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B. S. HOPKINS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

The Crystal Structure of Ammonium Pentachlorozincate[1]

BY HAROLD P. KLUG AND LEROY ALEXANDER[2]

Introduction

The group MX_5 occurs rather infrequently in the stoichiometry of inorganic compounds as compared with such groups as MX_3, MX_4, MX_6 and M_2X_7. It is well known also that crystal chemistry reveals numerous examples of three-, four-, six-, eight- and twelve-fold coöordination by a central atom, whereas a coördination of five is virtually unknown. Such unusual stoichiometry is occasionally found in complex compounds of the general formula A_mMX_n, where A is a univalent cation, M is a di- or trivalent metal, and X is a halogen. Examples are $(NH_4)_3ZnCl_5$, and $(NH_4)_2InCl_5 \cdot H_2O$, both of which have been under investigation in this Laboratory to determine the nature of the coördination groups present.

Although many halogen complexes of the general formula A_mMX_n have had their crystal structures studied, very few involving a stoichiometry of MX_5 have been examined. Brosset[3] determined the crystal structures of Tl_2AlF_5 and $K_2AlF_5 \cdot H_2O$, and in each case found the net composition AlF_5 to be achieved through infinite chains of AlF_6 octahedra extending through the crystal. These chains are formed by the common sharing of the halogen atoms of two opposite vertices of each octahedron with neighboring octahedra. The actual coördination about the aluminum then is six-fold, and there are no AlF_5 groups as such in these compounds.

Phosphorus pentachloride and pentabromide appear to be the only other compounds involving the stoichiometry of MX_5 which have had crystal structure investigations. Powell, Clark, and Wells[4] found no PCl_5 molecules in phosphorus pentachloride but instead a CsCl-type packing of ionic tetrahedral PCl_4^+ and octahedral PCl_6^- groups. The structure of phosphorus pentabromide, however, is entirely different.[5] It consists of a packing of tetrahedral PBr_4^+ and Br^- ions.

In view of the interesting results reported for compounds involving MX_5 groups, and the further fact that zinc-halogen complexes in general have had little crystal-chemical study, it seemed worthwhile to study $(NH_4)_3ZnCl_5$ thoroughly. This communication reports the results of a complete determination of its crystal structure. It is shown that the structure is to be regarded as a

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(1) Presented before the Division of Physical and Inorganic Chemistry, Cleveland meeting of the American Chemical Society, April, 1944.

(2) (a) Shevlin Fellow in Chemistry, 1942–1943. (b) From a thesis by Leroy Alexander, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, July, 1943. (c) Present address: General Electric Company, Pittsfield, Mass.

(3) Brosset, *Z. anorg. allgem. Chem.*, **235**, 139 (1937); "Electrochemical and X-Ray Crystallographic Investigation of Complex Aluminum Fluorides," Separate, Stockholm, 1942, 120 pp.

(4) Powell, Clark and Wells, *J. Chem. Soc.*, 642 (1942).

(5) Powell and Clark, *Nature*, **145**, 971 (1940).

packing of NH_4^+, Cl^-, and $ZnCl_4^=$ ions, and its chemical formula might be more accurately written as $(NH_4)_2ZnCl_4{\cdot}NH_4Cl$.

Crystallographic Data

Pierre[6] was the first to report the preparation of $(NH_4)_3ZnCl_5$. Marignac[7] also prepared it, and in addition obtained plate-like crystals of the salt $(NH_4)_2ZnCl_4$. Following this work as many as eight ammonium chlorozincates of various compositions were reported, but in 1898 Base,[8] in a systematic attempt to prepare them all, succeeded in obtaining only the two salts described by Marignac. Finally, Meerburg[9] applied the phase rule to the system NH_4Cl–$ZnCl_2$–H_2O and proved that only $(NH_4)_2ZnCl_4$ and $(NH_4)_3ZnCl_5$ are capable of existence in aqueous solution between 0 and 30°.

The pentachlorozincate was investigated crystallographically by Marignac, Rammelsberg,[10] and Johnsen,[11] who showed it to be rhombic bipyramidal with the axial ratios $a:b:c = 0.7822:1:0.6915$. Johnsen reported the density to be approximately 1.81. Marignac found the crystals to possess two habits, prismatic with elongation in the *a* direction, and nearly equi-dimensional in all directions. Twinning on the (110) face was reported to occur commonly.

Experimental

The crystals used in this study were prepared from reagent grade salts using three formula weights of ammonium chloride to one of zinc chloride. These were dissolved in the minimum amount of conductivity water, after which the solution was filtered and set aside in a desiccator over calcium chloride to evaporate. The marked tendency to twin was observed frequently, and the two crystal habits reported by Marignac were both obtained. In solutions of low acidity the equi-dimensional types predominated, while by increasing the acidity by the addition of hydrochloric acid it was sometimes possible to obtain only the prismatic variety. The crystals were pressed between filter papers to remove adhering mother liquor, and dried in an electric oven at 100° for about an hour. Gravimetric analysis for zinc by precipitation as the 8-hydroxyquinolate and for chloride by precipitation as silver chloride[12] confirmed their composition as $(NH_4)_3ZnCl_5$.

Preliminary Laue photographs showed orthorhombic symmetry, confirming the findings of the earlier crystallographic studies. Layer-line measurements from rotation photographs about each of the crystal axes were then used to obtain the approximate dimensions of the unit cell. These values were subsequently refined using pinacoid reflections in the equatorial layer lines of oscillation photographs. The revised lattice constants were found to be $a_0 = 8.74$, $b_0 = 9.84$, and $c_0 = 12.61$ Å. (all ± 0.02 Å.), corresponding to axial ratios of $a:b:c = 0.6930:0.7805:1$ in good agreement with those reported in the literature when the axes are appropriately interchanged. Using Johnsen's value for the density, 1.81, the unit cell was found to contain four molecules of the composition $(NH_4)_3ZnCl_5$.

The underlying lattice type and the space group were determined from Laue data with the aid of a pyroelectric test for a center of symmetry. Symmetrical and unsymmetrical Laue photographs taken with tungsten radiation ($\lambda_{\text{min.}} = 0.33$ Å.) were analyzed by means of gnomonic projections, and first-order reflections examined for extinctions. The presence of all types of pyramid reflections in the first order indicated a simple primitive lattice. Two clear-cut extinctions were found, ($hk0$) with (h) odd, and ($0kl$) with ($k + l$) odd. These established the space group as either D_{2h}^{16} or C_{2v}^{9}. A pyroelectric test by the method described by Martin[13] was negative, thus indicating the presence of a center of symmetry and uniquely fixing the space group as $D_{2h}^{16} - Pnma$.

Intensity data from more than six hundred planes were obtained from three series of 15° oscillations about the crystal axes using filtered CuK_α radiation. The reflections were indexed by the Bernal reciprocal lattice technique as described by Buerger.[14] The multiple film technique[15] was used, and the intensities were estimated visually using a calibrated scale. Non-equatorial reflections were corrected for reflection time by the method of Hettich.[16] An empirical correction was also made to place the intensities from all films on a common basis. Finally, the intensities were reduced to relative structure factors by multiplying by the reciprocals of the Lorentz and polarization factors and extracting the square root. No attempt was made to apply the temperature factor or the absorption factor except that small crystals were used to reduce the effect of the latter.

Determination of the Structure

The space group D_{2h}^{16}—$Pnma$ possesses two-fold screw axes parallel to each crystallographic axis, and symmetry planes perpendicular to them. A glide plane (n) with glide components of $b/2 + c/2$ is situated at $x = {}^1/_4$ and ${}^3/_4$, a mirror plane (m) at $y = {}^1/_4$ and ${}^3/_4$, and a glide plane (a) with

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[6] Pierre, *Ann. chim. phys.*, [3] **16**, 250 (1846).

[7] Marignac, *Ann. Mines*, [5] **12**, 1 (1857).

[8] Base, *Am. Chem. J.*, **20**, 660 (1898).

[9] Meerburg, *Z. anorg. Chem.*, **37**, 199 (1903).

[10] Rammelsberg, "Handbuch der krystallographischen Chemie," Berlin, 1855, p. 205.

[11] Johnsen, *Z. Krist.*, **41**, 527 (1906).

[12] Kolthoff and Sandell, "Textbook of Quantative Inorganic Analysis," The Macmillan Company, New York, N. Y., 1943, pp. 327 and 307.

[13] Martin, *Min. Mag.*, **22**, 519 (1931).

[14] Buerger, "X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 133–155, 195–198.

[15] de Lange, Robertson, and Woodward, *Proc. Roy. Soc.* (London), **A171**, 398 (1939).

[16] Hettich, *Z. Krist.*, **90**, 479 (1935).

a glide component of $a/_2$ at $z = {}^1/_4$ and ${}^3/_4$. The following sets of equivalent positions are available[17]

4: (*a*) $000;\ 0\tfrac{1}{2}0;\ \tfrac{1}{2}0\tfrac{1}{2};\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}.$ } (symmetry centers)
(*b*) $00\tfrac{1}{2};\ 0\tfrac{1}{2}\tfrac{1}{2};\ \tfrac{1}{2}00;\ \tfrac{1}{2}\tfrac{1}{2}0.$ }
(*c*) $x\tfrac{1}{4}z;\ \bar{x}\tfrac{3}{4}\bar{z};$
$\tfrac{1}{2} - x, \tfrac{3}{4}, \tfrac{1}{2} + z;\ \tfrac{1}{2} + x, \tfrac{1}{4}, \tfrac{1}{2} - z.$ (mirror plane)
8: (*d*) $xyz;\ \tfrac{1}{2} + x, \tfrac{1}{2} - y, \tfrac{1}{2} - z;\ \bar{x}, \tfrac{1}{2} + y, \bar{z};$
$\bar{x}\bar{y}\bar{z};\ \tfrac{1}{2} - x, \tfrac{1}{2} + y, \tfrac{1}{2} + z;\ x, \tfrac{1}{2} - y, z;$
$\tfrac{1}{2} - x, \bar{y}, \tfrac{1}{2} + z;$
$\tfrac{1}{2} + x, y, \tfrac{1}{2} - z.$ (general positions)

There must be placed in the unit cell with the above symmetry elements 4 zinc atoms, 12 ammonium groups, and 20 chlorine atoms.

In the only two compounds of similar stoichiometry which have been studied to date, namely Tl_2AlF_5 and $K_2AlF_5 \cdot H_2O$, the basic structural feature is an infinite chain of AlF_6 octahedra formed by the sharing of opposite corners. The Al–F distance in Tl_2AlF_5 is reported to be 1.91 Å. which is in good agreement with the sum of the ionic radii, 1.86 Å.[18] This is good evidence that the Al–F bond is essentially ionic.

It seemed, therefore, that a structure involving chains of $ZnCl_6$ octahedra might be predicted for $(NH_4)_3ZnCl_5$ if zinc could coördinate six chlorine atoms. In zinc chloride, which is reported to be isomorphous with cadmium chloride,[19] such octahedral coördination of chlorine exists. In cadmium chloride[20] the observed Cd–Cl distance is 2.66 Å. as compared with the sum of the ionic radii, 2.78 Å. This decrease is to be attributed to the partial covalent character of the bond. Since a Zn–Cl bond is expected to possess a comparable covalent character, an expected Zn–Cl distance of approximately 2.44 Å. in $(NH_4)_3ZnCl_5$ would be predicted from the sum of the ionic radii, 2.55 Å., provided octahedral coördination exists. It was observed that $b_0/4 = 9.84/4 = 2.46$ Å., a value almost exactly equal to the expected Zn–Cl distance of 2.44 Å. This suggests chains of $ZnCl_6$ octahedra extending in the *b* direction. Ammonium ions would be situated between the chains and hold the structure together. From the known structures of ammonium chloride it would be predicted that ammonium ions would be surrounded by six or eight chloride ions at a distance of approximately 3.30 Å.

Numerous attempts at predicting a structure on the basis of the above considerations were all unsuccessful. One difficulty always arose, namely, that the ammonium ions could not be accommodated without abnormally close approach between ammonium and chloride ions and leaving, at the same time, an excessively open structure in other regions of the cell. It was finally decided that further use of such trial-and-error methods was a waste of time, and that the problem should be attacked by one or more of the methods of Fourier analysis.

From the relatively strong diffracting power of zinc it was felt that at least the locations of the zinc atoms could be established by the use of one-dimensional Patterson–Harker[21] F^2 summations. The presence of a symmetry plane perpendicular to each crystallographic axis makes this method of attack feasible.

Because of the mirror plane parallel to (010) at $y = 0.25$ and 0.75, the distribution of atoms in the *b* direction is decidedly limited. An atom must lie precisely on the mirror plane or at a sufficient distance from it so as not to overlap. Thus ammonium ions with a radius of about 1.50 Å. and chloride ions with a radius of 1.81 Å. must either lie on the plane or at these or greater distances from it. Simple calculations then allow the prediction that the *y* parameter of the ammonium ions will either be exactly 0.25 or lie between +0.097 and −0.097 (or the corresponding limits 0.403 to 0.597). Similarly *y* for chloride ions will either be 0.25 or fall between +0.066 and −0.066 (or 0.434 and 0.566). Atoms lying on the mirror planes ($y = 0.25$) must occupy the set of positions 4(*c*), while if $y \neq 0 \neq 0.25$ these atoms must occupy the set of general positions 8(*d*). As there are twelve ammonium groups and twenty chlorine atoms to be placed, it is evident that some ammoniums and some chlorines may be situated in either the (*c*) or (*d*) positions with the parameter restrictions just explained. The other alternative is that some ammoniums and chlorines may be situated in symmetry centers with $y = 0$, in which case they would occupy a set of 4(*a*) or (*b*) positions. The case of the zinc atoms is different. They must occupy one of the three sets (*a*), (*b*), or (*c*), and therefore the *y* parameter must be either 0 or 0.25. It should be possible to distinguish between these two possibilities from the appearance of the plot of the Patterson–Harker function $P(0y0)$.

Using F^2 data from about 600 planes the function $P(0y0)$ was summed by the method of Patterson and Tunell.[22] The functions $P(\tfrac{1}{2}0z)$ and $P(x\tfrac{1}{2}\tfrac{1}{2})$ were also summed. The plot of $P(0y0)$, in contrast to the other two, was found to be particularly lacking (except for the peak at the origin) in any peak high enough to be attributed to a Zn–Zn interaction. It seemed reasonable to conclude, therefore, that the zinc atoms are on the symmetry planes ($y = 0.25$ and 0.75). From the most conspicuous maximum on $P(\tfrac{1}{2}0z)$ (see Fig. 3) it was concluded that the zinc atoms are at a distance of $z = 0.145$ from the *a* glide plane, corresponding to a parameter of $z = 0.105$ or 0.355. The very high peak on $P(x\tfrac{1}{2}\tfrac{1}{2})$ (see Fig. 1) suggested that zinc had an *x* parameter of 0.185 or 0.315. The four zinc atoms were thus assigned to

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(17) "International Tables for the Determination of Crystal Structures," Vol. I, p. 138.

(18) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1st ed., 1939, p. 326.

(19) Bruni and Ferrari, *Atti accad. Lincei*, **2**, 457 (1925); **4**, 10 (1926).

(20) Pauling and Hoard, *Z. Krist.*, **74**, 546 (1930).

(21) Patterson, *ibid.*, **90**, 517 (1935); Harker, *J. Chem. Phys.*, **4**, 381 (1936).

(22) Patterson and Tunell, *Am. Mineral*, **27**, 655 (1942).

a set of 4(*c*) equivalent positions with the approximate parameters $x = 0.315$ and $z = 0.105$.

In order to locate the chlorine atoms it was decided to enlist the aid of appropriate two-dimensional Patterson–Harker summations. First the function $P(x\frac{1}{2}z)$ for a summation perpendicular to *b*, making use of the *y* screw axis, was used. A plot of this function is shown in Fig. 1. The contour elevations are in arbitrary units. While this function should yield information relative to the *x* and *z* parameters of all of the atoms, much ambiguity was encountered in its interpretation because of the great multiplicity of factors which can contribute to its maxima. The plot is really a plane section through Patterson space at $y = {}^1/_2$, and it may contain maxima due to the following causes: (1) Two equivalent atoms related by a *y* screw axis. Several of these peaks are to be expected. (2) Two equivalent atoms related by the *n* glide. Such pairs will give maxima with the coördinates: x = twice the perpendicular distance of either atom from the *n* plane, $z = 0.50$. These peaks will lie along the line $z = 0.50$ and several are to be expected. (3) Any two *like* or *unlike* atoms lying on alternate mirror planes, since they are necessarily separated by a *y* interval of 0.50. The coördinates of these peaks will be x = the *x* component of the vector separating them in the crystal itself, and z = the *z* component of this vector. A considerable number of maxima of this kind should appear. (4) Finally, any of two *like* or *unlike* atoms in the structure which happen to be separated by a vector distance the *y* component of which is approximately 0.50. Maxima of this kind are apt to be numerous only if a number of atoms lie very close to the planes $y = 0$ and 0.50. The one dimensional summations indicated this to be the probable situation in $(NH_4)_3ZnCl_5$.

Peak no. 6 of Fig. 1 could be attributed to the interaction of two zinc atoms related by a screw axis if their parameters are $x = 0.310$ and $z = 0.109$. These values are in excellent agreement with the zinc parameters deduced from the one-dimensional summations. The very high peak no. 1 was taken to be due to the action of the *n* glide plane, and to represent a large number of atoms (including zinc) lying at distances from the glide plane ranging from $x = 0.03$ to 0.115. This too is in agreement with conclusions reached from the plot of $P(x\frac{1}{2}\frac{1}{2})$. The remaining peaks could not be identified until information from other two-dimensional summations was available.

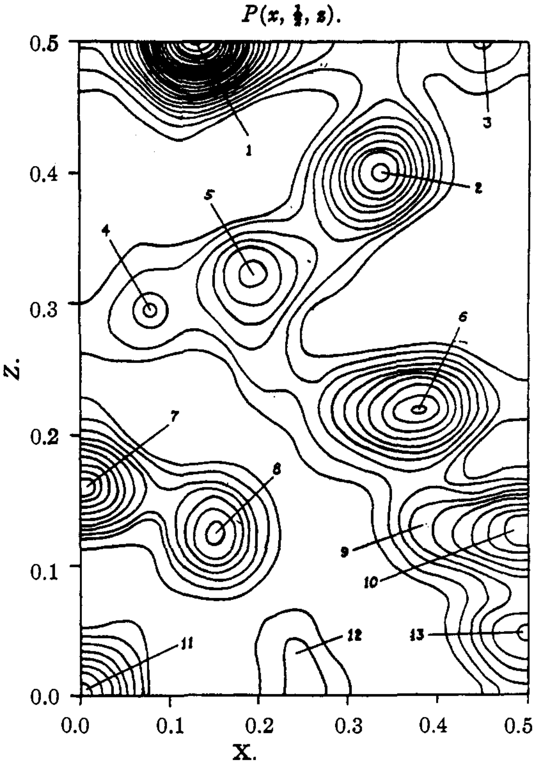

Fig. 1.—A plot of the function $P(x\ \frac{1}{2}\ z)$. The upper edge of the plot represents the function $P\ (x\ \frac{1}{2}\ \frac{1}{2})$. The contour elevations are in arbitrary units. Peaks nos. 1 and 6 lead to parameters $x = 0.315$ and $z = 0.105$ for the zinc atoms.

There was no evidence to indicate that in the *c* direction the bulk of the atoms lie on planes separated by intervals of $z = 0.50$, an arrangement which exists in the *b* direction and thereby introduces many unwanted maxima into the plot of $P(x\frac{1}{2}z)$. Accordingly the function $P(xy\frac{1}{2})$, making use of the *z* screw axis, was evaluated. The only important maxima not arising from the action of the *z* screw axis will be those due to the *n* glide plane. The latter will give no trouble since they will lie on the line $y = 0.50$. In fact, the previous one- and two-dimensional plots allow the prediction of a very large peak at $x = 0.130$ and $y = 0.50$ in the plot of $P(xy\frac{1}{2})$.

Figure 2 is the completed plot of $P(xy\frac{1}{2})$, and the very large maximum no. 1 at $x = 0.134$ and $y = 0.50$ verifies the prediction above. The only other high peak is no. 4 at $x = 0$ and $y = 0.310$. It turned out to be fundamentally important in arriving at the correct structure. First, it was noted that it could not be due to the action of the *z* screw axis because, if this were true, it would place an atom unpermissibly close to a mirror plane. It would require an atom to lie at a distance of $y = 0.095$ from a mirror plane, and it has been shown earlier that neither ammonium nor chloride ion can approach closer than a distance of $y = 0.153$ from such a plane. Likewise, peak no. 4 could not be due to the action of the *n* glide, since all peaks of that class fall at $x = x$, $y = 0.50$. It was therefore concluded that this peak is due to an accidental relationship in the structure involving two atoms of strong diffracting power separated by a vector distance with the components

$$x \cong 0 \qquad y = 0.310 \qquad z \cong 0.50$$

The height of the peak could only be attributed to a Zn–Cl interaction, with perhaps more than one chlorine per zinc atom. Calculations showed this

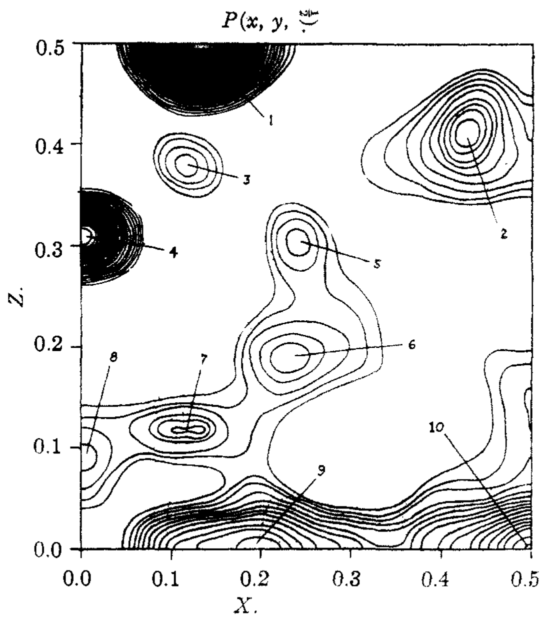

Fig. 2.—A plot of the function $P(x\ y\ \frac{1}{2})$. The very large peak no. 1 results from the action of the n glide plane, and represents a large number of interactions (including zinc). Peak no. 4 results from a Zn–Cl_D interaction.

would necessitate the presence of eight chlorine atoms in a set of general positions with the parameters

$$x \cong 0.185 \qquad y = 0.060 \qquad z \cong 0.105.$$

These will be designated from this point on as Cl_D atoms. The precise parameters given above lead to the improbably short Zn–Cl_D distance of 2.18 Å., but a slight permissible shift in the z parameter to $z = 0.055$ increases the Zn–Cl_D distance to approximately 2.30 Å., which is the expected Zn–Cl distance for tetrahedral covalent coördination.[23] The greater shift necessary to increase the interatomic distance to the octahedral coördination distances of 2.44 and 2.55 Å. previously discussed would probably change the z component of the vector so much as to prevent a conspicuous peak in the plot of $P(xy\frac{1}{2})$. This shift was also supported by the one dimensional plots $P(\frac{1}{2}0z)$ and $P(0y0)$. Accordingly, eight Cl_D atoms were tentatively assigned to a set of $8(d)$ positions with the shifted parameters just mentioned.

It now seemed very probable that a large number of atoms was located on the mirror planes at $y = 0.25$ and 0.75. If so, a plot of $P(x0z)$, even though the structure possesses no direct two-fold axis, would yield particularly valuable information in the present problem, since it should contain large maxima for Zn–Zn and Zn–Cl vectors. The zinc atoms were already known to lie on these planes, and it appeared probable that eight and perhaps all twelve of the remaining chlorines lay on them also.

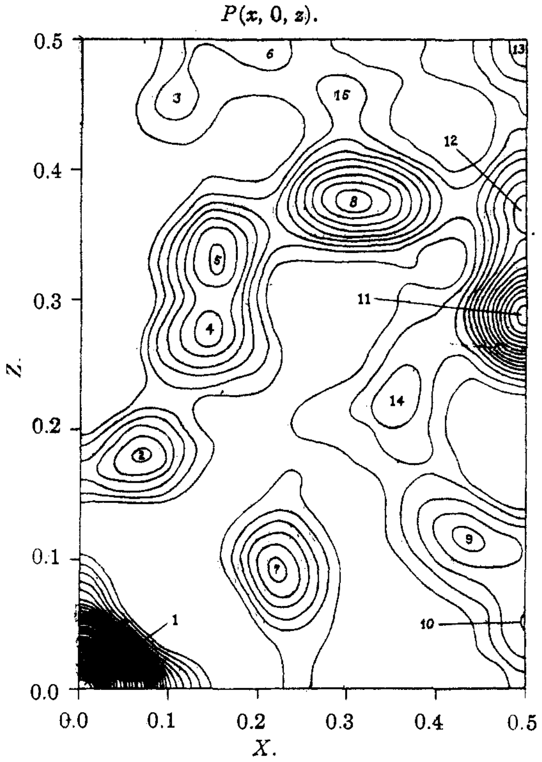

Fig. 3.—A plot of the function $P(x\ 0\ z)$. The right-hand edge of the plot represents the function $P(\frac{1}{2}\ 0\ z)$. This section gives parameter data for the large number of atoms located on the symmetry planes, even though the structure possesses no direct two-fold axis.

In the plot of $P(x0z)$, Fig. 3, peaks nos. 11 and 12, respectively, confirm the parameters previously assigned to zinc and Cl_D. Peaks nos. 2 and 7 were taken to represent Zn–Cl vectors, and calculation showed their magnitudes to be 2.31 and 2.27 Å., respectively, values almost identical with the Zn–Cl_D distance already fairly well established. The positions of these peaks not only give the absolute magnitudes of the interatomic vectors but also their directions. They thus lead to the placing of two sets of four chlorine atoms in the $4(c)$ positions with the approximate parameters: Cl_A with $x = 0.382$, $z = 0.282$; Cl_B with $x = 0.030$, $z = 0.480$. In placing these chlorine atoms as described, a tetrahedral grouping of chlorine about zinc results, all edges of the tetrahedron being of approximately the same length, 3.70 Å., a distance in good agreement with twice the ionic radius (1.81 Å.) of chlorine. The remaining four chlorine atoms, designated Cl_C, were found to be responsible for peaks nos. 4 and 5, and their required parameters were found to be approximately $x = 0.165$ and $z = -0.230$.

Scale drawings of the packing of the zinc and chlorine atoms, in the positions listed above, and assuming the accepted ionic radii, revealed the presence of very definite openings of approximately the necessary dimensions to accommodate

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(23) Pauling and Huggins, Z. Krist., 87, 205 (1934).

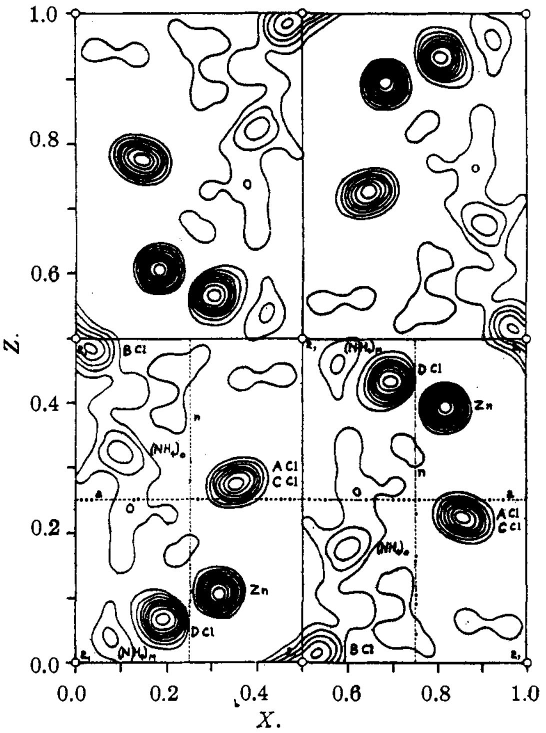

Fig. 4.—$\rho(x, z)$. Fourier projection of electron density on (010).

all twelve ammonium groups. Accordingly the ammonium groups were placed in these cavities and their approximate parameters determined. Structure factors were then calculated for a series of planes using the predicted values of the parameters. Their agreement with the observed F's was for the most part very satisfactory, and was taken as conclusive evidence that the approximate structure had been determined.

The preliminary values of the parameters were revised by preparing two Bragg projections of the electron density, one on (010) and the other on (001). These projections, Figs. 4 and 5, not only served to refine certain of the parameters but they also constitute a clear-cut portrayal of the atomic arrangement in $(NH_4)_3ZnCl_5$. Still further improvement in the agreement between calculated and observed structure factors was obtained by systematically varying one parameter at a time. The final choice of parameters is given in Table I. The possible limits of error are believed to be:

TABLE I

FINAL VALUES OF THE PARAMETERS

Atom or ion	x	y	z
4Zn	0.314	(0.250)	0.107
$4Cl_A$	.377	(.250)	.282
$4Cl_B$	.034	(.250)	.483
$4Cl_C$	.162	(.250)	− .229
$8Cl_D$	.190	.058	.064
$4(NH_4)_m$	.424	(.250)	− .458
$8(NH_4)_o$	.412	.000	− .180

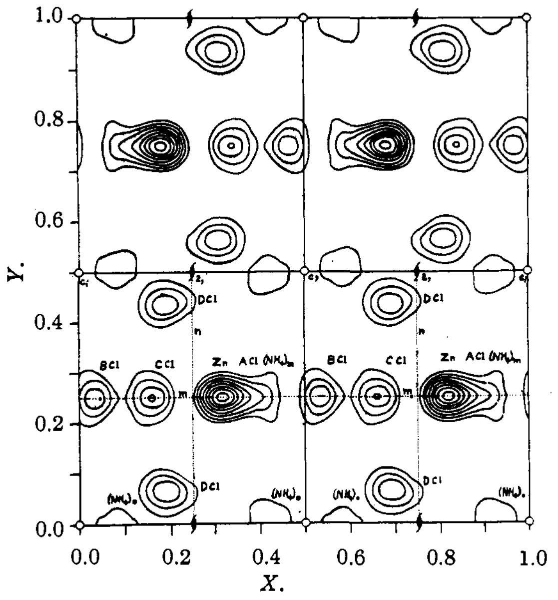

Fig. 5.—$\rho(x, y)$. Fourier projection of electron density on (001).

for Zn, Cl_B, Cl_C, Cl_D, and $(NH_4)_o$ ±0.003; for Cl_A, $(NH_4)_m$ ±0.005.

Using the parameter values in Table I, structure factors were calculated for more than 600 different reflections and compared with the observed values. In the entire list no unsatisfactory agreement was observed. A part[24] of these data is presented in Table II.

In the end, the peaks on the six Patterson-Harker diagrams were completely explained with the exception of the two small peaks, nos. 3 and 8, on $P(xy\frac{1}{2})$, Fig. 2, and the two smallest peaks on $P(0y0)$, all of which are believed to be spurious.

Discussion of the Structure

The atomic arrangement in $(NH_4)_3ZnCl_5$ is best understood by reference to Figs. 6 and 7. Figure 6 shows a packing drawing of the front half of the cell on the (010) face. For the sake of clarity in portraying the positions of the zinc atoms and the orientations of the $ZnCl_4^=$ tetrahedra found in the structure, the atoms on the mirror plane at $y = 0.25$ are shown as open circles, while atoms at the approximate levels $y = 0$ and 0.50 are represented as shaded circles (shaded atoms shown are actually those at $y = 0.50$) with their actual levels indicated by a pair of numerical values. By rotating the diagram through 180° about a perpendicular axis at its center, an accurate representation of the packing in the back half of the cell is obtained. Figure 7 is a pseudo-perspective drawing of the arrangement of part of the atoms in the unit cell. It aims to show important coördination groups in the structure, each kind of group being

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(24) In the interest of the conservation of space data from only 150 planes are presented here as a sample of the kind of agreement observed. Data from the remaining 450 planes are comparable and are available to anyone interested upon request.

TABLE II

STRUCTURE FACTOR DATA[24]

hkl	$F_{\text{Obs.}} \times 21$	$F_{\text{Calcd.}}$	*hkl*	$F_{\text{Obs.}} \times 21$	$F_{\text{Calcd.}}$
200	51	−78.2	048	59	50.3
400	61	−66.6	0.4.10	50	67.6
600	82	109.5	0.4.12	0	−23.9
800	66	−108.9	064	18	−29.4
10.0.0	21	47.5	066	108	89.9
020	108	−163.7	068	43	−43.6
040	177	301.5	0.6.10	27	−40.2
060	168	−216.2	0.6.12	0	24.9
080	80	116.4	082	48	−59.4
0.10.0	126	−185.5	084	0	23.8
0.12.0	56	112.5	086	0	8.4
002	44	39.8	088	88	108.5
004	44	39.9	0.8.10	48	95.8
006	96	−96.4	0.10.2	33	−30.5
008	17	−13.4	0.10.4	0	−21.9
0.0.10	39	35.5	0.10.6	60	77.9
0.0.12	0	−19.1	011	63	−85.3
220	0	−5.5	013	121	−130.5
240	31	−18.3	015	0	−1.8
260	78	65.0	017	54	41.9
2.10.0	66	60.2	019	37	26.6
420	29	31.5	0.1.11	85	−80.3
440	56	−54.0	031	37	21.7
480	32	−42.2	033	0	5.4
620	62	−67.4	035	109	−84.6
640	65	71.2	037	59	−59.7
660	89	−106.8	039	0	20.1
680	20	27.4	0.3.11	103	148.5
820	17	−5.6	051	78	−81.5
840	50	−48.3	053	176	−147.0
860	63	67.6	055	50	−45.7
880	0	17.3	057	32	24.0
210	36	56.3	059	40	43.1
230	87	−128.6	3.2.11	37	−47.5
250	0	3.1	5.2.11	0	12.4
270	52	−68.8	422	63	−65.9
290	49	41.8	622	51	47.9
410	42	−32.7	822	11	10.6
430	101	129.7	224	81	−80.8
450	0	10.2	424	44	25.0
470	96	86.2	624	11	14.3
490	45	−55.0	824	42	−61.9
610	..	..	226	45	−31.4
630	40	−32.0	426	76	−58.8
650	41	−58.9	626	22	8.7
670	31	−11.5	826	0	3.2
690	0	−7.6	228	44	48.4
810	42	−57.4	428	0	−0.2
830	51	65.4	628	61	−66.9
850	47	−49.1	2.2.10	34	48.9
870	37	55.3	6.2.10	35	−47.3
10.3.0	37	44.8	2.2.12	12	−13.7
022	39	−36.4	4.2.12	26	−29.4
024	74	−59.5	141	69	−54.2
028	139	−148.2	341	23	11.1
0.2.10	75	−97.0	541	68	−60.1
044	37	29.1	741	16	14.2
046	59	−41.4	941	21	25.3
242	38	35.4	414	84	75.1
442	89	81.7	614	90	−83.2
642	21	−2.5	814	47	−57.6
143	14	−10.9	115	113	149.2
311	76	99.0	315	0	13.8
511	57	73.3	515	0	−3.9
711	33	−42.3	715	70	54.6
911	59	80.1	915	10	−21.1
212	9	−4.6	216	20	−23.7
412	46	−49.1	416	16	−16.8
612	19	−7.1	616	48	−29.8
812	13	1.2	816	0	−6.8
10.1.2	36	−64.9	117	18	28.2
513	39	25.2	317	15	−20.5
713	51	68.8	517	24	9.4
913	0	2.1	717	52	77.8
214	78	−68.7	917	0	−9.6

outlined by a different kind of line. The *y* coordinates of the atoms are indicated by numbers on the various circles, and the traces of the mirror planes *m* are indicated on the top and bottom of the cell.

The unit cell of $(NH_4)_3ZnCl_5$ contains four tetrahedral $ZnCl_4$ groups. The calculated Zn–Cl distances are 2.23, 2.24, 2.24, and 2.27 Å. Allowing for a probable experimental error of ±0.03 Å. in measuring these distances, the zinc atom can be considered to be equidistant from the four chlorines at the corners of the tetrahedron. The six edges of the tetrahedron vary in length from 3.60 to 3.78 Å., indicating it to be a nearly regular tetrahedron. The average Zn–Cl distance, 2.25 Å., is slightly smaller than the sum of the accepted tetrahedral covalent radii,[24] 2.30 Å. Since the expected interionic distance for four-fold coordination of chlorine about zinc is about 2.35 Å.,[25] it can be concluded that the Zn–Cl bond is largely covalent in character. The average Cl–Cl separation within the tetrahedra is 3.67 Å., a value well in keeping with twice the ionic radius of chlorine, 3.62 Å. The closest approach of a chlorine atom outside a given tetrahedron to the central zinc atom is 4.06 Å., the distance to a Cl_A atom in a neighboring tetrahedron.

The environment of the four remaining chlorine atoms in the cell, Cl_C, is interesting. They are separated from the zinc atoms by distances of 4.44 and 4.83 Å., and each one is surrounded by a distorted octahedron (Fig. 7) of NH_4^+ ions as its nearest neighbors, with Cl_C–NH_4 distances of 3.14 3.35, 3.35, 3.48, 3.48, and 3.68 Å. The average of these distances, 3.41 Å. is slightly larger than the sum of the ionic radii for Cl^- and freely rotating NH_4^+, namely, 3.31 Å. From an examination of Figs. 6 and 7 it is apparent that each Cl_C–NH_4 octahedron shares two faces with neighboring octahedra in the *a* direction, thus forming continuous chains through the lattice. This is not to be interpreted as productive of a strongly bonded structure in the *a* direction because the Cl–NH_4

(25) Reference 18, pp. 347–350.

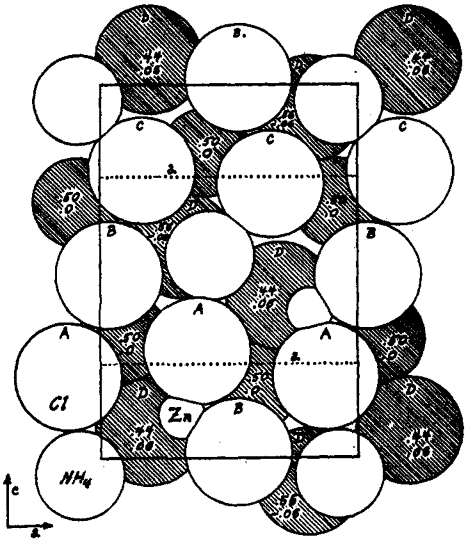

Fig. 6.—Packing drawing of the front half of the cell on the (010) face. Chlorine, ammonium, and zinc are represented by large, medium, and small circles, respectively. Open circles represent atoms lying on the mirror plane at $y = 0.25$, while shaded circles are atoms at the approximate levels $y = 0$ and 0.50.

bond is ionic, non-directional, and weak in magnitude compared with the Zn–Cl bond.

The structure may now be considered from the standpoint of the environment of the ammonium ions. The eight $(NH_4)_O$ groups are surrounded by distorted trigonal prism groupings of six chlorine atoms. One of these is shown in the lower part of Fig. 7 in dotted lines. Three of the chlorines lie on one mirror plane at $y = 0.25$ and the remaining three are on the next one at $y = 0.75$. The average Cl–$(NH_4)_O$ distance within the trigonal prism is 3.44 Å., compared with 3.41 Å. in the Cl_C–NH_4 octahedra. In addition each $(NH_4)_O$ is surrounded by three more chlorine atoms (Cl_D), in positions opposite the side faces of the prism, at a greater average distance, 3.63 Å. Since four of the six chlorine atoms at the corners of the trigonal prism are actually members of $ZnCl_4^=$ tetrahedra, it is seen that the prism does not exist as a distinct entity in the structure.

The environment of the four $(NH_4)_m$ groups is unsymmetrical and not capable of clear-cut portrayal in either Fig. 6 or 7. Each $(NH_4)_m$ group is surrounded by eight chlorine atoms at the corners of an irregular polygon with an average $(NH_4)_m$–Cl distance of 3.32 Å., a value in excellent agreement with 3.31 Å., the sum of the ionic radii. The closest approach of zinc atoms and ammonium ions in the structure is Zn–$(NH_4)_m$ = 3.89 Å.

The stoichiometric composition A_mMX_5 is achieved in $(NH_4)_3ZnCl_5$ by a packing of NH_4^+, tetrahedral $ZnCl_4^=$, and Cl^- ions. This is in marked contrast to the structures of Tl_2AlF_5 and $K_2AlF_5 \cdot H_2O$ in which a similar stoichiometry is

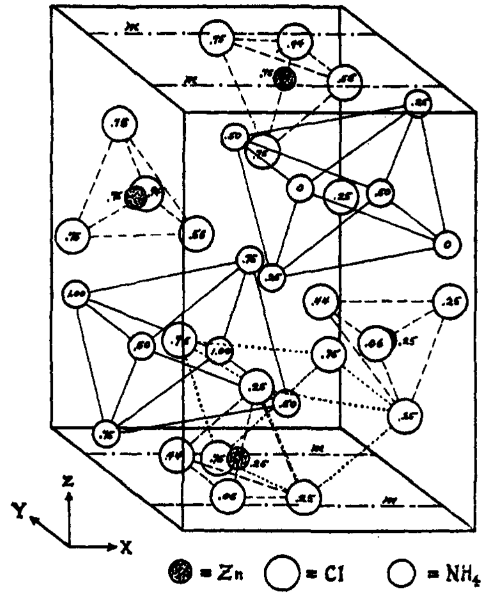

Fig. 7.—A pseudo-perspective drawing of part of the atoms in the cell to show important coördination groups in the structure. The tetrahedral $ZnCl_4$ groups, the octahedral coördination of NH_4 around Cl_C, and the trigonal prismatic arrangement of Cl around $(NH_4)_O$ are clearly shown.

attained through infinite-chain anions of the composition $AlF_5^=$ formed through the sharing of opposite vertices of AlF_6 octahedra. In view of the packing observed in $(NH_4)_3ZnCl_5$, it would appear that more accurate information concerning its chemical nature would be conveyed by writing its formula $(NH_4)_2ZnCl_4 \cdot NH_4Cl$.

Examination of the structure shows that the two kinds of anions, $ZnCl_4^=$ and Cl^-, are bound together by a fairly uniform distribution of NH_4^+ cations, and it may be concluded that the strength of the bonds is approximately the same in all directions through the crystal. This probably explains the absence of a cleavage plane in crystals of $(NH_4)_3ZnCl_5$.

Acknowledgment.—One of the authors (L. A.) wishes to express his gratitude and appreciation to the Graduate School of the University of Minnesota for the Shevlin Fellowship in chemistry under which a large part of this research was done.

Summary

The complete crystal structure of $(NH_4)_3ZnCl_5$ has been determined from Laue and rotating and oscillating crystal photographs by the Patterson–Harker and Bragg–Fourier methods. The crystal is orthorhombic bipyramidal, with $a_0 = 8.74$ Å., $b_0 = 9.84$ Å., and $c_0 = 12.61$ Å. The space group is D_{2h}^{16}-*Pnma*, and the unit cell contains four molecules of the composition $(NH_4)_3ZnCl_5$.

The positions of the atoms are fixed by sixteen parameters (Table I) whose values were obtained

with considerable accuracy. The zinc atoms are surrounded tetrahedrally by chlorine atoms at an average distance of 2.25 Å., and an extra chlorine atom not coördinated with the zinc is present to give the required stoichiometry. These extra chlorine atoms are octahedrally surrounded by ammonium ions at the average distance, 3.41 Å. One kind of ammonium ion is surrounded by a trigonal prism grouping of chlorine atoms at an average distance of 3.44 Å., while the other ammonium groups are surrounded by an irregular polygon of eight chlorine atoms at the average distance of 3.32 Å. The Zn–Cl bonds in the $ZnCl_4^=$ tetrahedra are essentially covalent, while all other bonds in the structure (except N–H) are essentially ionic in nature. The structure is a packing of NH_4^+, $ZnCl_4^=$, and Cl^- ions, and the formula of the compound would best be represented by $(NH_4)_2ZnCl_4\cdot NH_4Cl$.

MINNEAPOLIS MINNESOTA RECEIVED APRIL 7, 1944

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 481]

The Heat Capacity of Carbon Tetrachloride from 15 to 300°K. The Heats of Transition and of Fusion. The Entropy from Thermal Measurements Compared with the Entropy from Molecular Data

BY J. F. G. HICKS, J. G. HOOLEY[1a] AND C. C. STEPHENSON

The calculation of the thermodynamic functions of carbon tetrachloride from molecular data has been the subject of a number of papers.[1b-5] The entropy of carbon tetrachloride calculated from the existing thermal data[6-9] agrees quite well with the theoretical entropy value,[2] but this agreement is somewhat fortuitous because the thermal entropy may be in error by as much as one entropy unit. The thermal data of this paper reduce the uncertainty of the third law entropy value and give an answer which is more reliable than that calculated from molecular data.

Material.—Two samples of carbon tetrachloride were used for the measurements. Both samples were prepared from Merck C. P. material which was distilled three times in a vacuum-jacketed column, the first and last quarter being rejected each time. The second sample was protected from light at all times. Melting-point determinations indicate that both samples contained about 0.02 mole per cent. of liquid-soluble solid-insoluble impurity, although the absence of any marked premelting effect on the heat capacity measurements in the region below the melting point gives a much smaller figure.

The measurements below 265°K. were made with Sample I which weighed 136.86 g. in vacuum. Sample II, which weighed 134.06 g. in vacuum, was used for the other series. The molecular weight of carbon tetrachloride was taken as 153.84.

Method.—The apparatus, method of measurement, and calorimeter have been described in an earlier paper.[10] At the conclusion of the measurements, the thermometer was checked at the melting points of ice and mercury and found to agree with the original calibration to within 0.01°.

The calorie used in this work is defined equal to 4.1833 int. joules. The absolute temperature of the ice-point is taken as 273.19°K.

Melting Point.—The melting point was observed with various percentages of the carbon tetrachloride melted. The results are summarized in Table I. The amount of impurity was calculated from the change observed in the melting point, and the accepted value, 250.3 ± 0.1°K., has been corrected for the effect of this impurity.

TABLE I

MELTING POINT OF CARBON TETRACHLORIDE

	% Melted	Time, hr.	T, °K.
Sample I	12	2	250.111
	12	3	250.094
	25	4.5	250.153
	25	5	250.149
	50	7.5	250.235
	50	8.5	250.234
Sample II	15	3	250.084
	30	4.5	250.148
	30	5.5	250.144
	50	7.5	250.206

Accepted value 250.3 ± 0.1

Transition Temperature.—Determinations of the transition temperature are summarized in Table II.

TABLE II

TRANSITION TEMPERATURE AT 225.35°K.

Trial	% Transformed	Time	T, °K.
I	50	9	225.355
II	30	5	225.356
	50	9	225.346
	50	11	225.353
III	15	5	225.347
	25	13	225.394

Accepted value 225.35 ± 0.03°K.

Melting points and transition temperatures observed by other experimenters are given in Table

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