

Since the theory of solubility as here developed, showing the dependence of solubility on the solvent, is really nothing but a theory of solutions, the proper way of attacking the problem, when its complicated nature has been thus manifested, will be a more detailed systematic examination of single cases of equilibrium, rather than the broad consideration of an elaborate mass of material, such as is given in the present paper. The knowledge now available as to the general behavior of salts as saturating substances in salt solution is, however, of great value in such a closer study of single cases. The conclusive results achievable from experiments in this direction will be the subject matter of the next article in this series.

COPENHAGEN, DENMARK.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON.]

## THE CRYSTAL STRUCTURE OF AMMONIUM CHLOROPLATINATE.

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**Introduction.**—This study of the crystal structure of ammonium chloroplatinate is intended primarily to furnish an illustration of the application of that method of studying the structures of crystals which arises from the use of the theory of space groups.<sup>1</sup> At the same time it will show the possibilities and more especially the present limitations in the study of any but the very simplest of structures.

**Outline of the Determination.**—The study of the arrangement of the atoms in this crystal will be carried out through the following main steps: (1) a consideration of the X-ray reflection spectrum from some important crystal face, in order to determine the absolute dimensions of the unit cell and to indicate the number of chemical molecules to be associated with it; (2) a description, with the aid of the results of (1), the crystallographic data, and the theory of space groups, of all of the ways in which it is possible for the atoms of ammonium chloroplatinate to be arranged; (3) the obtaining of diffraction data suitable for distinguishing between these various possible structures and the determination of the correct one to represent the arrangement of the atoms within the crystals of this salt.

**The Specimens.**—The crystals that were employed for this investigation are clear octahedrons 2 to 3 mm. on their largest diameters. They were sufficiently small so that the Laue photographs, to be described later, were prepared by passing the X-rays through the entire crystal without

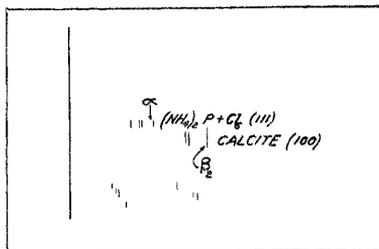
<sup>1</sup> P. Niggli, "Geometrische Krystallographie des Discontinuums," Leipzig, 1919; Ralph W. G. Wyckoff, *Am. J. Sci.*, 1, 127 (1921) and earlier papers.

first cutting a thin section. Owing to the fact that the crystals were smaller than the pin-hole beam of X-rays, the spots of these photographs were no longer elliptical but bore a shape that was conditioned by the shape of the crystal. The reflection spectra were obtained from faces that were not more than 2 mm. on a side. It is of interest to note that satisfactory data for the determination of the structure of a crystal at least in some instances can be obtained from such small crystals.

**The Reflection Spectrum and the Number of Chemical Molecules within the Unit Cell.**—A comparison X-ray spectrum from the cleavage

(100) face of calcite and from the octahedral (111) face of ammonium chloroplatinate was prepared in the usual manner by mounting the two crystals one above the other upon the rotating table of an X-ray spectrometer. The radiation was taken from a tungsten tube. The drawing of Fig. 1 shows the spectra that were thus obtained.<sup>2</sup>

Knowing the wave lengths of the reflected X-rays and also the spacing of calcite against the (100) plane, it is possible from the measurement of its spectrum



to eliminate errors in the spectrograph used by calculating in the following manner the distance from the crystal to the photographic plate.

Fig. 1.—A tracing of the comparison spectrum of the L-series lines of tungsten from the (100) face of calcite and the (111) face of ammonium chloroplatinate.

TABLE I.  
THE CALCITE SPECTRUM FROM THE (100) FACE.  
 $d/n = 3.0281 \times 10^{-8}$  cm.<sup>4</sup>

Line.	Wave length $\times 10^{-8}$ cm.	Distance (a) (on plate). Cm.	$\sin \theta$ .	$\tan \theta$ .	Distance (b) (crystal-plate). Cm.
$\beta_2$	1.242	4.34	0.2048	0.4377	9.91 <sup>5</sup>
$\gamma_1$	1.095	3.78	0.1807	0.3804	9.93 <sup>7</sup>
$\gamma_2, \gamma_3$	1.061	3.64	0.1751	0.3674	9.90 <sup>7</sup>
					9.91 <sup>7</sup>

By rearrangement of the equation  $n\lambda = 2d \sin \theta$ ,<sup>3</sup> it is seen that  $\sin \theta = n\lambda/2d$ ; furthermore  $\tan 2\theta$  gives the ratio of (a) the distance of a spectrum line from the central image upon the photographic plate and (b) the dis-

<sup>2</sup> Partly because of the comparatively long time that was required to obtain a satisfactory spectrum, the resulting photograph was so blackened by scattered radiation that its reproduction would not have been satisfactory. The drawing of Fig. 1 is made from a tracing of this spectrum.

<sup>3</sup> In this equation as usual  $n =$  the order of the reflection,  $\lambda =$  the wave length of the reflected X-rays,  $d =$  the spacing between like reflecting planes, and  $\theta$  the angle of the reflection.

<sup>4</sup> W. Duane, Nat. Research Council, *Bull.*, 1, 383 (1920).

tance from the crystal to the photographic plate. This latter distance ( $b$ ) can thus be calculated for this particular spectrum from the spectrum of calcite (Table I, p. 2293).

Since  $d/n = /2\lambda \sin \theta$ , the reflection from the (111) face of ammonium chloroplatinate can be calculated in a similar manner (Table II).

TABLE II.  
THE AMMONIUM CHLOROPLATINATE SPECTRUM FROM THE (111) FACE.

Line.	Wave length $\times 10^{-8}$ cm.	Distance ( $a$ ) (on plate). Cm.	$\tan 2\theta$ .	$\sin \theta$ .	$(d/n)_{111}$ . Cm.
$\alpha_1$	1.473	2.63	0.2652	0.1293	$5.690 \times 10^{-8}$
$\beta_1$	1.278	2.28	0.2299	0.1127	5.668
$\beta_2$	1.242	2.20	0.2218	0.1089	5.696
$\gamma_1$	1.095	1.94	0.1956	0.0964	5.678
					$5.683 \times 10^{-8}$

The number of chemical molecules associated with the unit cell of a cubic crystal, or rather, since the order of the observed reflection cannot be told with any degree of assurance, the ratio of the number of molecules to the cube of the order of the reflection,  $m/n^3$ , can be obtained from the following expression,

$$m/n^3 = \frac{(d/n)_{100}^3 \times \rho}{M}, \quad (1)$$

where  $M$ , the mass of a chemical molecule of the salt is equal to its molecular weight multiplied by the weight of an atom whose atomic weight is unity (roughly equal to the weight of a single atom of hydrogen =  $1.64 \times 10^{-24}$  g.), and  $\rho$  = the density of the crystal. The spacing of any plane ( $hkl$ ) is related to the spacing of the cube (100) plane of a cubic crystal by the following equation,

$$d_{hkl} = \frac{d_{100}}{\sqrt{h^2 + k^2 + l^2}}. \quad (2)$$

Substituting in Equation 1 the value of  $d_{100}$  obtained by transposing Equation 2, the value of  $m/n^3$  for a cubic crystal can be calculated from the measurement of the reflection spectrum from any crystal face through

$$m/n^3 = \frac{(d/n)_{hkl}^3 \times (h^2 + k^2 + l^2)^{3/2} \times \rho}{M}. \quad (3)$$

The values of the density of ammonium chloroplatinate which have been recorded are sufficiently discordant so that a redetermination seemed desirable. Using a pycnometer method<sup>5</sup> the density at 30° against water at 4° was found to be 3.065. The substitution of the appropriate values for ammonium chloroplatinate in Equation 3 gives for  $m/n^3$  the value of 4.021. If this value is considered in the light of a table giving values for

<sup>5</sup> J. Johnston and L. H. Adams, THIS JOURNAL, 34, 566 (1912).

$m/n^3$  for all possible values of  $m$  and  $n$ , it becomes evident that in this case either<sup>6</sup>  $m=4$  and  $n=1$ , or  $m=32$  and  $n=2$ .

If  $n=1$  then the application of Expression 2 to the spacing calculated for the (111) planes gives a length of the side of the unit cube of  $d_{100} = d_{111} \times \sqrt{3} = 9.843 \times 10^{-8}$  cm. If, however,  $n=2$ , this dimension is twice as great, namely,  $19.686 \times 10^{-8}$  cm.

**The Possible Arrangements for the Atoms in Ammonium Chloroplatinate.**—From a knowledge of all of the special cases of the space groups it is possible to write down all of the ways in which the atoms of ammonium chloroplatinate can be arranged within the unit cube, if the class of symmetry to which the crystal should be assigned is known.

Etch figures upon different faces of crystals of this salt have been studied,<sup>7</sup> so that from the standpoint of the crystallographer its *symmetry* is quite definitely established as that of the normal, or holohedral, class of the cubic system. Ammonium chloroplatinate must then be assigned to one of the 10 space groups,  $O_h^{1-10}$ , which possess this symmetry.

Two cases arise, one if it is assumed that  $m=4$  and  $n=1$ , the other if it is assumed that  $m=32$  and  $n=2$ . They will be discussed separately as follows.<sup>8</sup>

*I. Assuming that  $m=4$ ,  $n=1$ .* In Table III are stated the number and nature of the special cases of each of the 10 space groups  $O_h^{1-10}$ . The number outside of the parenthesis is the number of special cases having a particular number of equivalent positions (for like atoms) within the unit cell; the number in parenthesis is the number of variable parameters possessed by these arrangements.

Since ammonium chloroplatinate has the formula  $(NH_4)_2PtCl_6$  and since it is assumed here that 4 chemical molecules are to be contained within the unit cube, this cell must contain 4 platinum atoms, 8 nitrogen atoms, 24 chlorine atoms and 32 hydrogen atoms. An inspection of Table III shows that there are but two ways of arranging the 4 platinum atoms within the unit; (1) 3 of them must be alike and different from the fourth, both chemically and crystallographically; or (2) all 4 must be alike. If the 4 platinum atoms are not all alike (1), then the positions of the atoms within the unit cube must be those of special cases of the space group  $O_h^1$ ; otherwise (2) they must be assigned to either space group  $O_h^4$  or space group  $O_h^5$ . There is every reason to believe that the 4 platinum atoms are chemically, and hence also crystallographically, all alike (2). For the sake of completeness, however, both possibilities will be listed at this point. All of the special cases of these three space groups,  $O_h^1$ ,  $O_h^4$  and

<sup>6</sup> Ralph W. G. Wyckoff, *Am. J. Sci.*, **1**, 138 (1921).

<sup>7</sup> A. Ries, *Z. Kryst. Min.*, **36**, 321 (1902).

<sup>8</sup> The data for this discussion are taken from unpublished tables giving all of the special cases of the space groups.

TABLE III.  
THE SPECIAL CASES OF THE CUBIC HOLOHEDRAL SPACE GROUPS.

No. of equivalent positions.	Space group.				No. of equivalent positions.	Space group.		
	1. O <sub>h</sub> .	2. O <sub>h</sub> .	3. O <sub>h</sub> .	4. O <sub>h</sub> .		5. O <sub>h</sub> .	6. O <sub>h</sub> .	7. O <sub>h</sub> .
1	2(0)	....	....	....	1	....	....	....
2	....	1(0)	1(0)	1(0)	2	....	....	....
3	2(0)	....	....	....	3	....	....	....
4	....	....	....	2(0)	4	2(0)	....	....
6	2(1)	1(0)	3(0)	1(0)	6	....	....	....
8	1(1)	1(0)	1(0)	1(1)	8	1(0)	2(0)	2(0)
12	3(1)	1(0);1(1)	3(1)	1(0);1(1)	12	....	....	....
16	....	1(1)	1(1)	....	16	....	....	2(0)
24	3(2)	2(1)	1(1);1(2)	2(1);1(2)	24	1(0);1(1)	2(0)	....
32	....	....	....	....	32	1(1)	....	1(1)
48	1(3)	1(3)	1(3)	1(3)	48	3(1)	2(1)	2(1)
64	....	....	....	....	64	....	1(1)	....
96	....	....	....	....	96	2(2)	1(1);1(2)	1(1);1(2)
192	....	....	....	....	192	1(3)	1(3)	1(3)

No. of equivalent positions.	Space Group.		
	8. O <sub>h</sub> .	9. O <sub>h</sub> .	10. O <sub>h</sub> .
1	....	....	....
2	....	1(0)	....
3	....	....	....
4	....	....	....
6	....	1(0)	....
8	....	1(0)	....
12	....	1(0); 1(1)	....
16	1(0)	1(1)	2(0)
24	....	2(1)	2(0)
32	2(0)	....	1(1)
48	1(0)	1(1); 2(2)	2(1)
64	1(1)	....	....
96	2(1)	1(3)	1(3)
192	1(3)	....	....

O<sub>h</sub><sup>5</sup> (through 32 equivalent positions, the maximum number of like atoms possible within the unit cell) are as follows.

Space Group O<sub>h</sub><sup>1</sup>.

One equivalent position

1a. 000.

1b.  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ .

Three equivalent positions

3a.  $\frac{1}{2}\frac{1}{2}0$ ;  $\frac{1}{2}0\frac{1}{2}$ ;  $0\frac{1}{2}\frac{1}{2}$ .

3b.  $\frac{1}{2}00$ ;  $0\frac{1}{2}0$ ;  $00\frac{1}{2}$ .

Six equivalent positions

6a. u00; 0u0; 00u;  $\bar{u}00$ ;  $0\bar{u}0$ ;  $00\bar{u}$ .

6d.  $u\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}u\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}u$ ;  $\bar{u}\frac{1}{2}\frac{1}{2}$ ;  $\frac{1}{2}\frac{1}{2}\bar{u}$ ;  $\frac{1}{2}\bar{u}\frac{1}{2}$ .

*Eight equivalent positions*8c.  $uuu; u\bar{u}\bar{u}; \bar{u}u\bar{u}; \bar{u}\bar{u}u; \bar{u}\bar{u}\bar{u}; \bar{u}u; u\bar{u}; u\bar{u}\bar{u}$ .*Twelve equivalent positions*12f.  $u0\frac{1}{2}; \bar{u}0\frac{1}{2}; u\frac{1}{2}0; \bar{u}\frac{1}{2}0; \frac{1}{2}u0; \frac{1}{2}\bar{u}0;$  $0u\frac{1}{2}; 0\bar{u}\frac{1}{2}; 0\frac{1}{2}u; 0\frac{1}{2}\bar{u}; \frac{1}{2}0u; \frac{1}{2}0\bar{u}$ .12m.  $u\bar{u}0; u\bar{u}0; \bar{u}\bar{u}0; \bar{u}\bar{u}0; 0u\bar{u}; 0u\bar{u};$  $0\bar{u}\bar{u}; 0\bar{u}\bar{u}; \bar{u}0u; u0\bar{u}; \bar{u}0\bar{u}; u0\bar{u}$ .12n.  $u\bar{u}\frac{1}{2}; u\bar{u}\frac{1}{2}; \bar{u}\bar{u}\frac{1}{2}; \bar{u}\bar{u}\frac{1}{2}; \frac{1}{2}u\bar{u}; \frac{1}{2}u\bar{u};$  $\frac{1}{2}\bar{u}\bar{u}; \frac{1}{2}\bar{u}\bar{u}; \bar{u}\frac{1}{2}u; u\frac{1}{2}\bar{u}; \bar{u}\frac{1}{2}\bar{u}; u\frac{1}{2}\bar{u}$ .*Twenty-four equivalent positions*24o.  $0uv; 0\bar{u}\bar{v}; 0u\bar{v}; 0\bar{u}v; v0u; \bar{v}0\bar{u};$  $\bar{v}0u; v0\bar{u}; uv0; \bar{u}\bar{v}0; u\bar{v}0; \bar{u}v0;$  $u0v; \bar{u}0\bar{v}; u0\bar{v}; \bar{u}0v; 0vu; 0\bar{v}\bar{u};$  $0\bar{v}u; 0v\bar{u}; vu0; \bar{v}\bar{u}0; \bar{v}u0; v\bar{u}0$ .24p.  $\frac{1}{2}uv; \frac{1}{2}\bar{u}\bar{v}; \frac{1}{2}u\bar{v}; \frac{1}{2}\bar{u}v; v\frac{1}{2}u; \bar{v}\frac{1}{2}\bar{u};$  $\bar{v}\frac{1}{2}u; v\frac{1}{2}\bar{u}; uv\frac{1}{2}; \bar{u}\bar{v}\frac{1}{2}; u\bar{v}\frac{1}{2}; \bar{u}v\frac{1}{2};$  $u\frac{1}{2}v; \bar{u}\frac{1}{2}\bar{v}; u\frac{1}{2}\bar{v}; \bar{u}\frac{1}{2}v; \frac{1}{2}vu; \frac{1}{2}\bar{v}\bar{u};$  $\frac{1}{2}\bar{v}u; \frac{1}{2}v\bar{u}; vu\frac{1}{2}; \bar{v}\bar{u}\frac{1}{2}; \bar{v}u\frac{1}{2}; v\bar{u}\frac{1}{2}$ .24q.  $uuv; u\bar{u}\bar{v}; \bar{u}u\bar{v}; \bar{u}\bar{u}v; vu\bar{u}; \bar{v}u\bar{u};$  $\bar{v}\bar{u}u; v\bar{u}\bar{u}; uvu; \bar{u}\bar{v}u; u\bar{v}\bar{u}; \bar{u}v\bar{u};$  $\bar{u}\bar{u}\bar{v}; \bar{u}\bar{u}v; u\bar{u}\bar{v}; u\bar{u}v; \bar{v}\bar{u}\bar{u}; \bar{v}\bar{u}u;$  $vu\bar{u}; \bar{v}u\bar{u}; \bar{u}\bar{v}\bar{u}; u\bar{v}\bar{u}; \bar{u}\bar{v}u; u\bar{v}u$ .

## Space Group C

*Two equivalent positions*2a.  $000; \frac{1}{2}\frac{1}{2}\frac{1}{2}$ .*Four equivalent positions*4d.  $\frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}$ .4e.  $\frac{3}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}$ .*Six equivalent positions*6e.  $0\frac{1}{2}0; 00\frac{1}{2}; \frac{1}{2}00; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2}$ .*Eight equivalent positions*8d.  $uuu; \bar{u}\bar{u}\bar{u}; \frac{1}{2}-u, \frac{1}{2}-u, \frac{1}{2}-u; u+$  $u\bar{u}\bar{u}; \bar{u}\bar{u}u; \frac{1}{2}-u, u+\frac{1}{2}, u+\frac{1}{2}; u+$ *Twelve equivalent positions*12h.  $\frac{1}{2}0\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}\frac{1}{2}0;$  $\frac{1}{2}\frac{1}{2}0; \frac{1}{2}\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}0\frac{1}{2}$ .12a.  $u00; \bar{u}00; 0u0; u+\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}-u, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, u+\frac{1}{2}, \frac{1}{2};$  $0\bar{u}0; 00u; 00\bar{u}; \frac{1}{2}, \frac{1}{2}-u, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, u+\frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}-u$ .*Twenty-four equivalent positions*24f.  $u0\frac{1}{2}; u\frac{1}{2}0; \frac{1}{2}u0; u+\frac{1}{2}, \frac{1}{2}, 0; u+\frac{1}{2}, 0, \frac{1}{2}; 0, u+\frac{1}{2}, \frac{1}{2};$  $0u\frac{1}{2}; 0\frac{1}{2}u; \frac{1}{2}0u; \frac{1}{2}, u+\frac{1}{2}, 0; \frac{1}{2}, 0, u+\frac{1}{2}; 0, \frac{1}{2}, u+\frac{1}{2};$  $\bar{u}0\frac{1}{2}; \bar{u}\frac{1}{2}0; \frac{1}{2}\bar{u}0; \frac{1}{2}-u, \frac{1}{2}, 0; \frac{1}{2}-u, 0, \frac{1}{2}; 0, \frac{1}{2}-u, \frac{1}{2};$  $0\bar{u}\frac{1}{2}; 0\frac{1}{2}\bar{u}; \frac{1}{2}0\bar{u}; \frac{1}{2}, \frac{1}{2}-u, 0; \frac{1}{2}, 0, \frac{1}{2}-u; 0, \frac{1}{2}, \frac{1}{2}-u$ .24t.  $u, \frac{1}{2}-u, \frac{1}{2}; u, u+\frac{1}{2}, \frac{1}{2}; \bar{u}, \frac{1}{2}-u, \frac{1}{2}; \bar{u}, u+\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, u, \frac{1}{2}-u; \frac{1}{2}, u, u+\frac{1}{2};$  $\frac{1}{2}, \bar{u}, \frac{1}{2}-u; \frac{1}{2}, \bar{u}, u+\frac{1}{2}; \frac{1}{2}-u, \frac{1}{2}, u; u+\frac{1}{2}, \frac{1}{2}, u; \frac{1}{2}-u, \frac{1}{2}, \bar{u}; u+\frac{1}{2}, \frac{1}{2}, \bar{u};$  $\frac{1}{2}-u, u, \frac{1}{2}; u+\frac{1}{2}, u, \frac{1}{2}; \frac{1}{2}-u, \bar{u}, \frac{1}{2}; u+\frac{1}{2}, \bar{u}, \frac{1}{2}; u, \frac{1}{2}, \frac{1}{2}-u; u, \frac{1}{2}, u+\frac{1}{2};$  $\bar{u}, \frac{1}{2}, \frac{1}{2}-u; \bar{u}, \frac{1}{2}, u+\frac{1}{2}; \frac{1}{2}, \frac{1}{2}-u, u; \frac{1}{2}, u+\frac{1}{2}, u; \frac{1}{2}, \frac{1}{2}-u, \bar{u}; \frac{1}{2}, u+\frac{1}{2}, \bar{u}$ .24u.  $uuv; u\bar{u}\bar{v}; \bar{u}u\bar{v}; \frac{1}{2}-u, \frac{1}{2}-u, \frac{1}{2}-v; \frac{1}{2}-u, u+\frac{1}{2}, v+\frac{1}{2}; u+\frac{1}{2}, \frac{1}{2}-u, v+\frac{1}{2};$  $\bar{u}\bar{u}v; vu\bar{u}; \bar{v}u\bar{u}; u+\frac{1}{2}, u+\frac{1}{2}, \frac{1}{2}-v; \frac{1}{2}-v, \frac{1}{2}-u, \frac{1}{2}-u; v+\frac{1}{2}, \frac{1}{2}-u, u+\frac{1}{2};$  $\bar{v}\bar{u}u; v\bar{u}\bar{u}; uvu; v+\frac{1}{2}, u+\frac{1}{2}, \frac{1}{2}-u; \frac{1}{2}-v, u+\frac{1}{2}, u+\frac{1}{2}; \frac{1}{2}-u, \frac{1}{2}-v, \frac{1}{2}-u;$  $\bar{u}\bar{u}u; u\bar{v}\bar{u}; \bar{u}v\bar{u}; u+\frac{1}{2}, v+\frac{1}{2}, \frac{1}{2}-u; \frac{1}{2}-u, v+\frac{1}{2}, u+\frac{1}{2}; u+\frac{1}{2}, \frac{1}{2}-v, u+\frac{1}{2}$ .

Space Group  $O_h^5$ .

## Four equivalent positions

4b.  $000; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}$ .

4c.  $\frac{1}{2}\frac{1}{2}\frac{1}{2}; 00\frac{1}{2}; 0\frac{1}{2}0; \frac{1}{2}00$ .

## Eight equivalent positions

8e.  $\frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}; \frac{1}{4}\frac{3}{4}\frac{1}{4}; \frac{3}{4}\frac{1}{4}\frac{1}{4}; \frac{3}{4}\frac{3}{4}\frac{3}{4}$ .

## Twenty-four equivalent positions

24c.  $\frac{1}{4}\frac{1}{4}0; \frac{1}{4}\frac{3}{4}0; \frac{3}{4}\frac{1}{4}0; \frac{3}{4}\frac{3}{4}0; 0\frac{1}{4}\frac{1}{4}; 0\frac{1}{4}\frac{3}{4}; 0\frac{3}{4}\frac{1}{4}; 0\frac{3}{4}\frac{3}{4};$   
 $\frac{1}{4}0\frac{1}{4}; \frac{1}{4}0\frac{3}{4}; \frac{3}{4}0\frac{1}{4}; \frac{3}{4}0\frac{3}{4}; \frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}; \frac{1}{4}\frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4};$   
 $\frac{3}{4}\frac{1}{4}\frac{1}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}; \frac{3}{4}\frac{3}{4}\frac{3}{4}; \frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}; \frac{1}{4}\frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4};$

24a.  $u00; \bar{u}00; 0u0; u+\frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}-u, \frac{1}{2}, 0; \frac{1}{2}, u+\frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}-u, 0; \frac{1}{2}\frac{1}{2}u;$   
 $0\bar{u}0; 00u; 00\bar{u}; u+\frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}-u, 0, \frac{1}{2}; \frac{1}{2}, 0, u+\frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}-u; \frac{1}{2}\frac{1}{2}\bar{u};$   
 $\frac{1}{2}u\frac{1}{2}; \frac{1}{2}\bar{u}\frac{1}{2}; u\frac{1}{2}\frac{1}{2}; 0, u+\frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2}-u, \frac{1}{2}; 0, \frac{1}{2}, u+\frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}-u; \bar{u}\frac{1}{2}\frac{1}{2}$ .

## Thirty-two equivalent positions

32a.  $uuu; u+\frac{1}{2}, u+\frac{1}{2}, u; u+\frac{1}{2}, u, u+\frac{1}{2}; u, u+\frac{1}{2}, u+\frac{1}{2};$   
 $u\bar{u}\bar{u}; u+\frac{1}{2}, \frac{1}{2}-u, \bar{u}; u+\frac{1}{2}, \bar{u}, \frac{1}{2}-u; u, \frac{1}{2}-u, \frac{1}{2}-u;$   
 $\bar{u}u\bar{u}; \frac{1}{2}-u, u+\frac{1}{2}, \bar{u}; \frac{1}{2}-u, u, \frac{1}{2}-u; \bar{u}, u+\frac{1}{2}, \frac{1}{2}-u;$   
 $\bar{u}\bar{u}\bar{u}; \frac{1}{2}-u, \frac{1}{2}-u, \bar{u}; \frac{1}{2}-u, \bar{u}, \frac{1}{2}-u; \bar{u}, \frac{1}{2}-u, \frac{1}{2}-u;$   
 $\bar{u}uu; \frac{1}{2}-u, u+\frac{1}{2}, u; \frac{1}{2}-u, u, u+\frac{1}{2}; \bar{u}, u+\frac{1}{2}, u+\frac{1}{2};$   
 $u\bar{u}u; u+\frac{1}{2}, \frac{1}{2}-u, u; u+\frac{1}{2}, \bar{u}, u+\frac{1}{2}; u, \frac{1}{2}-u, u+\frac{1}{2};$   
 $uu\bar{u}; u+\frac{1}{2}, u+\frac{1}{2}, \bar{u}; u+\frac{1}{2}, u, \frac{1}{2}-u; u, u+\frac{1}{2}, \frac{1}{2}-u.$

If 3 of the platinum atoms are alike and different from the fourth platinum atom, then it would be anticipated from the chemical composition of the salt that 6 of the ammonium groups and 18 of the chlorine atoms would be alike but different in some manner from, respectively, the other 2 ammonium groups and the other 6 chlorine atoms (which would be alike among themselves). The space group  $O_h^1$  has no special case having 18 equivalent positions within the unit. Furthermore, suitable special cases do not exist for assuming, for instance, that all of the hydrogen atoms in an ammonium group are not alike or that some of the chlorine atoms about the platinum atoms are different from others, while still maintaining a "three group alike and one group different" arrangement to correspond with the platinum atoms. As a consequence any arrangement of the atoms of ammonium chloroplatinate based upon this space group  $O_h^1$  seems thoroughly improbable from the standpoint of its chemistry. Considered, however, solely as a geometrical problem there are ways of arranging the requisite number of atoms within the unit cell. They are as follows. Possible arrangement (a): *platinum* atoms, 1a or 1b, and 3a or 3b; *chlorine* atoms, 2 of the arrangements having 12 equivalent positions, or 3 sets of the 8 equivalent positions obtained by assigning 3 different values to  $u$ , or 4 sets of 6 equivalent positions obtained in a similar manner; *nitrogen* atoms, 8 equivalent positions obtained by assigning some value to  $u$  of 8c; *hydrogen* atoms, 4 sets of 8 equivalent positions obtained by assigning 4 different values to the  $u$  of 8c, or 2 sets of the 12 equivalent positions and one of the 8 equivalent positions, or 4 different sets of 6 equivalent positions and one of 8 equivalent positions, etc.

It has already been pointed out that if all 4 of the platinum atoms are alike the arrangement of the atoms must be that of either  $O_h^4$  or of  $O_h^5$ . There is every reason to believe that all 4 of the hydrogen atoms in the ammonium radical are chemically identical.<sup>9</sup> If this is correct then these hydrogen atoms by the very definition of their likeness have neighboring atoms arranged in the same way about each. Since in neither of these space groups are there more than 2 special cases having 4 equivalent positions within the unit and since one of these two special cases must be taken up by the platinum atoms, it follows that all 8 of the nitrogen atoms must be alike. Then if the 4 hydrogen atoms of the ammonium group are taken as alike, there must be 32 equivalent hydrogen atoms within the unit cell. This is possible only with the space group  $O_h^5$ . It may consequently be concluded, if the chemical nature of ammonium chloroplatinate is taken into account, that its symmetry is that of the space group  $O_h^5$ .

Two types of ways of arranging the atoms of ammonium chloroplatinate according to the special cases of this space group,  $O_h^5$ , exist. They are as follows. Possible arrangement (b): *platinum* atoms, 4b or 4c; *chlorine* atoms, 24a; *nitrogen* atoms, 8e; *hydrogen* atoms, 32a. Possible arrangement (c): *platinum* atoms, 4b or 4c; *chlorine* atoms, 24c; *nitrogen* atoms, 8e; *hydrogen* atoms, 32a.

In any grouping developed from  $O_h^5$ , a study of its special cases will show that all of the chlorine atoms must be alike and equally distant from a platinum atom. From the chemical nature of ammonium chloroplatinate, again, it is evident that the chlorine atoms are more tightly bound to the platinum atoms than to the ammonium radicals; and according to any reasonable law of force between atoms this would indicate that the chlorine atoms should be nearer to the platinum atoms than to the nitrogen atoms. In arrangement (c) the chlorine atoms lie closer to the nitrogen atoms than to the platinum atoms so that once more employing chemical evidence it can be stated with a considerable degree of probability that the arrangement of the atoms in ammonium chloroplatinate crystals *must* be that defined by arrangement (b).<sup>10</sup>

If this sort of chemical evidence is ignored there are a considerable

<sup>9</sup> For instance the fact that different but isomeric compounds obtained by substituting different organic radicals in place of the hydrogens of ammonium are not obtained seems to point conclusively in this direction.

<sup>10</sup> This discussion has not taken into account the idea of atomic spheres of influence of definite size (W. L. Bragg, *Phil. Mag.*, [6] **40**, 169 (1920)). Upon this basis also the chlorine atoms should be nearer to the platinum than to the nitrogen atoms, if the radius of the platinum atom is taken from the recent determination of the structure of the metal (A. W. Hull, *Phys. Rev.*, **17**, 571 (1921)) and if the dimensions of the ammonium group are obtained from measurements made on ammonium chloride (W. H. and W. L. Bragg, "X-rays and Crystal Structure," Bell and Sons, London, 1918, p. 111).

number of different ways in which the requisite number of atoms of platinum, nitrogen, chlorine and hydrogen can be grouped within unit cells, and with the existing lack of precise knowledge concerning the laws of scattering it would be a practically hopeless task to try to eliminate them absolutely upon the basis of their predicted diffraction effects. These other possible arrangements would be developed from the space group  $O_h^4$  and would be of the following type. Possible arrangement (d): *platinum* atoms, 4d or 4e; *chlorine* atoms, one set of 24 equivalent positions, or 2 sets of 12 equivalent positions, or 3 sets of 8 equivalent positions, or one set of 12, one of 8 and one of 4 equivalent positions, or arrangements developed by putting 6e and 2a in place of any of the above sets of 8 equivalent positions; *nitrogen* atoms, 8d; *hydrogen* atoms, one set of 24 and 8d, or one set of 24 equivalent positions, 6e and 2a, or 2 sets of 12 or 3 sets of 8 in place of one set of 24 equivalent positions in either of the above, or 4 sets of 8 equivalent positions.

II. *Assuming that  $m=32$ ,  $n=2$ .* If this is the correct amount of mass to be associated with the unit cube, each unit must contain 32 platinum atoms, 64 nitrogen atoms, 192 chlorine atoms and 256 hydrogen atoms. If all 4 of the hydrogen atoms in ammonium are alike it is impossible to associate 32 molecules with the unit cell (unless it be assumed that some of the platinum atoms are different from others) because the maximum number of equivalent positions within the unit cell of any space group is 192. If, however, it is allowed that some of the hydrogen atoms in ammonium may be different from others, then a considerable number of geometrically possible, though chemically far from understandable, groupings can be developed. A consideration of Table IV shows that 3 space groups,  $O_h^5$ ,  $O_h^7$  and  $O_h^8$ , possess special cases with 32 equivalent positions within the unit cube. Two of these, the first two, also show as many as 192 equivalent positions within the unit cell. From either of these if all chemical evidence is disregarded, and in fact from  $O_h^8$  also, it would be possible to build up very complicated arrangements for the atoms of ammonium chloroplatinate. To eliminate with certainty these groupings by a comparison of the diffraction effects which they would produce with those found by experiment is practically impossible in the present state of our knowledge. Since, in the light of chemical evidence, they are at least highly improbable, they will be omitted from further consideration.

**Distinguishing between the Possible Arrangements.**—By making the single assumption that all of the 4 hydrogen atoms of the ammonium radical are chemically exactly alike, it has been shown that the atoms of ammonium chloroplatinate must be placed either according to arrangement (b) or arrangement (c). Of these two, one of them, (c), can be ruled out upon similar grounds. It is, however, possible to distinguish between these two arrangements from the difference in the diffraction effects which

they will produce, so that it is perhaps worth while, if only for purposes of illustration, to show by this instance the method of picking out diffraction effects which will be characteristic of different crystallographically possible arrangements and thus by investigating these characteristic effects to choose the correct grouping.

Calculations of terms proportional to the intensity of reflection from any plane (hkl) in any order,  $n$ , of the spectrum have been made by means of an expression of the form

$$I \propto f(d/n) \sum_r [\sigma_r \cos 2\pi n(hx_r + ky_r + lz_r)]^2 + \sum_r [\sigma_r \sin 2\pi n(hx_r + ky_r + lz_r)]^2 \quad (4)$$

where  $I$  is the intensity of reflection,  $f(d/n)$  is a function of the spacing between like planes whose form is not known with great certainty (for the present it does not enter into this discussion), and  $\sigma_r$ , the scattering power of the atom  $r$  for X-rays, seems to be roughly proportional to the atomic number. The summation is to be taken to cover each of the atoms within the unit cube. For convenience in writing  $A$  will be written for the summation of the cosine terms (not squared) and  $B$  for the summation of the corresponding sine terms. This expression (4) would be written  $I \propto f(d/n)[A^2+B^2]$ .

Applied to the different kinds of atoms of arrangements (b) and (c) this expression gives terms for the intensity of reflection from any plane as follows.

#### *Platinum atoms*

4b. When  $n=1$ : if  $h=2m$ ,  $k=2p+1$ ,  $l=2q+1$ , where  $m$ ,  $p$  and  $q$  are any integers (indices=one even, two odd), then  $A=0$ ; the similar sine term,  $B=0$ , also; if  $h=2m$ ,  $k=2p$ ,  $l=2q+1$  (two even, one odd indices), then,  $A=0$ ,  $B=0$ ; if  $h=2m+1$ ,  $k=2p+1$ ,  $l=2q+1$  (all odd indices), then,  $A=4Pt$ ,  $B=0$ . 4c. When  $n=1$ : if  $h=2m$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m$ ,  $k=2p$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m+1$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=-4Pt$ ,  $B=0$ .

#### *Nitrogen atoms*

Sc. When  $n=1$ : if  $h=2m$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m$ ,  $k=2p$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m+1$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ .

#### *Chlorine atoms*

24c. When  $n=1$ : if  $h=2m$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m$ ,  $k=2p$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m+1$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ .

24a. When  $n=1$ : if  $h=2m$ ,  $h=2p+1$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m$ ,  $k=2p$ ,  $l=2q+1$ , then  $A=0$ ,  $B=0$ ; if  $h=2m+1$ ,  $k=2p+1$ ,  $l=2q+1$ , then  $A=Cl[8 \cos 2\pi u(2m+1) + 8 \cos 2\pi u(2p+1) + 8 \cos 2\pi u(2q+1)]$ ,  $B=0$ .

*Hydrogen atoms*

The term for the hydrogen atoms will not be taken into consideration for, since the scattering power of an atom of hydrogen is so slight, the effect even of 3 such atoms can scarcely be qualitatively observed.

The value of (4) for arrangements (b) and (c) can be written directly by combining the terms for each of the atomic positions. When  $n=1$  they thus become (neglecting the hydrogen terms).

Arrangement (b): when the indices are either 2 even and 1 odd or 2 odd and 1 even,  $A=0, B=0$ ; when the indices are all odd,  $A = \pm 4Pt + 8 Cl[\cos 2\pi hu + \cos 2\pi ku + \cos 2\pi lu]$ ,  $B=0$ ;.....(5)

Arrangement (c): except when the indices are all odd  $A=0, B=0$ ; then  $A = \pm 4Pt$ ,  $B=0$ . .....(6)

When  $n=2$ : all terms will have appreciable values in the second order so that in dealing with such qualitative measures of diffraction as are now available, discussion will be limited to the first-order region.

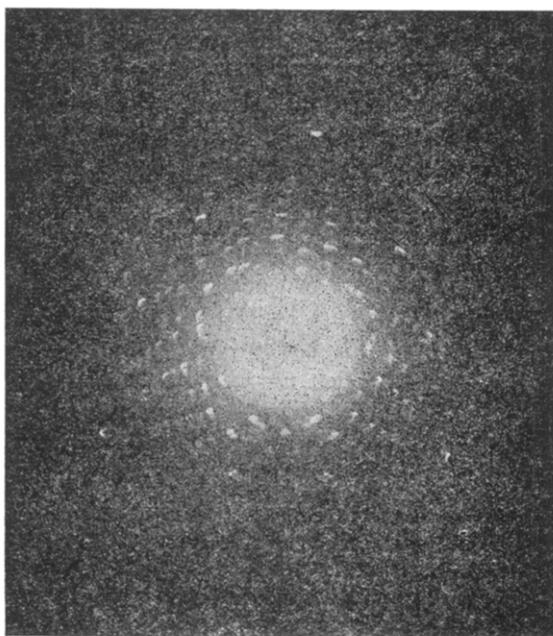


Fig. 2.—A print of the Laue photograph obtained by passing the X-rays in a direction roughly normal to the (111) face of ammonium chloroplatinate.

It is evident that for either (b) or (c) only planes all of whose indices are odd will give first order reflections. Both are in agreement with the results of the reflection spectrum photograph. The most satisfactory way of assuring the correctness of one or the other of these two possibil-

ities and of deciding between them lies then in considering the reflections in the first order from a large number of planes. This is most satisfactorily done at the present time by the study of Laue photographs. This same study should give as well an indication of the position of the chlorine atoms. Their location cannot now be expected with great accuracy without an excessive amount of labor because (1) the hydrogen atoms, though present in a considerable number and hence of quantitative importance, are as already suggested qualitatively insignificant, and (2) because the scattering power of platinum is so great compared with that of chlorine that small changes in the position of the chlorine atoms would be likewise qualitatively of small account. As soon as these reflections can be satisfactorily treated in a quantitative fashion this placing of the chlorine atoms should be easily made.

Two Laue photographs were studied in detail by the customary methods. One, taken normal to the (111) plane, showed reflections from about 400

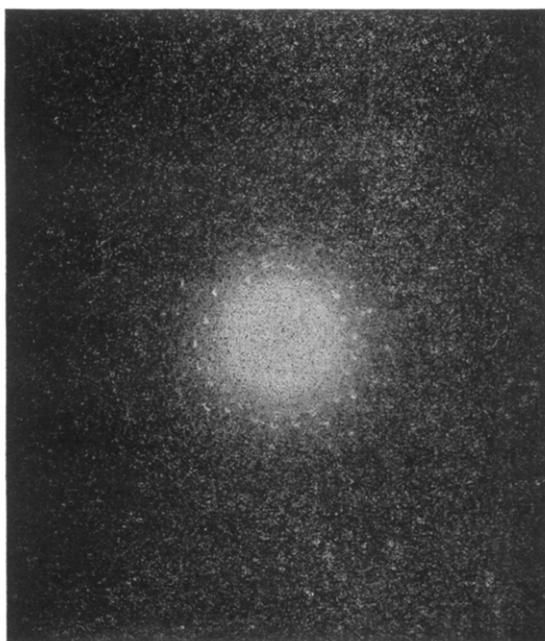


Fig. 3.—A print of the Laue photograph obtained by passing the X-rays in a direction roughly normal to the (100) face of ammonium chloroplatinate.

planes (Fig. 2); the other, tilted somewhat from a normal to the cube plane, contained about 200 spots (Fig. 3). The gnomonic projections of these two photographs are shown in Figs. 4 and 5. By enlarging by the amount shown in the first two figures, these projections will duplicate

the conditions of the original experiment so that from them can be obtained all of the data now available from these photographs. A rough measure of the intensities of the spots is given by the size of the spots in the central reproduction of the photograph, the most intense spots being made the largest. The reproductions of the original photographs (Figs. 2 and 3) are added to make possible slightly more accurate estimations of the intensities of the brighter spots (the only ones that show). A spot can be identified with the projection of its plane in the usual manner, most conveniently by using some such ruler as that already described; and its distance from the central spot and the indices of its reflecting plane can be

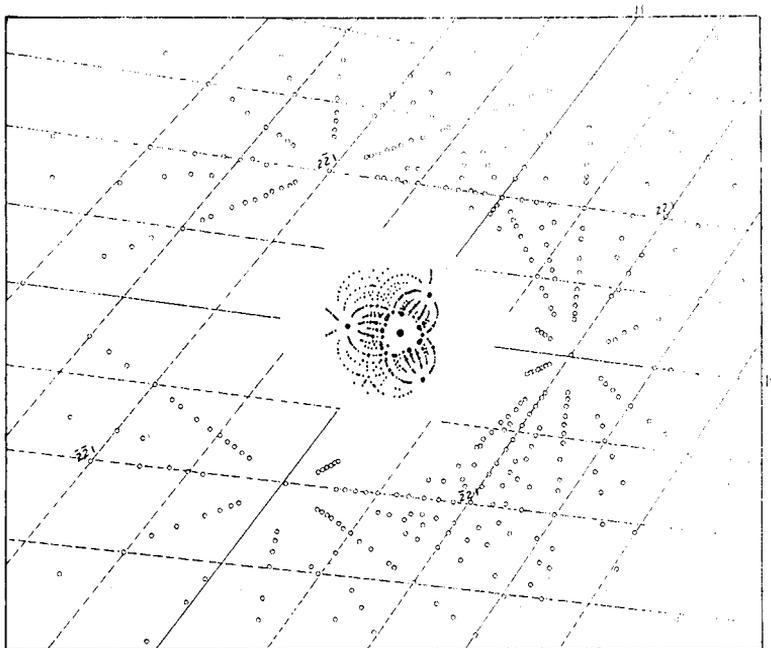


Fig. 4.—The gnomonic projection of the Laue photograph of Fig. 2. Reduced.

directly obtained from measurement upon the central reproduction and upon the projection respectively.<sup>11</sup> The angle  $\theta$  of the reflection can be calculated for any spot from a knowledge of the distance from the crystal to the

<sup>11</sup> It would not be feasible to record the measurements upon approximately 600 planes together with the calculations of the wave lengths producing the spots and their estimated intensities. The inclusion of this mass of data would give an utterly false impression of their present value. Rather than leave out all results, however, the condensed description outlined in the text has been used. In spite of its obvious disadvantages it is possible with such reproductions as are shown here to record in a short space all of these data in such a form that those sufficiently interested can work them out with an approximation to the original accuracy.

photographic plate (which in both of these cases was 5 cm.) and from a measurement of the distance of the spot from the undiffracted image. Combined with a knowledge of the indices of the reflecting plane and by using Expression 2 and the equation  $n\lambda = 2d \sin \theta$ , this evaluation of  $\theta$  makes possible the determination of  $n\lambda$  for each spot.

In neither of these photographs were any spots observed in the first order region (assuming that the number of molecules to be associated with the unit cell is 4 and hence that the reflection observed from the (111) face in the spectrum photograph was of the first order) except those all of whose indices are odd numbers. Some of the indices of these first order

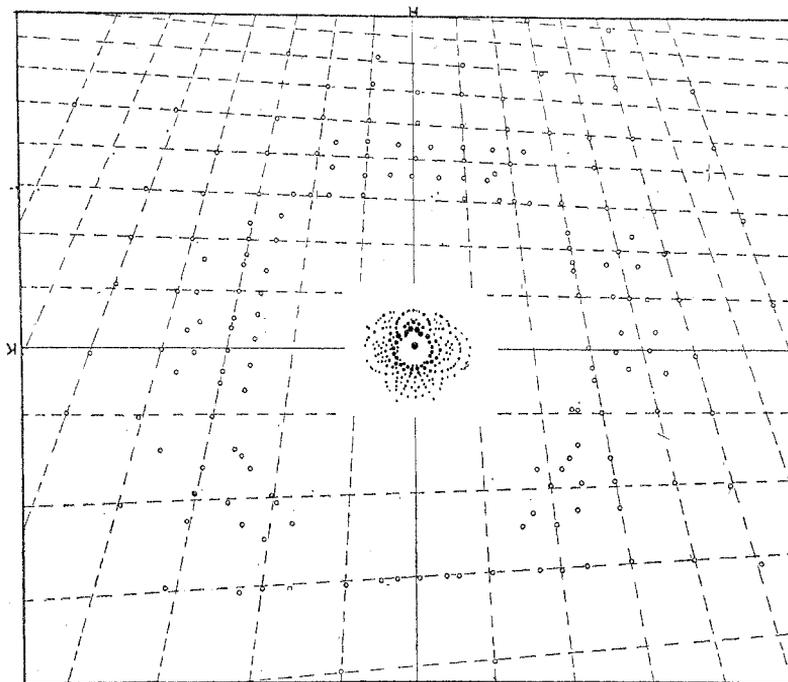


Fig. 5.—The gnomonic projection of the Laue photograph of Fig. 3. Reduced.

planes are such complicated ones as  $(\bar{9} \ 11 \ 5)$  or  $(5 \ \bar{13} \ 3)$  so that the complete absence of any but all-odd planes leaves no doubt as to the truth of the general statement that only planes having all odd indices are found in the first order region. This observation is very strong evidence for the correctness of either arrangement (b) or arrangement (c).

The terms proportional to the amplitude (square root of the intensity) of the first order reflections from arrangements (b) and (c) have been shown to be arrangement (c),  $A = 4Pt$ ; arrangement (b), with the platinum atoms at  $4b$ ,  $A_{4b} = 4Pt + 8Cl[\cos 2\pi hu + \cos 2\pi ku + \cos 2\pi lu]$ ; with the platinum atoms at  $4c$ ,  $A_{4c} = -Pt + 8Cl[\cos 2\pi hu + \cos 2\pi ku + \cos 2\pi lu]$ . But  $A_{4c} =$

$-A_{4b}$  if  $u_{4c} = u_{4b} + \frac{1}{2}$  so that it will be sufficient to discuss but one case (the one involving  $4b$  will be chosen).

It is customary to assume that  $f(d_{hkl}/n)$  in Equation 4 has the form of  $(d_{hkl}/n)^2$ . If this is true and if the atoms are arranged according to (c) then the intensity of the first order reflections from the different planes (hkl), at the same wave lengths, should stand in the order of the value of  $1/(h^2 + k^2 + l^2)$ . If, on the other hand, the chlorine atoms have the arrangement (b), this order of intensities will be inverted in part by reason of the term which these chlorine atoms contribute towards the amplitude. Such irregularities are found in the results from the Laue photographs and this may be taken to show that the correct arrangement is that of (b).<sup>12</sup>

A more detailed discussion of such reflections should give an indication of the value of  $u$  for the chlorine atoms. From the results of the study of the Laue photographs, for instance, the following comparisons of the intensity of reflection of waves of practically the same length from different planes are possible

$$\begin{aligned}(173) &< (171) \text{ (by a small amount),} \\ (171) &< (191), \\ (751) &< (171), \\ (751) &< (191) \text{ (by a considerable amount).}\end{aligned}$$

The positions of the chlorine atoms are defined by  $u$  which must consequently be assigned such a value that the above experimental facts must be accounted for when the value of  $(h^2 + k^2 + l^2)$  is taken into consideration (a qualitative ordering of the intensity of the reflections on the basis of this  $f(d/n)$  factor is sufficient). This  $u$  is most readily found by plotting it for each of these planes (Fig. 6) against the corresponding amplitude of reflection as determined through the intensity Equation 5. It is obvious from the form of arrangement 24a that the function will be symmetrical about  $u=0.5$  so that it is sufficient to consider  $u$  from  $u=0$  to  $u=0.5$ . The data given here allow two possible positions for the chlorine atoms, one about  $u=0.1$ , the other close to  $u=0.225$  (Fig. 6). The first of these seems improbable because it would bring the centers of the chlorine and platinum atoms nearer together than is to be anticipated; no data were found, however, definitely to rule out this possibility. If the second position is the correct one the value for  $u$  must lie between  $u=0.22$  and  $u=0.24$ .

It is of interest to calculate, using the idea of closely packed atomic spheres,<sup>13</sup> the expected distance of the chlorine from the platinum atoms

<sup>12</sup> Variations from the normal decline of intensity with increasing values of  $(h^2 + k^2 + l^2)$ , though of but slight amount, would be produced in (c) by the hydrogen atoms. The observed effects seem to be much greater, however, than would be expected from the introduction of this factor into the intensity equation for (c).

<sup>13</sup> W. L. Bragg, *Phil. Mag.*, [6] 40, 169 (1920).

and to compare this distance with the results of the above determination. The radius of the platinum atom, as calculated from the structure of platinum metal<sup>14</sup> is  $1.39 \times 10^{-8}$  cm. To chlorine has been assigned the radius  $1.05 \times 10^{-8}$  cm.<sup>13</sup> Upon this basis then the distance from chlorine to platinum should be  $2.44 \times 10^{-8}$  cm. Taking  $u=0.23$  and knowing the length of the unit cube to be  $9.843 \times 10^{-8}$  cm., this distance is  $2.26 \times 10^{-8}$  cm. (If  $u=0.24$ , it is  $2.36 \times 10^{-8}$  cm.)

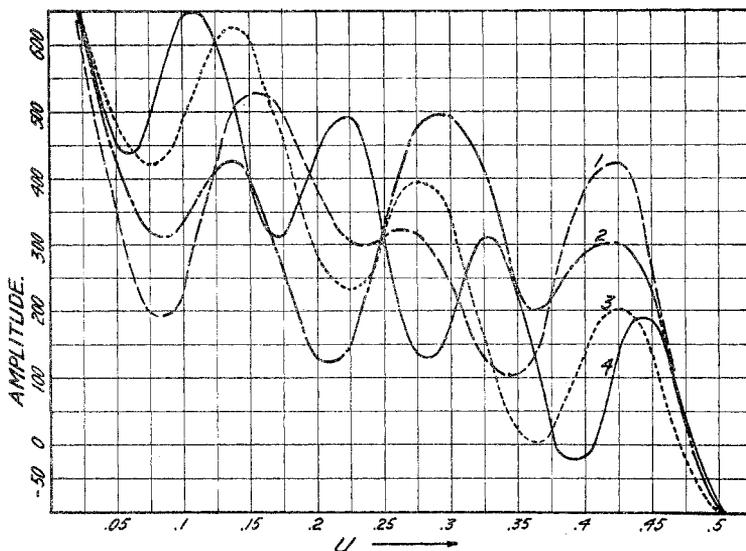


Fig. 6.—Curve 1 = planes of the form (571); Curve 2 = (173);  
Curve 3 = (171); Curve 4 = (191).

As soon as careful measurements of intensity become possible and satisfactory knowledge of the nature of scattering is available, the more accurate placing of the chlorine atoms in ammonium chloroplatinate and a comparison between their positions in this compound and in other chloroplatinates, as well as a comparison of the structures of these crystals with the analogous fluosilicates, chlorostannates, bromoplatinates, etc., will be easily accomplished and will be of considerable interest.

**Conclusion.**—Making use of the single assumption, which seems to be itself entirely justified, that the 4 hydrogen atoms in the ammonium group are all chemically alike, it has been shown that the atoms in the unit cube of ammonium chloroplatinate have the following coordinate positions: *platinum* atoms, 4b; *chlorine* atoms, 24a, the value of  $u$  probably lying between  $u=0.22$  and  $u=0.24$ ; *nitrogen* atoms, 8e; *hydrogen* atoms, 32a, the value of  $u_H$  being unknown. The length of the side of this unit cube is  $9.843 \times 10^{-8}$  cm. The arrangement of its atoms is shown in Fig.

<sup>14</sup> A. W. Hull, *Phys. Rev.*, **17**, 571 (1921).

7: Fig. 7a shows the positions of only the platinum and nitrogen atoms within a unit cell; Fig. 7b gives the arrangement of all of the atoms within a small cube which has one-eighth of the volume (and one-half the length of side) of this unit.

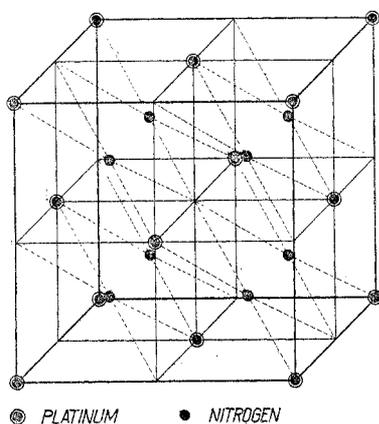


Fig. 7a.

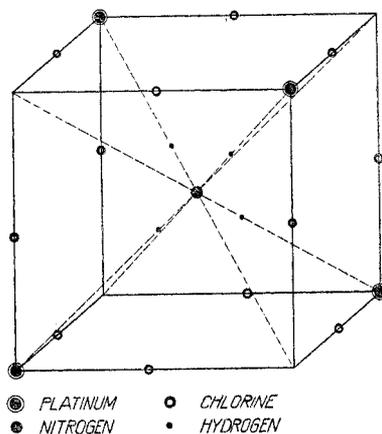


Fig. 7b.

The arrangement of the atoms within the unit cell of ammonium chloroplatinate. Fig. 7a shows the positions of the platinum and nitrogen atoms within the unit; Fig. 7b gives the positions of all of the atoms within the small cube that has one-eighth of the volume of the unit.

**The Chemical Significance of this Crystal Structure.**—This crystal structure of ammonium chloroplatinate is most easily described by saying that it is the same as that of fluorspar ( $\text{CaF}_2$ ) if for the bivalent positive calcium atoms bivalent negative  $\text{PtCl}_6$  groups are substituted and if the monovalent fluorine atoms are replaced by monovalent ammonium radicals. There can be no doubt but that  $\text{PtCl}_6$  groups of atoms function in solution as doubly (negatively) charged ions and that the ammonium radicals under the same conditions are singly charged (positively). Since their crystallization is a strictly analogous process to the crystallization of such salts as the alkali halides, for which there is considerable evidence that the atoms remain ions (that is, remain electrically charged) in the solid state, it is natural to assume that very probably there exists within the crystal of ammonium chloroplatinate the ions of  $\text{PtCl}_6$  and of  $\text{NH}_4$ . The fact that the corresponding compound calcium fluoride  $\text{CaF}_2$ , which from the chemical nature of its elements is presumably also an "ion" compound, has an analogous structure, would seem to indicate that this arrangement is the most stable, or at least is an exceedingly stable, way of grouping one doubly charged and two singly charged (of opposite sign to the doubly charged) atoms or groups of atoms in the crystalline state.

### Summary.

Crystals of ammonium chloroplatinate  $((\text{NH}_4)_2\text{PtCl}_6)$  probably have a structure which is analogous to that commonly assumed for fluorspar, if  $\text{PtCl}_6$  groups replace the calcium atoms and if  $\text{NH}_4$  groups are introduced in place of the fluorine atoms. This determination was made by and serves as an illustration of the general method (previously discussed) for the study of the structure of crystals which is based upon the theory of space groups.

The only assumption made that is not required in the ordinary determination of the wave length of X-rays from a reflection spectrum was that the 4 hydrogen atoms of the ammonium radical are exactly alike; with this exception, that in attempting to place the chlorine atoms with accuracy, it was assumed that atoms scatter X-rays in an amount which is roughly proportional to their atomic numbers and that in a lattice arrangement of atoms the intensities of reflection follow qualitatively the order of  $1/(\text{h}^2 + \text{k}^2 + \text{l}^2)$ .

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### A DIFFERENTIAL THERMOMETER.

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One type of differential thermometer measures the difference of temperature existing at the same location at different times; a second type measures the difference in temperature existing simultaneously at different points in space. The thermometer here described is of the latter type.

A well-known differential thermoscope of this type consists of two glass bulbs containing air, otherwise closed but communicating with each other through a U-tube partly filled with oil, whose change of level indicates change of temperature by responding to change of gas pressure within the bulbs. When this instrument is developed into a differential thermometer, certain disadvantages become apparent, of which three will here be mentioned. (1) When the manometric liquid is caused to run into one of the bulbs by accidental tilting, perhaps during transportation, then it is difficult to return the liquid into precisely the same position as it occupied when the instrument was scaled. If stopcocks are introduced in the effort to avoid this inconvenience, the cure may become worse than the disease because of zero-creep. (2) In the presence of permanent gas, the manometric liquid becomes, in practice, not infrequently broken into threads, separated by short columns of the gas. This inconvenience, albeit only temporary, is nevertheless annoying. (3) Although oils furnish very sensitive manometric liquids, their use, or, indeed, the use of any liquid