C_6H_{12}N_4$.



(A)



(B)

Figure 2. Rotation photographs about the three-fold axis taken with CuKα radiation. (A) $SnCl_4 \cdot 4C_6H_{12}N_4$; (B) $TiCl_4 \cdot 4C_6H_{12}N_4$.

theoretical values C = 38.4°/o, H = 6.4°/o. Since it is well-known that accurate microcombustion analyses are often difficult for unusual compounds, these results were concluded to be in reasonable agreement.

The fact that these analyses are in approximate agreement with the formula and the results of the X-ray analysis are also in agreement leaves little doubt that the composition of crystals of both the tin and titanium compounds is $MCl_4 \cdot 4C_6H_{12}N_4$.

Laue photographs showed that the X-ray symmetry was $D_{3d}-\bar{3}m$. A pyroelectric test was made by the liquid air method described above. On being pulled above the surface, the crystal showed the characteristic gyrations of a charged body and a considerable tendency to stick to the walls of the Dewar flask. It was concluded to be pyroelectric, and therefore to lack a center of symmetry. The actual point group of the structure then must be D_3-32 or $C_{3v}-3m$.

The layer line spacing in the rotation photograph about the three-fold axis showed the hexagonal $\underset{\sim}{c}$ axis length to be 8.9 Å. It was found that the reflections could be indexed on a hexagonal lattice with a = 8.9 Å. The indices of the reflections observed suggested that they might possibly conform to the extinction rule for rhombohedral centering, H – K + L or H – K – L always equal to an integer divisible by three.

The hexagonal $\underset{\sim}{a}$ axis 8.9 Å. in length was defined as the vector parallel to the incident beam when the Laue pattern of Figure 3 is obtained, with the observer looking in the same direction as the beam.

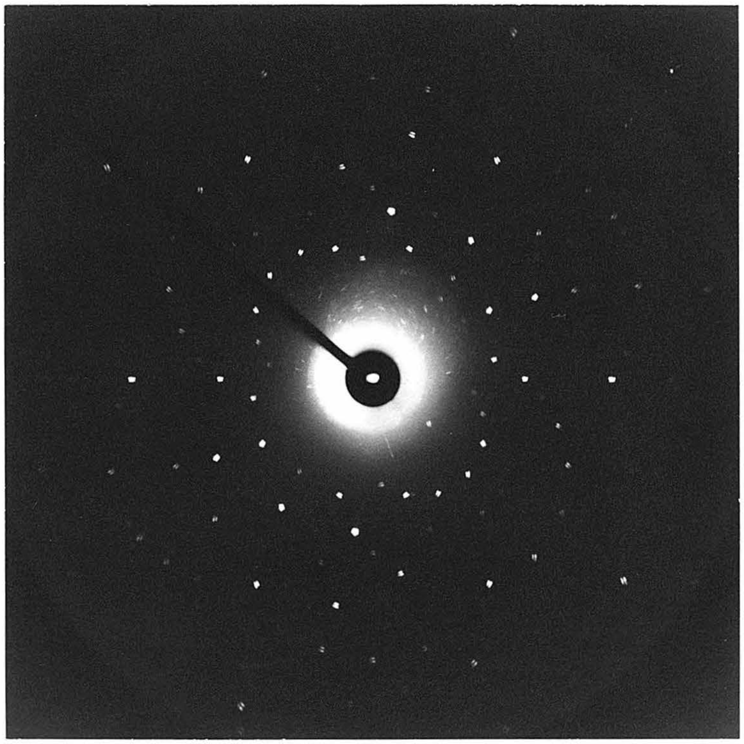


Figure 3. Laue pattern defining the $\underset{\sim}{a}$ axis in $SnCl_4 \cdot 4C_6H_{12}N_4$. The X-ray beam was directed along $+\underset{\sim}{a}$ when this pattern was produced; the side of the film shown was toward the crystal. The $\underset{\sim}{c}$ axis is vertical.

Heavily exposed Laue photographs were prepared with the beam along the $\underset{\sim}{c}$ axis and with increasing angles of inclination up to 8°. When indexed on these axes they showed no reflections in conflict with the chosen unit cell, and also no reflections not obeying the rule $H - K - L = 3n$, although 107 first-order reflections were observed in the most asymmetric photograph. It was therefore concluded that the true unit cell was the rhombohedral one with

$$\begin{aligned} \underset{\sim}{a}_r &= \tfrac{1}{3}(-\underset{\sim}{a} - 2\underset{\sim}{b} + \underset{\sim}{c}), \\ \underset{\sim}{b}_r &= \tfrac{1}{3}(2\underset{\sim}{a} + \underset{\sim}{b} + \underset{\sim}{c}), \\ \text{and} \quad \underset{\sim}{c}_r &= \tfrac{1}{3}(-\underset{\sim}{a} + \underset{\sim}{b} + \underset{\sim}{c}). \end{aligned}$$

The indices HKL referred to the axes $\underset{\sim}{a}, \underset{\sim}{b}, \underset{\sim}{c}$ of the triply primitive hexagonal unit were retained in all calculations.

Sets of oscillation photographs about the $\underset{\sim}{a}$ axis of $SnCl_4 \cdot 4C_6H_{12}N_4$ were taken with CuKα and MoKα radiation, the latter on multiple films. All of these were indexed; the CuKα photographs, having spots near the edge of the film, were used for a final determination of the lattice constants, while the MoKα oscillations were used for intensity estimates.

The lattice constants were calculated by a least squares reduction of 19 measurements on 10 non-equivalent reflections. The best values were

$$\begin{aligned} a = b &= 8.95 \pm 0.01 \text{ Å}. \\ c &= 8.95 \pm 0.01 \text{ Å}. \end{aligned}$$

The axial ratio c/a is unity within experimental error. This corresponds to a rhombohedral angle $\alpha = 97.2°$.

The density of $SnCl_4 \cdot 4C_6H_{12}N_4$ was determined with the following results:

fine powder, flotation method—1.68, 1.69 g./cm.^{3};
fine powder, pycnometer method—1.62;
larger needles, flotation method—1.42.

Since large crystals might be expected to contain voids and inclusions more frequently, the last value was discarded and the mean taken to be 1.65.

The number of molecules per hexagonal unit cell corresponding to this density is 0.752; that is, each rhombohedral unit contains 0.251 molecules. The fact that this number is so near to one-quarter made it seem probable that there was randomness in the structure, with each unit cell containing on the average one molecule of hexamethylene tetramine, one chlorine atom, and one-quarter of a tin atom.

No evidence of superlattice formation was ever noticed in this investigation. In view of the stability of hexamethylene tetramine crystals and the fact that these complexes decompose rather than sublime, it seems unlikely that any heat treatment will produce a more ordered structure. It is remotely possible, however, that different conditions of formation—such as precipitation over a period of months—might favor an ordered structure with a larger unit cell.

In spite of the additional complications introduced by randomness in the structure, it was decided to make use of the intensity data to find out as much as possible about the compound.

The space groups[1] isomorphous with point groups D_3–32 and C_{3v}–3m and based on a rhombohedral lattice are

D_3^7–R32,

C_{3v}^5–R3m,

and C_{3v}^6–R3c.

The third of these requires that reflections HOL and OKL be absent except when L is even. A considerable number of observed reflections did not obey this rule, and the space group C_{3v}^6–R3c accordingly was discarded.

The only special positions which require only three atoms in the hexagonal unit are the following:

for D_3^7–R32: 3(a) 0 0 0; 3(b) 0 0 $\frac{1}{2}$;

for C_{3v}^5–R3m: 3(a) 0 0 z.

These x y z coordinates and those in the following discussion are fractions of the hexagonal unit cell edges. In all cases the complete set of positions is to be obtained by adding to the coordinates listed the translations (0 0 0; $\frac{1}{3}$ $\frac{2}{3}$ $\frac{2}{3}$; $\frac{2}{3}$ $\frac{1}{3}$ $\frac{1}{3}$).

The symmetry required at each of these special positions is that of the isomorphous point group—D_3–32 or C_{3v}–3m. If a hexamethylene tetramine molecule is to be placed in one of these special positions, its symmetry must be at least as great as required by the space group. Since the free hexamethylene tetramine molecule has point group T_d–$\bar{4}$3m it has no two-fold axis normal to a three-fold axis and cannot provide the

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[1] In all discussions of space groups and special positions the terminology of the "Internationale Tabellen" (10) is used.

symmetry D_3–32. On the other hand, the alternative point group C_{3v}–3m is a sub-group of T_d. These considerations made it appear likely that the true space group was C^5_{3v}–R3m.

A Harker section along one of the mirror planes in Patterson space was calculated in an attempt to gain information on the relation between the heavy atoms and the hexamethylene tetramine molecules.

The mirror planes are loci of points $x\ \bar{x}\ z$; therefore the desired function was

$$P(x\ \bar{x}\ z) = \sum_H \sum_K \sum_L |F_{HKL}|^2 \cos 2\pi \left[(H - K)x + Lz\right].$$

The result of this calculation is shown in Figure 4. There are peaks near the origin such as would be expected from the interatomic vectors within a hexamethylene tetramine molecule. If this molecule is assumed to lie with a three-fold axis along the $\underset{\sim}{c}$ axis and with one of its mirror planes parallel to the plane of the section, then one nitrogen is on the $\underset{\sim}{c}$ axis. It can be taken at the origin with no loss in generality. Extending upward from this nitrogen are the vectors to three adjacent carbons; one of these vectors lies in the plane parallel to the section. The corresponding peak in the Patterson function should appear in Figure 4 above the origin either to the right or to the left. It does in fact appear to the left. This defines the orientation of the molecules in the crystal as that corresponding to this choice and not the other alternative, which would differ by a 30° rotation of the molecule about the $\underset{\sim}{c}$ axis.

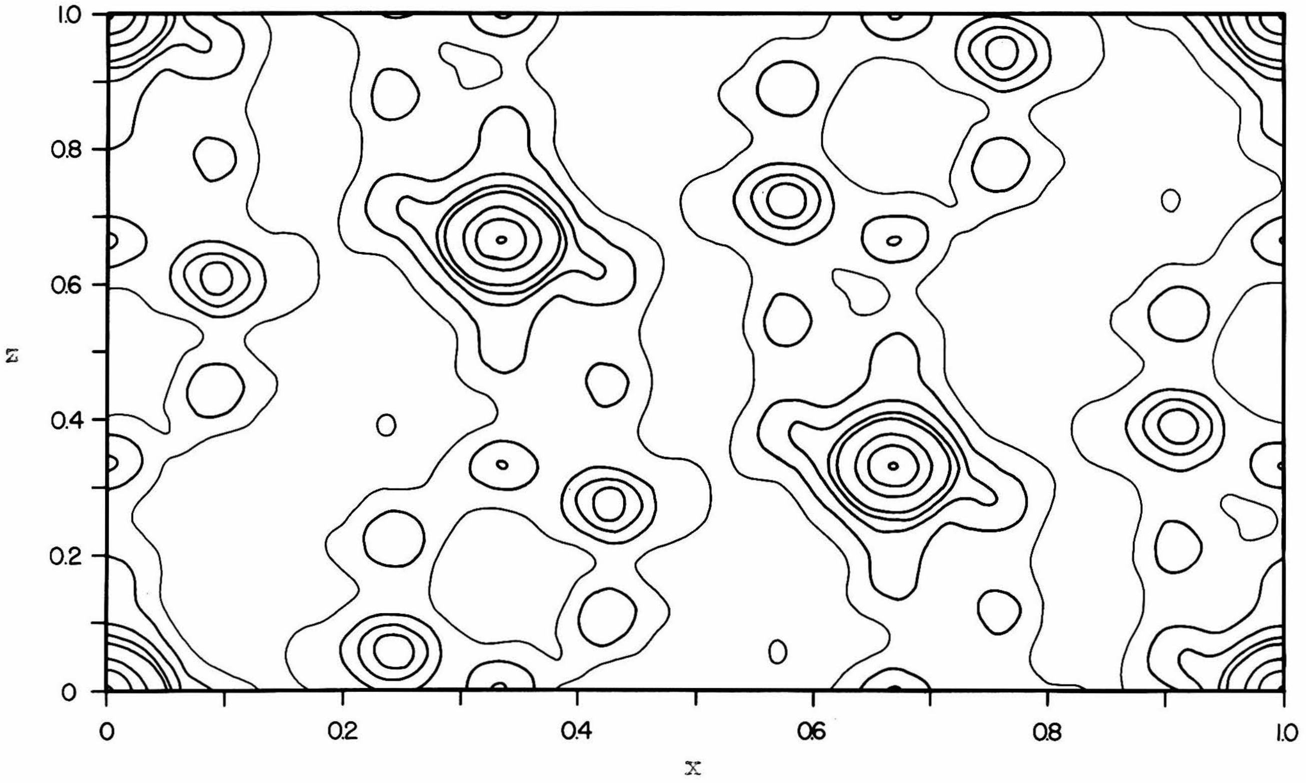


Figure 4. Harker section $P(x\,\bar{x}\,z)$ for $SnCl_4 \cdot 4C_6H_{12}N_4$.

Values of the contour lines on an arbitrary scale:
0 (drawn lighter than the rest), 500, 1000, 1500,
2000, 4000, 6000, 8000.

The other important feature of Figure 4 is the set of maxima centered at the point $0\ 0\ \frac{1}{2}$. These are just the peaks which would be expected if a heavy atom were also on the $\underset{\sim}{c}$ axis, half-way between the centers of the hexamethylene tetramine molecules. If a nitrogen atom is placed at $0\ 0\ 0$ as before, with the rest of the hexamethylene tetramine molecule extending upward, then the heavy atom must be placed to correspond with one of the heavy atom—nitrogen peaks—that is, either at $0\ 0\ \frac{1}{3}$ or at $0\ 0\ \frac{2}{3}$. The molecule of hexamethylene tetramine, however, extends almost up to $z = \frac{1}{3}$; therefore the heavy atom must lie at $0\ 0\ \frac{2}{3}$.

The random nature of the structure makes it difficult to decide whether the heavy atom is the one chlorine atom or the one-quarter tin atom present in the average rhombohedral unit cell. At first the hypothesis was tested that molecules of stannic chloride were present in the crystal, in spite of the great conflict between required interatomic distances and known van der Waals radii which this entailed. It was postulated that stannic chloride molecules are randomly distributed among the unit cells in one or more positions so that the average fulfills the symmetry requirements of the space group. If the molecule were assumed to be approximately tetrahedral it might be placed with its three-fold axis along the $\underset{\sim}{c}$ axis. But this would require a chlorine atom and the tin atom to fit between the hexamethylene tetramine molecules along the $\underset{\sim}{c}$ axis in a space which is small even for the chlorine atom alone. Calculations of $|F|$'s were made for several models of this type for a group of ten reflections with low values of $(\sin \theta)/\lambda$, and it was decided that no good agreement could be obtained in this way.

A slightly more reasonable packing of $SnCl_4$ molecules among those of hexamethylene tetramine was with the two-fold axis approximately along the $\underset{\sim}{c}$ axis. This would probably divide the average of one chlorine atom per rhombohedral unit among 12 or 24 positions, so that the effect of the chlorine would not be much greater than that of hydrogen in most structure determinations on organic compounds, and might well be negligible.

A set of F's was calculated assuming the presence of one-quarter of a tin atom at $0\ 0\ \frac{2}{3}$ and a hexamethylene tetramine molecule as described, with a nitrogen atom at $0\ 0\ 0$. The non-centrosymmetric structure gave complex F's in general. The observed values of the modulus $|F|$ were then used with the calculated phase angles to compute the function

$$\mathrm{\rlap{S}1}\,(x\ z) = \sum_{H} \sum_{L} F_{HOL} \exp\left[-\,2\pi i\ (Hx + Lz)\right]$$

corresponding to a projection of all the electron density in the unit cell, in a direction parallel to the zone $[0\ 1\ 0]$, onto a plane.

The result of this calculation is shown in Figure 5, plotted to represent the projection on a plane normal to the zone $[0\ 1\ 0]$. Aside from a slight horizontal elongation of the heavy atom peak there seems to be no effect ascribable to atoms other than those assumed in the calculation.

Other Fourier syntheses were made with similar results. A part-cell projection and Fourier sections along the planes $x\ 0\ z$ and $x\ \bar{x}\ z$ showed only the hexamethylene tetramine molecule and the heavy atom.

In an attempt to predict the most likely orientation of a stannic chloride molecule in this structure, a diagram of the van der Waals radii (16, p. 189) in the plane $x\ \bar{x}\ z$ was drawn as shown in Figure 6. There seemed no reason for a tin atom to assume the position ascribed to it;

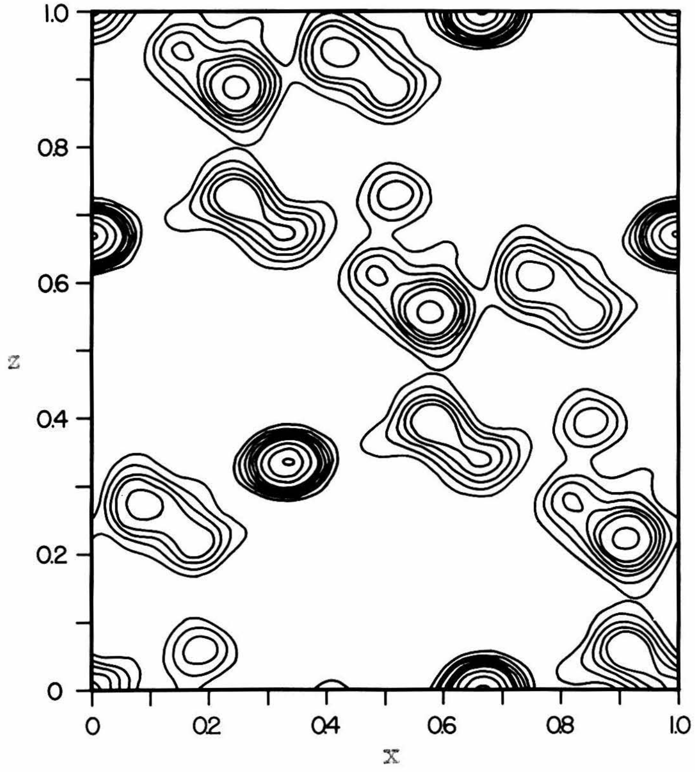


Figure 5. Fourier projection Si(x z) for $SnCl_4 \cdot 4C_6H_{12}N_4$, plotted on a plane normal to [0 1 0].

Values of the contour lines on an arbitrary scale: 0, 200, 400, 600, 800, 1000, 1500, 2000, 2500. Lowest value of the function: —580

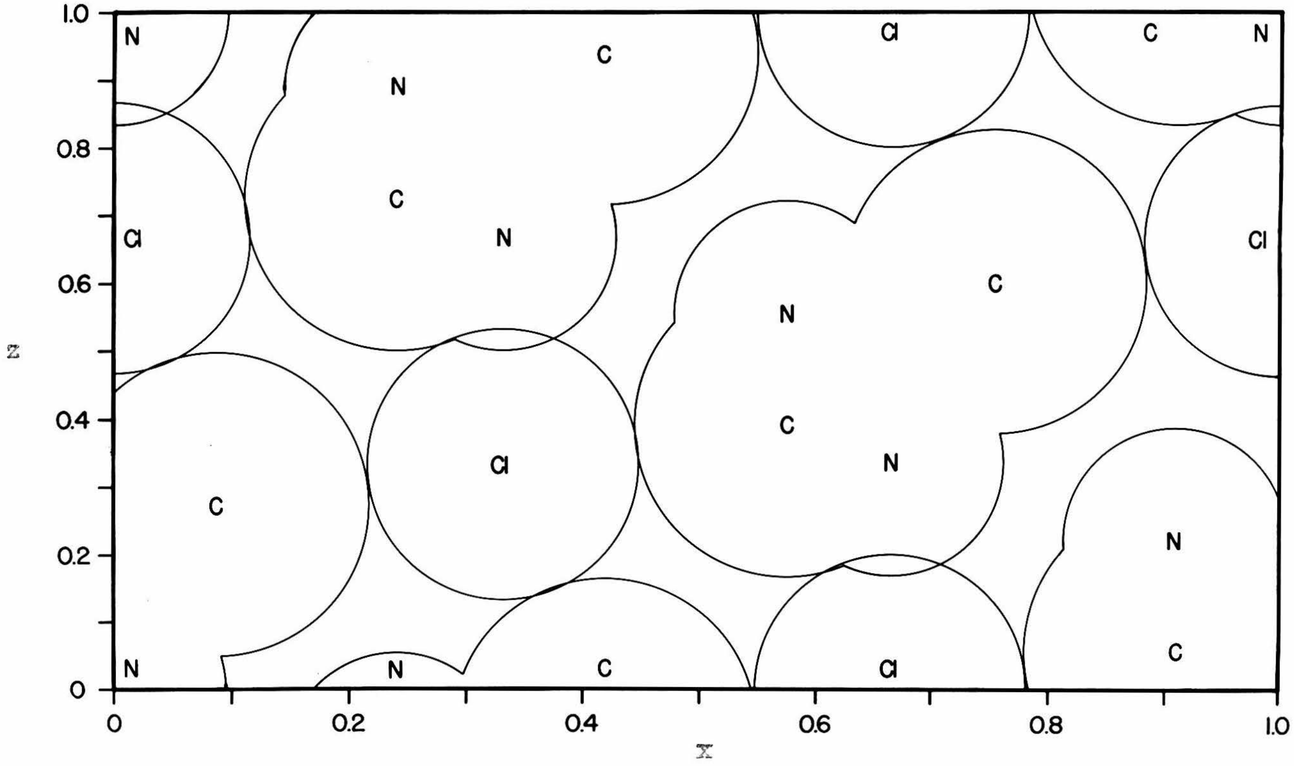


Figure 6. Arrangement of atoms in the plane $x \bar{x} z$ of $SnCl_4 \cdot 4C_6H_{12}N_4$, showing van der Waals radii.

but it became apparent that a chlorine atom would fit fairly well in just that place.

A new set of structure factors was calculated assuming a chloride ion at $0\ 0\ \frac{2}{3}$ instead of the one-quarter tin atom. From their phase angles and the observed $|F|$ values a summation

$$\rho(x\ \bar{x}\ z) = \sum_{H}\sum_{K}\sum_{L} F_{HKL} \exp\left[-2\pi i\,(Hx - Kx + Lz)\right]$$

was calculated corresponding to the electron density along one of the mirror planes in the structure. The result is shown in Figure 7. No peaks representing the tin atoms are visible.

A final test of the structure with one-quarter of a tin atom at $0\ 0\ \frac{2}{3}$ was made by calculating structure factors for a number of reflections which appear with about equal intensities on rotation photographs from both the tin and the titanium compounds. The ratios of corresponding pairs of intensities on the two photographs are indistinguishable with the naked eye. Since the corresponding reflections occur at the same point on the film all corrections necessary to obtain $|F|^2$ are the same, and a satisfactory model must yield similar $|F|^2$ ratios for both the tin and titanium compounds.

The reflections chosen are shown in Figure 2. The two rotation photographs have approximately the same total blackening at corresponding spots, but the two crystals were of different shapes. The spots are numbered for comparison with Table 1, in which are listed the calculated $|F|^2$ values.

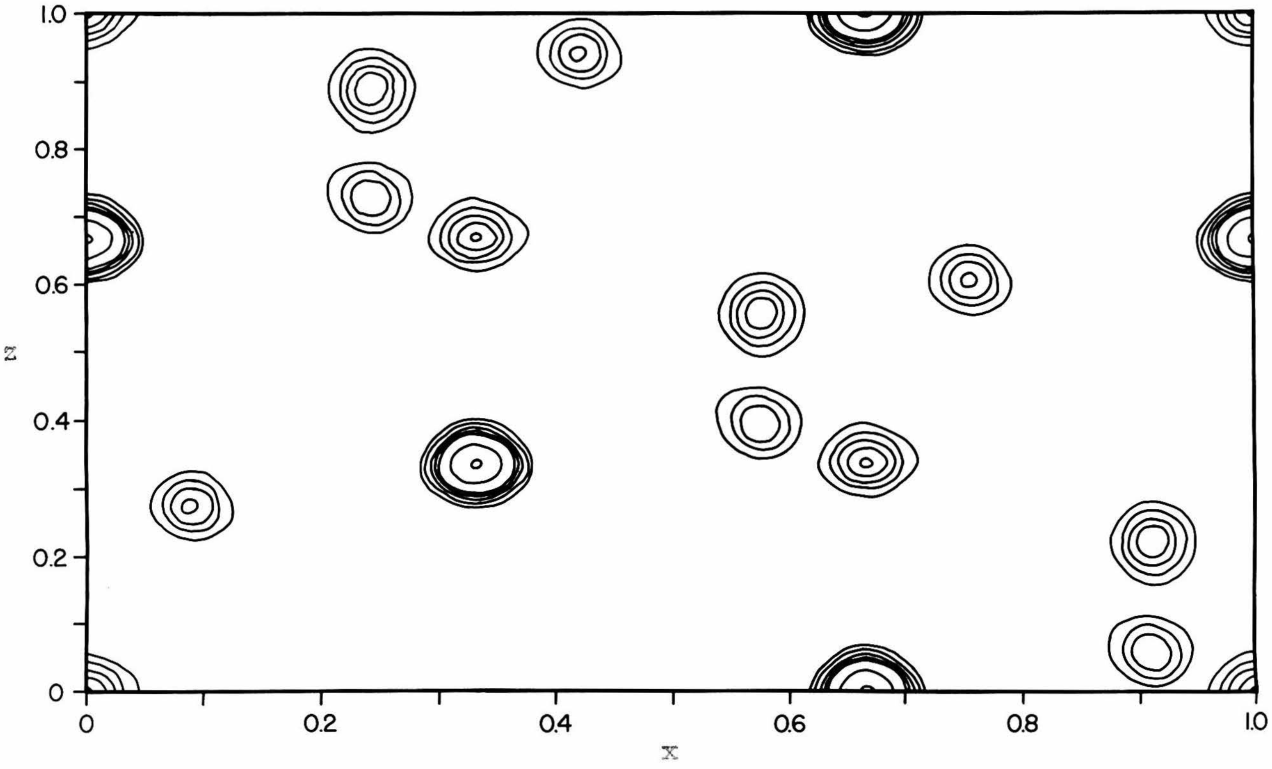


Figure 7. Fourier section $\rho(x\,\bar{x}\,z)$ for $SnCl_4 \cdot 4C_6H_{12}N_4$.

Values of the contour lines on an arbitrary scale: 100, 200, 300, 400, 500, 1000, 1500. Lowest value of the function: −50.

Table 1

$|F|^2$ Values for $MCl_4 \cdot 4C_6H_{12}N_4$ with One-Quarter of a Metal Atom at 0 0 $\frac{2}{3}$

Spot No.	HKL	$\|F\|^2$ Calcd. (Sn)	$\|F\|^2$ Calcd. (Ti)	$\|F\|^2$ Observed (Sn)
1	220	16	0.6	20
2	051	73	25	46
3	511	38	12	25
4	431	23	57	27
5	161	64	35	50
6	351	3.5	17	2.9

The discrepancies calculated for the titanium compound are obviously too large to have been overlooked.

The structure with one chlorine atom at 0 0 $\frac{2}{3}$ was therefore concluded to be the true one. It explains immediately the formulas $MCl_4 \cdot 4C_6H_{12}N_4$ and the isomorphism of complexes of two metals so far apart in the periodic table as tin and titanium. Furthermore, this structure provides an economy of postulates, since it requires only the assumption that the tin atom is randomly distributed. Otherwise all four of the chlorines must be assumed to be distributed at random.

The packing of the atoms in this structure agrees reasonably well with the known van der Waals radii, as shown in Figure 6. There is space for the stannic ion near a chlorine atom in any of the four channels shown at its right and left, slightly above and below. In the crystal there are twelve of these channels around each chlorine. It seems likely that the three which are equivalent to the one shown at upper right are somewhat favored, since they allow the tin to be placed at a distance approximating the sum of the covalent radii from two nitrogens as well as one of the two chlorines.

In principle this structure is simply a modification of the structure of hexamethylene tetramine itself, which has a molecule at each point of a body-centered cubic lattice. The axes of the primitive rhombohedron are the vectors from the molecule at a cube center to those at three tetrahedrally related corners. The rhombohedral angle 109.5° corresponds to a hexagonal axial ratio $c/a = 0.61$. The modification of the hexamethylene tetramine structure consists in reducing the rhombohedral angle to 97.2° and increasing the ratio c/a to 1.00. The space made available at the center of the rhombohedron is occupied by a chlorine atom.

The distance between hexamethylene tetramine molecules nearest to each other in the distorted structure is 5.96 Å., changed only slightly from the original 6.08 Å. It is evident that the hexamethylene tetramine molecules tend to compress the chlorine atom in a vertical direction, from the noticeable overlapping of van der Waals radii indicated in Figure 6.

It seems probable that these compounds are somewhat similar to the clathrate compounds of hydroquinone investigated by Palin and Powell (15) in being held together mainly by the hydrogen-bonded framework of large organic molecules. Quite possibly the molecular ratio is variable, with 1:4 being the maximum proportion of tetrachloride molecules.

Some further calculations were made to check the possibility of a random orientation of hexamethylene tetramine molecules. It was thought possible that one in four, say, of these might be turned upside down; such an inversion through the center of the molecule would bring two nitrogens closer together and possibly provide a more suitable environment for the tin atoms. Calculated |F| values are shown in Table 2 for models with none, one–quarter, and one–half of the molecules inverted, together with observed |F|'s having their scale factor adjusted for the best fit to the non–random model. The reflections listed are most of the ones on which the change had much effect; therefore this scale factor should be suitable for all three models.

Table 2

Comparison of |F|'s for $SnCl_4 \cdot 4C_6H_{12}N_4$ with Partly Inverted Hexamethylene Tetramine Molecules

HKL	|F| Calcd., None Inverted	|F| Calcd., 1/4 Inverted	|F| Calcd., 1/2 Inverted	|F| Observed
030	8.7	4.8	2.2	8.3
202	8.3	6.4	6.6	6.4
006	5.5	3.0	1.0	7.9
036	3.3	2.2	1.7	3.8
048	2.7	1.4	0.7	2.6
072	3.5	1.8	0.4	4.4
104	9.4	4.9	0.6	9.7
140	6.6	5.7	5.3	5.2
502	4.5	2.6	1.4	5.0
128	2.2	0.2	0.2	3.0
2.1.10	1.4	1.0	0.7	3.0
312	8.5	4.1	0.7	10.2
434	3.9	2.1	0.2	3.6
446	1.7	0.9	0.7	2.8

These figures leave little doubt that half the hexamethylene tetramine molecules cannot be inverted. It is rather more difficult to decide about the inversion of one-quarter of the molecules; but a comparison for reflections 030, 048, 104, 128, 312, and 502 indicates that this model is also unsatisfactory.

The best fit of calculated $|F|$'s to the experimental data is shown by the complete list of structure factors in Appendix 1. The C—N bonds in hexamethylene tetramine were assumed to be tetrahedral in all calculations. A C—N bond length of 1.45 Å. was used originally, but the early Fourier sections indicated 1.48 Å. to be somewhat more suitable. The latter value was used thereafter. All the structure factors were calculated with the chlorine at $z = \frac{2}{3}$. The last Fourier section seemed to indicate that 0.664 would be a somewhat better value; this is exactly half-way between the geometrical centers of the hexamethylene tetramine molecules. Further refinement of the parameter was judged not worth while.

The final adjustment of scale factor and temperature factor was made by least squares as described above.

The total isotropic temperature factor finally arrived at was $B = 3.4$ Å^2.

The final value of the expression

$$\frac{\sum |(|F_{obs}| - |F_{calc}|)|}{\sum |F_{obs}|}$$

was 0.153.

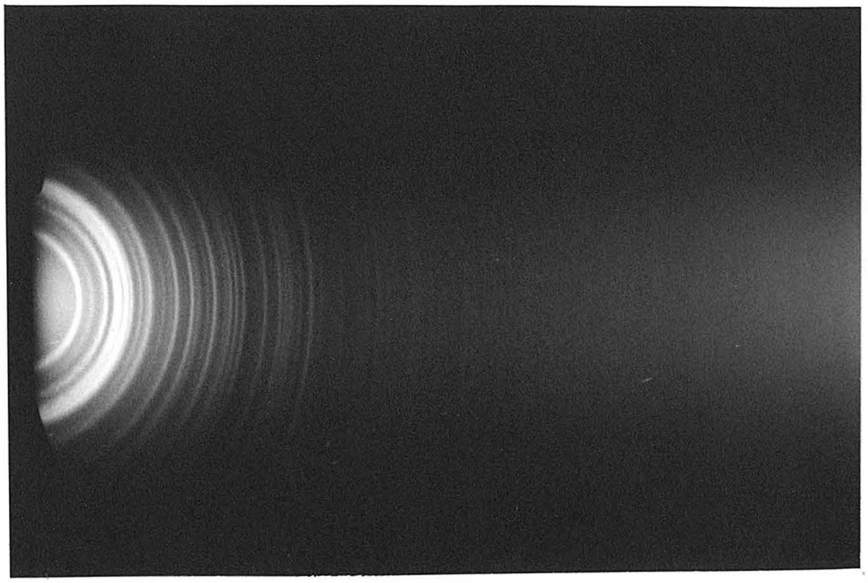
Powder photographs with CuKα radiation were made from the two precipitates. The patterns are shown in Figure 8. They exhibit many similarities but are not identical; this is the result to be expected if the packing in the crystal is dependent mainly on the relative sizes of hexamethylene tetramine and the halide ion.

A single crystal of $MnCl_2 \cdot 2C_6H_{12}N_4$ was mounted with its needle axis vertical, and Laue photographs were taken. The Laue symmetry was found to be D_{2h}–mmm. Crystal axes were chosen corresponding to the Laue photographs obtained when the axes were parallel to the beam. The Laue patterns with $\underset{\sim}{a}$ and $\underset{\sim}{b}$ respectively parallel to the beam while $\underset{\sim}{c}$ is vertical are shown in Figure 9.

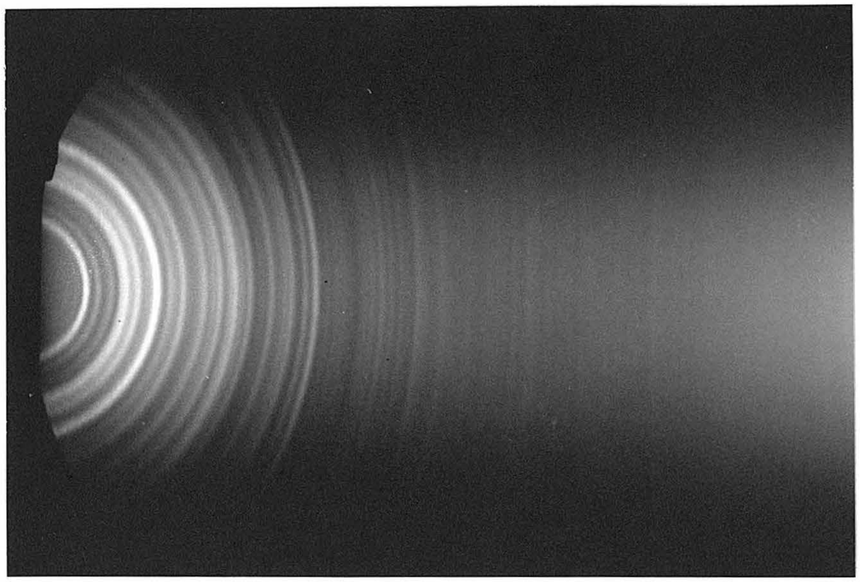
A set of four 24° oscillation photographs about the $\underset{\sim}{c}$ axis was made with CuKα radiation. The layer-line spacing gave the length of the $\underset{\sim}{c}$ axis as 7.23 Å. It was found that all the reflections on these oscillation photographs could be indexed with axes $a = 11.86$ Å., $b = 21.92$ Å.

The two symmetric Laue photographs with the beam along $\underset{\sim}{a}$ and $\underset{\sim}{b}$ shown in Figure 9 were indexed on this lattice by means of a gnomonic projection. No reflections were found which contradicted the assumed unit cell. The numbers of symmetry-independent reflections found to be definitely first-order were 25 and 12, respectively. All these are repeated four times on each photograph by the symmetry operations.

The density of this compound was determined by the pycnometer method with benzene as the liquid displaced. The resulting value, 1.55 g./cm.^{3},



(A)



(B)

Figure 8. Powder photographs of manganous halide complexes taken with CuKα radiation. (A) $MnCl_2 \cdot 2C_6H_{12}N_4$; (B) $MnBr_2 \cdot 2C_6H_{12}N_4$.

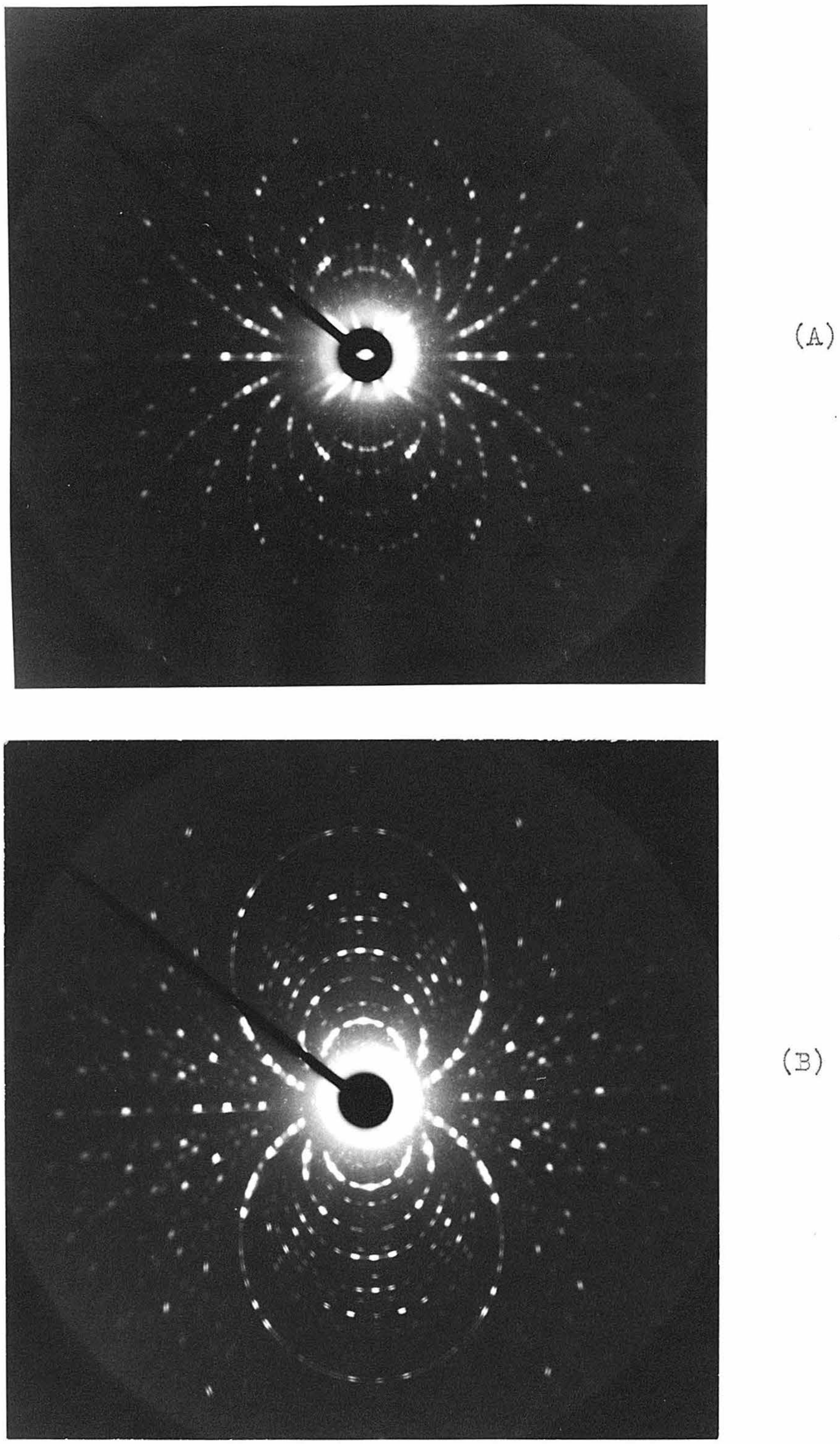


Figure 9. Laue photographs of $MnCl_2 \cdot 2C_6H_{12}N_4$ with $\underset{\sim}{c}$ vertical. (A) $\underset{\sim}{a}$ along beam; (B) $\underset{\sim}{b}$ along beam.

corresponds to 4.3 molecules $MnCl_2 \cdot 2C_6H_{12}N_4$ per unit cell. A redetermination of this figure would be desirable, but it seems probable that the true value is four.

The Laue photographs contained some reflections with an odd value of each of the following quantities: (H + K); (K + L); (H + L); (H + K + L). Therefore the orthorhombic lattice must be simple and not centered.

Indexing of the oscillation photographs about *c* gave reflections of the following types:

0 K L: K odd; L odd; (K + L) odd;
H 0 L; H odd; L odd;
H K 0: H odd; (H + K) odd.

Thus the mirror plane normal to *a* must be an ordinary mirror plane, if any, and not a glide plane. Normal to *b* there may be a mirror plane or an *n* glide plane; normal to *c* may be a mirror plane or a *b* glide plane.

In the zone H K 0 a total of 133 reflections were indexed, and all were found to have K even. This seems to establish the presence of the *b* glide normal to *c*. So few reflections in the zone H 0 L were available that the presence of the *n* glide plane must be considered only probable, subject to further confirmation.

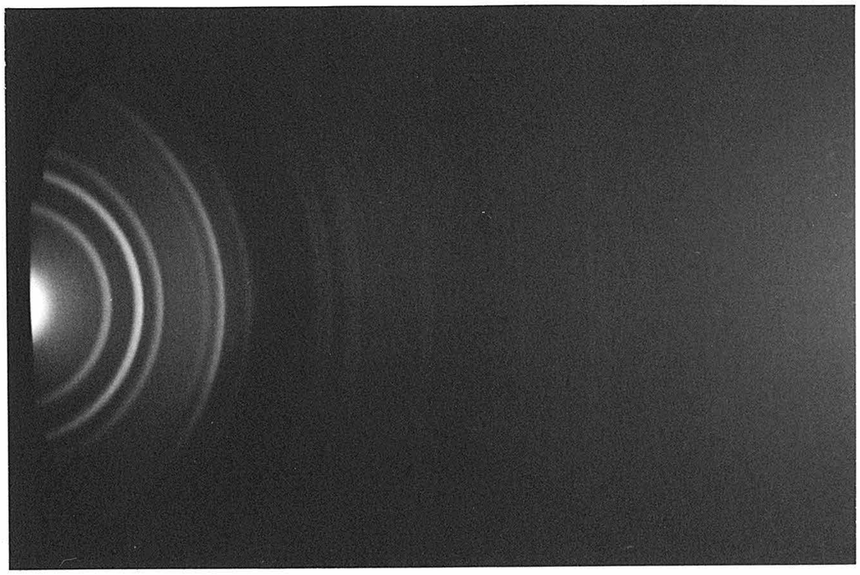
No definite statement can be made, at this early stage in the structure determination, about the probable arrangement of molecules in the crystal.

(C) Other Complexes

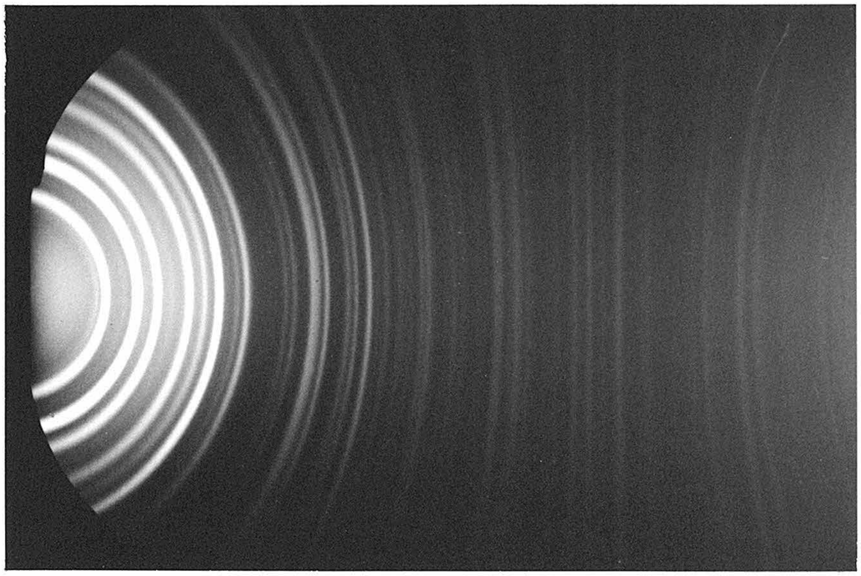
The structure found for the compounds $SnCl_4 \cdot 4C_6H_{12}N_4$ and $TiCl_4 \cdot 4C_6H_{12}N_4$ seems to be determined mainly by the packing of chlorine and hexamethylene tetramine; this indicates that other chlorides might give similar precipitates, or even precipitates whose X-ray diffraction patterns were completely indistinguishable. In this connection the observation of Duff and Bills (7) is of interest, that the complexes with $SnCl_4$, $SnCl_2$, $SbCl_3$, and $SbCl_5$ all form crystals of similar appearance.

As a test of the possibility that these precipitates might be isomorphous the compounds with $SnCl_2$ and $SbCl_3$ were prepared. The stannous chloride used was the dihydrate; the antimonous chloride was nominally anhydrous, but it had been partly used some time before and there was a layer of liquid over the solid $SbCl_3$. This was drained off as well as possible before the solid was used.

The powder photographs of the two precipitates obtained with $CuK\alpha$ radiation are shown in Figure 10. Comparison with those of the $SnCl_4$ and $TiCl_4$ compounds in Figure 1 reveals that the $SnCl_2$ compound gives exactly the same pattern. Furthermore, the $SbCl_3$ compound produced a pattern which is essentially the same except that a number of additional lines are present; a few of them are quite strong. This may indicate that the $SbCl_3$ compound has a superstructure imposed on the basic structure of the other three, representing a regular distribution of the metal atoms instead of the random distribution found in the other three compounds.



(A)



(B)

Figure 10. Powder photographs of hexamethylene tetramine complexes: (A) with $SnCl_2$; (B) with $SbCl_3$.

Conclusion

The most important factors governing the structures of the hexamethylene tetramine complexes seem to be packing of the anions among the hexamethylene tetramine molecules and the weak hydrogen bonding between these molecules. It is desirable that other compounds of this type be investigated. The crystal investigated should preferably have no atoms in random positions, in order that the complete structure can be ascertained.

In addition to structure determinations it would be desirable to investigate the equilibria involved in precipitation of these compounds and to find out the range of compositions over which the structure is stable. Such investigations will require much careful experimental work, because the preparation of sizable samples and the performance of accurate analyses of these materials are difficult.

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Appendix 1

Structure Factors for $SnCl_4 \cdot 4C_6H_{12}N_4$

HKL	|F| Calcd.	|F| Obs.	HKL	|F| Calcd.	|F| Obs.
003	21.1	24.5	119	3.5	4.3
006	5.5	7.9	1.1.12	1.3	2.6
009	2.0	4.8	122	8.4	8.1
012	23.6	21.6	125	5.8	5.3
015	15.8	18.1	128	2.2	3.0
018	3.6	4.8	131	11.4	9.8
0.1.11	1.6	3.4	134	6.5	5.3
021	3.7	4.3	137	7.8	7.8
024	6.1	5.8	1.3.10	2.6	2.8
027	7.0	7.2	140	6.6	5.2
0.2.10	2.8	3.6	143	6.2	5.6
030	8.7	8.3	146	2.5	2.6
033	8.2	6.3	149	3.2	4.2
036	3.3	3.8	1.4.12	2.5	3.0
039	4.6	6.3	152	4.3	3.7
0.3.12	3.3	5.0	155	3.1	3.1
042	6.8	5.9	158	1.9	2.6
045	6.7	6.3	161	7.2	6.6
048	2.7	2.6	164	4.3	3.4
051	8.2	6.3	173	4.7	4.8
054	2.9	4.5	176	5.9	6.6
057	4.8	4.8	202	8.3	6.4
063	6.1	5.8	205	3.9	3.4
066	6.6	6.8	208	4.0	5.7
072	3.5	4.4	2.0.11	2.5	3.6
081	6.3	6.6	211	18.7	19.2
084	3.6	3.3	214	9.3	9.3
101	18.1	16.5	2.1.10	1.4	3.0
104	9.4	9.7	220	4.8	4.2
107	5.2	6.2	223	10.0	8.5
1.0.10	2.5	3.7	226	8.6	7.2
110	30.3	24.3	229	3.6	4.8
113	14.4	14.2	2.2.12	1.6	3.6
116	6.0	6.0	232	7.2	6.4

HKL	|F| Calcd.	|F| Obs.	HKL	|F| Calcd.	|F| Obs.
235	5.7	5.8	437	2.9	3.8
244	3.5	3.3	4.3.10	1.3	3.7
247	3.7	4.8	440	12.5	12.0
250	10.1	7.9	443	5.4	4.8
253	6.4	5.0	446	1.7	2.8
256	3.7	3.0	452	3.7	2.6
271	4.4	2.8	455	3.5	3.0
303	14.4	14.1	461	2.1	2.0
306	15.2	15.1	464	1.9	2.0
309	4.0	4.8	502	4.5	5.0
312	8.5	10.2	508	3.1	3.8
315	2.5	2.8	511	6.2	4.7
318	4.9	5.5	514	4.4	4.1
3.1.11	2.8	4.3	517	2.2	2.2
321	8.3	6.2	523	5.3	4.4
324	5.5	4.6	532	5.1	4.4
330	16.0	15.8	535	5.2	5.3
333	7.6	5.8	553	2.4	1.9
336	2.9	1.6	603	4.7	3.4
342	7.4	6.7	606	3.4	4.2
345	7.6	7.3	609	2.5	3.6
351	1.0	1.6	612	4.1	3.9
354	2.3	2.4	615	3.6	3.4
401	19.9	20.7	630	4.2	2.6
404	10.3	9.5	633	3.7	3.5
407	3.0	4.7	636	2.8	3.0
413	9.3	9.1	651	3.1	2.8
416	9.9	9.3	701	5.0	4.2
419	2.8	4.2	704	3.7	2.8
422	6.1	4.7	707	4.9	4.6
425	4.9	4.6	713	2.7	2.8
428	2.8	3.6	731	4.7	3.8
431	3.5	4.8	734	2.4	2.0
434	3.9	3.6	746	3.5	4.8
			811	2.7	2.0

Propositions

1. (A) A useful way to compare complex ions which differ only in the nuclear charge of the central atom is to plot corresponding internuclear distances against the reciprocal of this nuclear charge. A linear relationship may be expected.

(B) There is a great need for accurate determinations of the structures of the common anions.

2. Considerable effort is now being expended in attempts to prepare commercially usable crystals of quartz by hydrothermal methods (1, 2). Experiments should also be made with slow hydrolysis of ethyl orthosilicate, which gives controllable precipitation of silica without use of high temperatures and pressures.

3. The method of least squares should be used in fitting the Schomaker–Stevenson equation to observed interatomic distances (3, 4).

4. (A) In calculating interatomic distances for X-ray and electron diffraction investigations, a proposed (5) analog computer for the function $r = (a^2 + b^2 + c^2)^{\frac{1}{2}}$ would not help with the major chore, which is the calculation of rectangular coordinates a, b, and c from sets of non-orthogonal coordinates. An inherently simpler computer made up of resistance networks would be very useful for performing these matrix multiplications.

(B) Use of such a computer would make extremely easy the preparation of perspective or stereoscopic drawings of crystal structures by the method of Bond (6).

5. It would be interesting to investigate the structure of the cubic ice crystals formed in repeatedly frozen water, whose freezing point gradually drops to –72° C. (7) It may be that the repeated breakdown of ordinary ice destroys metastable six-membered "boat" rings of water molecules which tend to form the hexagonal wurtzite structure, and that the cubic sphalerite structure forms instead.

6. The interpretation of carotenoid absorption spectra may be facilitated by the sharpening effect of low temperatures. The early work (8) with this method should be extended by systematic application of the convenient techniques now available (9).

7. A sensitive instrument for detection of gravitational anomalies or determination of g could be made by use of a vertical tube containing a gas thermostated near its critical point. The difference in density between the top and bottom would be measured by an interferometer or an absorption photometer, whose optical parts could be permanently sealed in the tube. This device should be quite insensitive to acceleration except in the vertical direction.

8. (A) A simple, sensitive detector of pyroelectricity or piezoelectricity could be made by attaching a suitable crystal holder to a pH meter.

(B) The liquid air test for pyroelectricity is not a safe indication either of absence or of presence of a center of symmetry. It is to be expected that rotational transitions which remove the central symmetry will occur in many crystals on such great cooling.

(C) A sensitive Giebe–Scheibe apparatus with a wider frequency range than that of Stokes (10) should be constructed as a permanent addition to the equipment of These Laboratories.

9. The number of symbols available for use in mathematical expressions is much too small. The use of Russian (11) or Japanese letters has the disadvantage of their complete unfamiliarity. I propose that pronounceable English syllables be introduced, made of a consonant followed by a vowel. One universal rule then gives the pronunciation of any such pair. In printing, the use of logotypes containing both letters or of upper–case consonants followed by lower–case vowels would make these symbols at least as convenient as others.

10. (A) The Fourier synthesis using $(F_o - F_c)$ instead of (F_o) as suggested by Booth (12) has the advantage, in addition to those he mentions, of reducing the effects of finite termination of the series.

(B) Booth's rule that the change in each atomic position be made proportional to the gradient in the $(F_o - F_c)$ synthesis is valid only if all the changes are smaller than 0.2 – 0.3 Å. The greatest advantage of this synthesis, however, should accrue when the changes required are much greater.

11. A good way to keep one's style clear and terse is to pick a short time each day in which no words are used which have more than one syll.

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