THE CRYSTAL STRUCTURE OF AMMONIUM HEXACHLOROPLUMBATE [$(NH_4)_2PbCl_6$].

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INTRODUCTION.

Ammonium chloroplumbate is said to form cubic crystals.[1] The crystal structures of the analogous salts—ammonium chloroplatinate,[2] ammonium fluosilicate,[3] and potassium and ammonium chlorostannates[4]—have been studied in detail. If ammonium chloroplumbate is isotropic its atomic arrangement would be expected to resemble that of these other compounds. The present investigation was undertaken to determine whether such structural isomorphism exists and to add to the available information accurate diffraction data upon this salt of lead.

The ammonium chloroplumbate used in this study was made by the method of Friedrich.[4a] An analysis of this preparation gave the following results:[4b]

NH_4	Calc.		7.91	per cent.
	Found	Aver.	7.70	" "
Pb	Calc.		45.44	" "
	Found	Aver.	44.42	" "
Cl	Calc.		46.67	" "
	Found	Aver.	46.84	" "

Although the analytical results are not in close agreement with the calculated percentages, they suffice to identify the substance as $(NH_4)_2PbCl_6$. Their variation from the theoretical amount is doubtless to be ascribed to the slow breakdown of the salt on standing.

The minute crystals forming this preparation appear to be completely isotropic. Since large single specimens were not available, the X-ray diffraction observations have necessarily been limited to making powder photographs.

[1] Groth, P., Chemische Kristallographie, 1, 468 (Leipzig, 1906).
[2] Wyckoff, R. W. G. and Posnjak, E. W., J. Am. Chem. Soc. 43, 2292, 1921.
[3] Bozorth, R. M., J. Am. Chem. Soc., 44, 1066, 1922.
[4] Dickinson, R. G., J. Am. Chem. Soc., 44, 276, 1922.
[4a] Friedrich, Ber. 26, 1434, 1893.
[4b] These analyses were made by Mr. H. A. Lovenberg.

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Two series of powder photographs have been prepared—one of $(NH_4)_2PbCl_6$ alone, and the other of $(NH_4)_2PbCl_6$ mixed with MgO to serve as a standard. The spacings of the diffraction lines of $(NH_4)_2PbCl_6$ found from these photographs are listed in column 1 of Table I; their estimated relative intensities are recorded in column 2. If these lines arise from a crystal having cubic symmetry the squares of the sines of their angles of reflection must stand in the ratio of whole numbers. Within the limit of experimental error this integral ratio is maintained for all of the lines observed from $(NH_4)_2PbCl_6$. The integers arising from these ratios are

TABLE I. Powder Diffraction Data from $(NH_4)_2PbCl_6$.

Spacing	Estimated Intensity	Indices	a_0
5.836A°	8	111(1)	10.11A°
5.081	7	100(2)	10.16
3.611	4	110(2)	10.21
3.070	7	113(1)	10.18
2.548	6	100(4)	10.19
2.341	5	133(1)	10.20
2.257	5	120(2)	10.09
2.070	2	112(2)	10.14
1.950	4	111(3); 115(1)	10.13
1.794	4	110(4)	10.15
(1.702)	5	135(1) 100(6); 122(2)	....
1.597	0.5	130(2)	10.10
1.542	1	335(1)	10.11
1.464	1	111(4)	10.14
(1.412)	3	711(1) 023(2)	....
1.352	0.5	321(2)	10.12
1.315	2	731(1); 553(1)	10.10
1.267	0.5	100(8)	10.14
1.228	2	140(2); 223(2)	10.13
1.163	0.5	157(1)	10.07
1.131	1.5	120(4)	10.12
		Average =	10.14A°

the values of $h^2 + k^2 + l^2$ for the several reflecting planes. The indices assigned to each of the observed reflections through these values of $h^2 + k^2 + l^2$ are stated in column 3 of Table I. Lengths of the edge, a_0, of the unit cube calculated from these spacings and assignments of indices are given in column 4.

An accurate determination of a_0 for $(NH_4)_2PbCl_6$ was made by averaging the data from the comparison photographs. For this purpose reflections with the largest spacings were excluded because of their greater limit of experimental error. Several reflections appear on the photographs either as partially resolved pairs of reflections or were proved to be such composite reflections by the subsequent analysis. These likewise were not employed in the accurate estimate of a_0. The values of a_0 averaged from each of the eight comparison films, after making the exclusions that have been outlined, are stated in Table II. Their average, $a_0 = 10.14$A°, is chosen as the length of the edge of the unit cube of $(NH_4)_2PbCl_6$. For these calculations a_0 for the standard[5] crystal, MgO, is taken to be 4.20_3A°.

No determination of the density of $(NH_4)_2PbCl_6$ appears ever to have been made. The powder data meet the requirements of a fundamental face centered cubic lattice in showing odd order reflections only from planes with all odd indices. This indication of the presence of four molecules in the unit

TABLE II. Average Values of a_0 calculated from Each of Eight Comparison Films.

Film No.	a_0
1	10.11A°
2	10.11
3	10.16
4	10.15
5	10.16
6	10.15
7	10.15
8	10.14
	10.14A°

cube is strengthened by the predominance of the scattering power of the lead atoms in $(NH_4)_2PbCl_6$. This predominance seems to preclude the possibility of an arrangement existing with other than four molecules which, nevertheless, could yield data corresponding sufficiently closely to those of Table I. In order to check this assignment, however, an approximate estimation was made of the density of $(NH_4)_2$-

[5] Wyckoff, R. W. G., this Journal, 10, 107, 1925; Zeit. f. Krist, 62, 529. 1925.

$PbCl_6$. The usual pyknometric procedure was followed and benzene was chosen as the wetting liquid. Only a fraction of a gram of the salt was available. For this reason, and because of the small size of the crystals in this preparation, the resulting density, $\rho = 2.60$, is undoubtedly somewhat too low. Nevertheless the density calculated for four molecules in the unit is the only one which makes a reasonably close approach to this observed density. [ρ (calculated for three molecules) $= 2.16$; ρ (calculated for four molecules) $= 2.89$]. It is thus necessary to conclude that the unit of $(NH_4)_2PbCl_6$, like those of its platinum, tin and silicon analogues, contains four molecules.

The same arguments[6] which limit the probable structures of these other crystals to the following arrangements I and II are clearly applicable to $(NH_4)_2PbCl_6$. These possible atomic groupings[7] are:

I				II			
	Pb atoms :		(4b)		Pb atoms :		(4b)
	N " :		(8e)		N " :		(8e)
	Cl " :		(24a)		Cl " :		(24c)
	H " :		(32a)		H " :		(32a)

A distinction between these two arrangements was drawn for the crystals previously studied by examining their first-order Laue reflections from planes with all odd indices. For the chloroplumbate it must be made by calculating the relative intensities of typical powder reflections according to I and II. Presumably because of the strong absorption in the sample only very qualitative estimates of relative intensity are possible on the photographs. It is thus sufficient to employ the usual semi-empirical formula[8]

$$I \propto (A^2 + B^2) \times \left(\frac{d}{n}\right)^{2.35} \times j \qquad (1)$$

in calculating intensities of powder reflections. Because of the small scattering power of hydrogen its atoms have been neglected in the following calculations. For the members of

[6] Wyckoff, R. W. G. and Posnjak, E. W., op. cit.; Dickinson, R. G., op. cit.

[7] The coördinate designations used here are those employed in Wyckoff, R. W. G., An Analytical Expression of the Results of the Theory of Space Groups (Washington, 1922), p. 103, et seq.

[8] Wyckoff, R. W. G., The Structure of Crystals, p. 201 (New York, 1924).

this isomorphous group thus far investigated the correct arrangement has proved to be I with u for chlorine (or fluorine) not far from one-fourth. When $u = 0.25$ the values of A in expression (1) reduce to the following (B = 0):

If n is odd:
  If h, k and l are all odd
    $A = 4\overline{Pb}$
If n is even:
  If h, k and l are two odd and one even
    If $n = 2$, 6, etc.
      $A = 4\overline{Pb} + 8\overline{N} - 8\overline{Cl}$
    If $n = 4$, 8, etc.
      $A = 4\overline{Pb} + 8\overline{N} + 24\overline{Cl}$
  If h, k and l are two even and one odd
    If $n = 2$, 6, etc.
      $A = 4\overline{Pb} - 8\overline{N} + 8\overline{Cl}$
    If $n = 4$, 8, etc.
      $A = 4\overline{Pb} + 8\overline{N} + 24\overline{Cl}$
  If h, k and l are all odd
    If $n = 2$, 6, etc.
      $A = 4\overline{Pb} - 8\overline{N} - 24\overline{Cl}$
    If $n = 4$, 8, etc.
      $A = 4\overline{Pb} + 8\overline{N} + 24\overline{Cl}$.

The intensities calculated for all possible reflections with $h^2 + k^2 + l^2$ less than the maximum measured on the film ($\Sigma h^2 = 84$) are compared with the observed estimated intensities in Fig. 1. Except for the too great observed intensity of the pair 111(3); 115(1) the agreement is satisfactory. First order reflections from structure II have the same structure factors as those from structure I when $u = 0.25$. Second order reflections, however, are different from these two arrangements. For grouping II, A has the following values (B = 0):

If $n = 2$
  If h, k and l are two odd and one even
    $A = 4\overline{Pb} + 8\overline{N} - 8\overline{Cl}$
  If h, k and l are two even and one odd
    $A = 4\overline{Pb} - 8\overline{N} - 8\overline{Cl}$
  If h, k and l are all odd
    $A = 4\overline{Pb} - 8\overline{N} + 24\overline{Cl}$

The relative intensities of the simplest possible reflections as calculated from these A terms are compared in Table III with observations and with the corresponding intensities calculated for arrangement I. It is obvious that grouping II is not possible for $(NH_4)_2PbCl_6$.

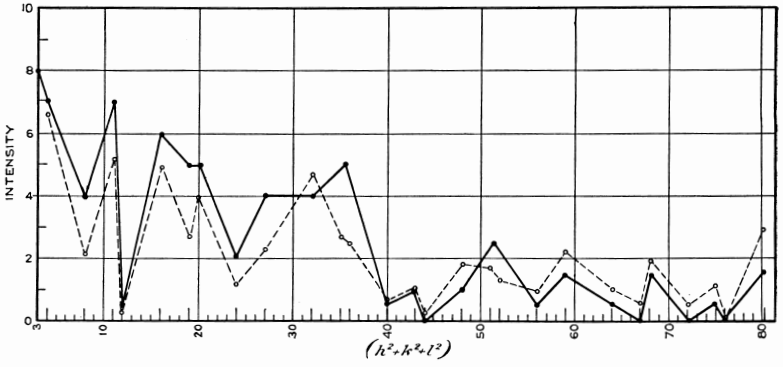

Fig. 1.—A plot showing the extent of the agreement between observed intensities and those calculated for every reflection less than $\Sigma h^2 = 84$ possible for arrangement I with $u = 0.25$. Observed intensities are connected by full, calculated intensities by the dotted, lines.

A better fit between the observed intensity of 111(3); 115(1) and the intensity calculated from structure I is naturally to be sought by assuming values of u near to, but not exactly equal to, one-fourth. The value of A for odd order reflections from I is (B = 0):

$$A = 4Pb + 8Cl\{\cos 2\pi nhu + \cos 2\pi nku + \cos 2\pi nlu\}.$$

Intensities calculated for values of u between 0.20 and 0.25

TABLE III. A Comparison between the Observed Intensities of Reflection of Simple Powder Lines and the Intensities calculated for Arrangements I and II.

Indices	Observed Intensity	Calculated Intensity For I	For II
111(1)	8	8	8
100(2)	7	7	0.7
110(2)	4	2.2	2.2
113(1)	7	5.2	5.2
111(2)	0.5	0.3	6.7
100(4)	6	4.9	4.9
133(1)	5	2.65	2.65
120(2)	5	4.0	0.4

using this expression are listed in Table IV. Since in the immediate neighborhood of $u = 0.25$ even order reflections suffer much slower changes in intensity with changes in u, it may be concluded that arrangement I with u for chlorine approximately equal to 0.23 explains well the general intensity relations and must be taken as the correct crystal structure of $(NH_4)_2PbCl_6$.

Like the other salts isomorphous with it the structure of $(NH_4)_2PbCl_6$ is most simply pictured as a modification of the CaF_2 arrangement. From this standpoint NH_4 groups replace fluorine atoms and $PbCl_6$ groups occupy the calcium positions. If $u = 0.23$ the lead-chlorine distance is 2.33A°; if $u = 0.25$ it is 2.53A°.

TABLE IV. Calculated Intensities of the Composite Line 111(3); 115(1) for Different Values of u.

u	Intensity For 111(3)	Intensity For 115(1)	Total
0.20	0	5.07	5.07
0.21	0.02	4.65	4.67
0.22	0.06	4.04	4.10
0.23	0.18	3.30	3.48
0.24	0.36	2.53	2.89
0.25	0.60	1.81	2.41

SUMMARY.

From a study of powder photographs of $(NH_4)_2PbCl_6$ it is shown that this compound has the same type of atomic arrangement as $(NH_4)_2PtCl_6$—Pb at 4b, N at 8e, Cl at 24a, and H presumably at 32a. The assumption that u for chlorine is one-fourth leads to a series of calculated intensities that are in generally satisfactory agreement with observation. An even better fit is, however, obtained by assuming that u is slightly less than 0.25. The length of the edge of the unit cube containing four molecules is 10.14A°. The density calculated from this structure is 2.89.

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