

260. *The Crystalline Structure of Tetramminoplatinous Chloride.*

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WERNER's view that 4-co-ordinated compounds of bivalent platinum possess a planar configuration has several times been contested (*e.g.*, Reihlen, *Annalen*, 1926, **447**, 211; Angell, Drew, and Wardlaw, *J.*, 1930, **349**); and recently, evidence has been offered of the existence of three isomerides of diamminoplatinous chloride (Drew, Pinkard, and Wardlaw, this vol., p. 988), indicating the inadequacy of this formulation. On the other hand, Pauling has shown theoretically (*J. Amer. Chem. Soc.*, 1931, **53**, 1367) that the bivalent transitional elements nickel, palladium, and platinum can form 4-covalent compounds with a planar configuration: apart from previously available evidence of a purely chemical nature, his conclusions appear to be supported by an investigation of nickel derivatives of benzylmethylglyoxime (Sugden, this vol., p. 246) and by the results of the X-ray analysis of potassium chloropalladite

and chloroplatinite (Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 774, 2404) which indicated a planar structure for the $[\text{MCl}_4]''$ anion.

Since no evidence has been brought forward regarding the configuration of a *kation* of the type $[\text{MX}_4]''$ ($\text{M} = \text{Ni}, \text{Pd}, \text{or Pt}$) in the crystalline state, an investigation of the structure of tetramminoplatinous chloride, $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$, has been undertaken. It has been found that in this case also the four ammonia groups are coplanar with the platinum atom. Taking this result in conjunction with that of Dickinson, it appears fairly certain that the bonds to any four identical groups co-ordinated to a platinum atom lie in a plane. The question now arises as to whether this planar configuration persists when these four groups are not all the same; it is hoped that information on this point will be obtained from a study of the diammines and mixed tetrammines of platinum and palladium.

Tetramminoplatinous chloride crystallises from water as a monohydrate in white tetragonal prisms, which show a tendency to discolour after several recrystallisations. Goniometric measurements have been recorded by Sella (*Mem. Accad. Sci. Torino*, 1858, **17**, 337) and by Kurnakow and Andrejewski (*Z. anorg. Chem.*, 1930, **189**, 137); their results, confirmed approximately in the present investigation, are as follows: The crystals are tetragonal, exhibiting the forms $a\{100\}$ and $o\{111\}$; axial ratio $a : c = 1 : 0.562$ (Sella), $1 : 0.566$ (Kurnakow and Andrejewski); weak double refraction, negative; $\omega = 1.672$, $\epsilon = 1.667$; no appreciable cleavage.

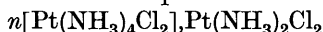
Other results obtained by Kurnakow and Andrejewski, however, are not confirmed. These writers consider that the brown coloration of tetrammine crystals, occurring on recrystallisation and accompanied by loss of ammonia, is due to the formation of mixed crystals of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ with $4[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. (The latter substance is also tetragonal with $a : c = 1 : 1.11$ approx.) On general grounds this seems very unlikely; the two compounds are not isomorphous, and almost certainly have lattices of considerably different dimensions; they have very different habits, the crystals of the double compound always showing $\{001\}$ very well developed. Further, the variations which are observed in the colour of the double compound, and considered by Kurnakow and Andrejewski to support their views, are definitely not due to admixture of tetrammine hydrate. (Those authors made no measurements to show that the angles of the supposed mixed crystals lie between those of the two components or that they vary in a regular manner with chemical composition.) Several crystals of the double compound were examined and found to be divided into three kinds, according to the value of the axial ratio. They all exhibited weak negative double refraction, the refractive indices being approxi-

ately 1.66. The main results are summarised in Table I; it is possible that if more material had been available, more than three kinds of crystal would have been observed. Only one crystal of type (c) was found. In the first column, the double compound is denoted by 4T.D., and the tetrammine hydrate by T.

TABLE I.

Substance.	Colour.	Pt, %.	c/a .	d .
4T.D. (a)	Very pale yellow	61.0	0.952	2.90
(b)	Almost colourless	59.1	1.103	2.90
(c)	Bright yellow	58.6	1.18	2.90
T.	Colourless	55.1	$\frac{1}{2} \times 1.13$	2.57

The crystals of the double compound examined by Kurnakow and Andrejewski were light yellow to brownish-yellow, $c/a = 1.111$; Pt, 59.2—60.0% [Calc. for $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$; Pt, 55.4; for $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$: Pt, 65.0; for T.D.: Pt, 59.6]. It can be seen from the above table that there is a considerable variation in the properties of the double compound, and although there is a rough relation between the axial ratio and platinum content, this relation is not such as to be explicable on the supposition that mixed crystals of the tetrammine hydrate and the double compound are formed. All the crystals (a), (b), and (c) had the same habit, with {001} prominent, very different from the prismatic form of the tetrammine. It seems possible that more than one compound of the formula



exists; the material available was insufficient to make a more detailed investigation on this point. From an examination of discoloured tetrammine crystals, it appears probable that the brown colour is due to the presence of diammine as a definite entity and not as a mixed crystal. The brown coloration is not diffused uniformly through the crystals, but very small yellowish-brown crystals seem to be present on the larger tetrammine crystals. It is concluded that there is no evidence for the existence of mixed crystals of the tetrammine with the double tetrammine-diammine compound. It is clear that further work on the latter substance is necessary.

The X-ray examination of the tetrammine was carried out on fairly well-developed colourless crystals prepared by dissolving β -diamminoplatinous chloride in ammonia (Found by micro-analysis: Pt, 55.1. Calc.: Pt, 55.4%). By means of rotation photographs using copper K_α radiation, the dimensions of the unit cell were found to be $a = 7.39 \pm 0.02$, $c = 4.21 \pm 0.02$ Å.U. The axial ratio is thus $a : c = 1 : 0.570$, agreeing with the goniometric values within the probable error of the latter. There is one molecule of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ in the cell, so the a -axes assigned by previous

investigators are the axes of the true unit cell. The calculated density is 2.54 g./c.c., that determined directly being approx. 2.57.

As would be expected with one molecule to the cell, there are no halvings, all the observed spacings agreeing with the calculated. A Laue photograph taken with the X-ray beam parallel to the c -axis showed full ditetragonal symmetry, so that the space-group, on this evidence, might be D_{2d}^1 , C_{4v}^1 , D_4^1 or D_{4h}^1 . The symmetry cannot be determined more definitely by X-ray methods alone. Since all the (111) faces appear equally developed on the crystals, it may be inferred that the crystal class is either D_4 or D_{4h} ; in either case this would lead to a planar configuration for the $[\text{Pt}(\text{NH}_3)_4]$ complex. To substantiate this conclusion, the crystals were tested for piezo-electricity by the method of Giebe and Schiebe (*Z. Physik*, 1925, **33**, 335, 760); no effect was detectable either with the c -axis parallel or perpendicular to the electric field. I have to thank Messrs. J. D. Bernal and W. A. Wooster for carrying out this test. The absence of a piezo-electric effect indicates that the crystals are centro-symmetrical so that the class must be D_{4h} , since it is the only one of the four possibilities which is not polar. The space-group of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ is thus D_{4h}^1 ($P4/mmm$).

Since there is the substance of one molecule only in the unit cell, it appears that the crystals have an ionic lattice. If molecules of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ were present, *i.e.*, if the structure were such that with each platinum atom two chlorine atoms were more closely associated than any others, then, since the molecule would possess the full D_{4h} symmetry, it would necessarily have a bipyramidal configuration with the chlorine atoms at equal distances from the platinum atom along the c -axis. Apart from the improbability of such a structure on general grounds, the length of the c -axis (4.21 Å.U.) is far too small to accommodate one platinum and two chlorine atoms. Thus the structure is ionic, as would be expected from chemical evidence. The complex kation $[\text{Pt}(\text{NH}_3)_4]^{2+}$ has the full D_{4h} symmetry, *i.e.*, the platinum atom is situated at the centre of a square composed of four ammonia groups. Further, each ammonia group has two planes of symmetry, from which it is to be inferred that the group as a whole is rotating about the Pt-N bond. (An alternative is that the four nitrogen valencies are coplanar, an extremely improbable condition.) This result could probably be verified by investigations of the specific heat and Raman spectrum of the crystals. It may be noted that in the case of hexammino-chlorides of bivalent cobalt (Stoll, *Diss.*, Zurich, 1926) and nickel (Wyckoff, *J. Amer. Chem. Soc.*, 1922, **44**, 1239) the symmetry of the ammonia groups is too high to be accounted for except by rotation about the covalent bond.

The preceding results are deduced from symmetry considerations ; further detailed information can only be obtained by making use of the intensities of the X-ray reflexions from the various lattice planes. In the subjoined table some of the principal intensities, estimated visually, are given. The abbreviations are *vs*, very strong ; *s*, strong ; *ms*, moderately strong ; *m*, moderate ; *w*, weak ; and *vw*, very weak.

<i>hkl.</i>	<i>I.</i>	<i>hkl.</i>	<i>I.</i>	<i>hkl.</i>	<i>I.</i>	<i>hkl.</i>	<i>I.</i>
100	<i>m</i>	400	<i>vs</i>	201	<i>vw</i>	002	<i>vs</i>
200	<i>s</i>	110	<i>m</i>	402	<i>vs</i>	003	<i>w</i>
300	<i>m</i>	220	<i>vs</i>	001	<i>ms</i>		

Now, since the intensities of the orders of (001) do not fall off regularly, it may be inferred that the chlorine ions do not lie in the same plane as the $[\text{Pt}(\text{NH}_3)_4]^{++}$ ions. A platinum atom being placed at the corner of the unit cell, the only positions available for the chlorine ions, in accordance with the symmetry requirements, are therefore the centres of the {100} faces. Next, the ammonia groups may lie either in the {100} or the {110} planes, but since nearly all the available space in the {100} planes is occupied by chlorine ions, the amonias must lie in the {110} planes. The distance Pt-NH₃ can only be determined by resorting again to considerations of X-ray reflexion intensities ; the value which gives the most symmetrical distribution and the best agreement with the intensities is approximately one-fourth of the length of the [110] axis.

There is, finally, the position of the water molecule to consider. The symmetry requires that the oxygen atom should lie either (*a*) mid-way between neighbouring platinum atoms along the *c*-axis, (*b*) at the cell-centre, or (*c*) at the centre of the (001) face. The possibility (*a*) may be ruled out because the space available is insufficient to accommodate a water molecule. In addition, it is known that the water content of the tetrammine varies somewhat, and that the crystals can be dehydrated merely by the action of phosphoric oxide at room temperature ; these facts indicate that the water is present in comparatively loose combination, whereas in case (*a*) it would be very closely locked into the crystal and could not be removed without complete disruption of the structure. Thus the suggestion which has sometimes been made, that water of crystallisation in platinous compounds gives rise to a six-point system around the platinum atom is, in this instance at any rate, not verified by experiment. It is difficult to discriminate between the possibilities (*b*) and (*c*), but the latter would make the (001) planes rather crowded, while the centre of the cell would be comparatively empty. The most satisfactory arrangement is obtained

with the oxygen atom at the cell centre. If the water molecule is fixed, it must be linear and parallel to the c -axis, but if, as seems likely, it is free to rotate, the hydrogen atoms may be situated anywhere in the space available.

The positions of all the atoms and ions (except the hydrogens) have thus been fixed; the structure obtained is depicted in Figs. 1 and 2, which show views along the c - and the a -axis respectively. The NH_3 group is represented as a sphere of radius 1.4 \AA.U. ; the radii of the other atoms are approximately those given by Goldschmidt (e.g., *Trans. Faraday Soc.*, 1929, **25**, 282). The results may be summarised by giving the parameters as follows: $a = 7.39$, $c = 4.21 \text{ \AA.U.}$; atomic co-ordinates—Pt, $(0, 0, 0)$; Cl, $(\frac{1}{2}, 0, \frac{1}{2})$, and $(0, \frac{1}{2}, \frac{1}{2})$; NH_3 , $(u, u, 0)$, $(-u, u, 0)$, $(u, -u, 0)$, and $(-u, -u, 0)$,

FIG. 1.

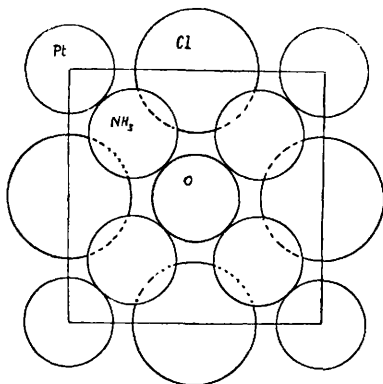
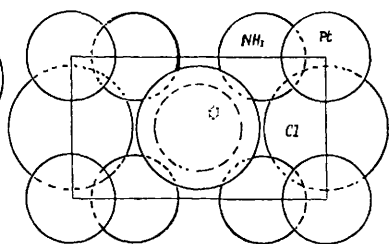


FIG. 2.



where $u = \frac{1}{4}$ app.; O, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. This structure leads to reflexion intensities which are in good agreement with all those given above; in particular, as can be seen from Fig. 2, the (201) planes, containing platinum atoms only, are interleaved by planes containing $4(\text{NH}_3)$, Cl_2 , and O, for which the sum of the atomic numbers is 82, almost the same as that for platinum (78). Thus the (201) reflexion should be very weak and the (402) very strong. This is very marked in the photographs, in which the (201) reflexion is barely visible, while its second order is very much stronger than any other plane of so large a spacing. In addition to the complete agreement in the matter of intensities, the proposed structure provides an explanation of other properties of the crystals; it can be seen that the water molecules are comparatively loosely held, and are situated in such a position that they can escape without disrupting the crystal. Further, since the units of the structure are arranged in planes parallel to (001) , *negative* double refraction would be expected,

but on account of the symmetrical three-dimensional distribution of the chlorine ions, the double refraction should be weak, as actually found.

The main features of the structure may now be summarised. *Each platinum atom is surrounded by four ammonia groups in a square, and at a greater distance by 8 equidistant chlorine ions. Each ammonia group is at the centre of 4 coplanar chlorine ions, while each chlorine ion is surrounded by 8 ammonias.* The arrangement of the chlorine ions approaches a cubic packing; it is anticipated that this effect would be more pronounced for the corresponding bromide and iodide, whose axial ratios, c/a , should thus approximate more closely to the value 0.707.

It is of interest to compare the results of this investigation with those of previous work (*loc. cit.*). The present structure is of the type H 15 (Ewald and Hermann, "Strukturbericht") and is the same in essentials as that determined for K_2PtCl_4 (Dickinson, *loc. cit.*), the similarity extending to the actual values of the cell dimensions, which are, for the chloroplatinite, $a = 6.99$, $c = 4.13$, and for the tetrammine, $a = 7.38$, $c = 4.21$ Å.U. In Table II the various interatomic distances are summarised and compared with previous values.

TABLE II.

Distance.	Value, Å.U.		Reference to previous work.
	Present paper.	Previous work.	
Pt-Pt	4.21	4.13	K_2PtCl_4 ; Wyckoff.
Pt-NH ₃	2.62		
Co-NH ₃		2.5	Co(NH ₃) ₆ Cl ₂ ; Stoll.
Ni-NH ₃		2.4	Ni(NH ₃) ₆ Cl ₂ ; Wyckoff.
Cl-NH ₃	3.36	3.57	
		3.49	Co(NH ₃) ₆ Cl ₂ ; Stoll."
Pt-Cl	4.25		
Co-Cl		4.27	
Ni-Cl		4.37	Ni(NH ₃) ₆ Cl ₂ ; Wyckoff."

Considering the diversity of the substances from which these results are drawn, the agreement exhibited in the above table is remarkable. The increase in the distance Cl-NH₃ on passing from the tetrammine to, *e.g.*, the hexammines is roughly the amount to be expected as the chlorine ion increases its co-ordination number from 8 to 12 (this term being used in Goldschmidt's sense, *i.e.*, the number of atoms or ions of kind A surrounding an atom or ion of kind B in the crystal lattice). The difference between the Pt-NH₃ and the Co (or Ni)-NH₃ distances is also approximately the amount to be expected from the respective radii of the metal atoms. The agreement shown in these instances affords further justification for assigning the value 0.25 to the parameter u .

The value 1.81 Å.U. is generally accepted as the radius of the

chlorine ion with co-ordination number 6; if an increase of 3% is assumed in this value for co-ordination number 8, the "radius" of the NH_3 group is found to be 1.49 Å.U. The radius of the platinum atom (co-ordination number 4) being taken as 1.22 Å.U., the ammonia radius is calculated as 1.41 Å.U. These values agree with that usually ascribed to the NH_3 group in ionised lattices. The value deduced from the Pt-NH₃ distance would be expected to be smaller than the other, if, as suggested above, the ammonia group, consisting of a rather flat pyramid, is rotating about the covalent bond.

An interesting confirmation of the planar configuration of the platinum valencies is afforded by the results of the examination of cooperite (PtS) shortly to be published by Mr. F. A. Bannister, to whom I am indebted for advance information. It appears that each platinum atom is surrounded by four equidistant coplanar sulphur atoms, which, however, form a rectangle, and not, as might be expected, a square. The sulphur valencies have the usual approximately tetrahedral configuration.

Since it now seems to be established that in bivalent complexes of the type $[\text{PtX}_4]$, whether positive or negative, the four bonds to the platinum atom are coplanar and directed to the corners of a square, it will be of considerable interest to investigate the configuration of complexes of the type $[\text{PtX}_2\text{Y}_2]$. In this case, the four valencies will no longer possess tetragonal symmetry, but according to the theory developed by Pauling, they would still be planar. A preliminary examination of α - $[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2]\text{Cl}_2$ has been made; the crystals of the monohydrate are monoclinic (probably sphenoidal), with axial ratios $a : b : c = 1.788 : 1 : 1.172$; $\beta = 113^\circ 31'$. There is more than one molecule in the unit cell. It is clear that the symmetry of the complex in this case is much lower than that of the tetrammine, but it is influenced here partly by the orientation of the pyridine rings as well as by the distribution of the platinum valencies. For this reason, although it is expected that the further examination of this substance and its β -isomeride will yield useful information on the points raised above, it is hoped to obtain more definite evidence from an examination of the compounds $[\text{Pt}(\text{NH}_3)_2(\text{NH}_2\text{OH})_2]\text{Cl}_2$.

Summary.

(1) The crystalline structure of tetramminoplatinous chloride monohydrate has been investigated by means of X-rays, and determined with a considerable degree of certainty.

(2) The four platinum covalencies in the complex $[\text{Pt}(\text{NH}_3)_4]$ are found to be coplanar and directed to the corners of a square.

(3) The principal interatomic distances in the crystal have been determined and found to agree with previous measurements.

(4) The conclusion of Kurnakow and Andrejewski that the tetrammine $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ forms mixed crystals with the double compound $4\{\text{Pt}(\text{NH}_3)_4\text{Cl}_2\}, \text{Pt}(\text{NH}_3)_2\text{Cl}_2$ is not confirmed.

(5) The possible configuration of complexes of the type $[\text{PtX}_2\text{Y}_2]$ is discussed, and preliminary crystallographic data are given for $\alpha\text{-}[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2]\text{Cl}_2$.

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