

260. *The Molecular Structure of Some Co-ordination Compounds of Platinum and Palladium.*

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IN extension of our previous work (J., 1932, 1912, 2527), we have carried out X-ray examinations of the following crystalline substances: bisethylenediaminoplatinous chloride, $[\text{Pt en}_2]\text{Cl}_2$; bisethylenediaminopalladous chloride; tetramminopalladous chloride,

* Microanalysis.

[Pd(NH₃)₄]Cl₂·H₂O; and the α - and β -diamminoplatinic tetrachlorides, [Pt(NH₃)₂Cl₄]. We have also re-examined tetramminoplatinous chloride and ammonium chloropalladite. These compounds have given further evidence of the planar distribution of platinum and palladous valencies, but, in addition, the results have led to the conclusion that the valencies of the metal atom are not all crystallographically equivalent, but are differentiated into pairs. More precisely, only those valencies which are *trans* to each other are equivalent; this applies to all the compounds mentioned with the exception of ammonium chloropalladite, *i.e.*, to all those in which the metal atom is the centre of a positive or neutral complex. The differentiation of valencies is undoubtedly intimately connected with the distribution of shared electrons, and is presumably due to slight differences in energy between the various sub-groups in the same principal quantum group of the central atom. Thus the difference between the pairs of valencies lies in the strength of the bond, and is not a difference of type, so that it cannot be expected to give rise to isomerism, but should be of importance in problems of elimination and substitution. This assumes that these purely crystallographic results are significant for chemical reactions; this is not an important point, however, since pairing of valencies has already been suggested (Drew, Pinkard, and Wardlaw, J., 1932, 1006) as the most satisfactory way of explaining the reactions of the simple and mixed tetramminoplatinous halides. The present work confirms this suggestion, and, by showing that it is the *trans*-valencies which are equivalent, affords a physical basis for Werner's hypothesis of *trans*-elimination. Whether this pairing is general or is confined to the amines, is a matter for further investigation.

The examination of the α -diamminoplatinic tetrachloride shows that the ammonia groups must be *trans* to each other, the six bonds to the platinum atom being distributed octahedrally. For the β -tetrachloride, the results are not so definite on account of the poor quality of the crystals, but they are most simply explained by an octahedral distribution of valencies, the ammonia radicals being in *cis*-positions.

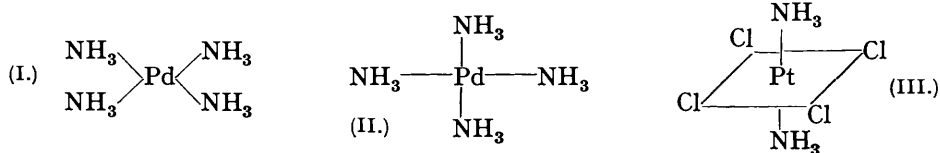
The more detailed arguments on which the above statements are based are now set out for each substance in turn.

Bisethylenediaminoplatinous Chloride.—This substance, in which two chelate groups are attached to the platinum atom in *cis*-positions, crystallises in the triclinic system and the complex ion is found to possess a centre of symmetry only. It follows immediately that the four nitrogen atoms are coplanar with the platinum atom, and further, that only the *trans* platinum–nitrogen bonds are equivalent. (For brevity, a condition in which *trans*-valencies only are equivalent will be referred to in future as “*trans*-pairing.”) If all four bonds were equivalent, the ion would possess at least an axis of symmetry, for Burgers has shown (*Proc. Roy. Soc., A*, 1927, 116, 553) that the ion [NH₃·C₂H₄·NH₃]⁺ in ethylenediamine sulphate possesses a two-fold axis (*i.e.*, the two nitrogens are equivalent), so that we may reasonably assume that the same applies to the neutral molecule. Thus, in the present case the pairing is to be ascribed to the central atom itself, and not to the attached groups.

Bisethylenediaminopalladous Chloride.—This substance is isomorphous with the preceding, and precisely the same considerations apply.

Tetramminopalladous Chloride.—This substance is tetragonal, and the examination shows that there are four molecules in the unit cell, the symmetry of the complex being either three mutually perpendicular planes or a four-fold axis. The latter would mean that the four Pd–N valencies were equivalent, but that the ion would be arranged unsymmetrically in the lattice relative to the chlorine ions. This is unlikely, since it would imply distortion of the chlorine ions, resulting in colour and reduced solubility (as, *e.g.*, in Magnus's salt), whereas actually the tetrammines are typical ionic substances, colourless and highly soluble. Thus we conclude that the tetrammine ion has three planes of symmetry, so that again the four nitrogens must be coplanar with the central atom, and the valencies must be paired. The required symmetry can be obtained with either of the arrangements (I) or (II). Of these, (II) (*trans*-pairing) is much to be preferred on various grounds; (I) represents four equal groups held by bonds of equal strength but distributed unequally with respect to each other, *i.e.*, we have in effect a pairing of valency angles. Apart from the fact that there is no very plausible theoretical reason for this arrangement,

it is clear that if there were any tendency towards it, symmetrical chelate groups such as ethylenediamine would be the most favourable for its development. Actually, as we have



seen, the only possible arrangement in $[\text{Pd en}_2]\text{Cl}_2$ is that corresponding to (II). For $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$, therefore, the evidence points strongly to "trans-pairing."

Tetramminoplatinous Chloride.—This substance is completely isomorphous with the preceding, but the earlier investigation (J., 1932, 1912) showed that the unit cell contained only one molecule, which therefore possessed full ditetragonal symmetry. In view of the preceding results, the work on the platinum compound was repeated, and it was found that the photographs with exceedingly long exposures showed weak reflexions corresponding to a larger cell containing four molecules. Thus the two tetrammines have exactly the same structure, although in the platinum compound the differentiation of the valencies must be very slight. (In this connexion it is significant that whereas two *cis*- and *trans*-isomerides of most platinous compounds, PtA_2X_2 , are known, apparently only one corresponding palladous compound can be obtained; evidently, the difference in the strength of the two pairs of bonds in palladium makes the one isomeride much less stable than the other.) The previously published description of tetramminoplatinous chloride needs modification as a result of this later work, although the earlier description is still very nearly correct. The principal correction (*loc. cit.*, p. 1918) is that "each platinum atom is surrounded by four ammonia groups in a rhombus, the angle of which is very slightly different from 90° " (instead of "in a square").

α -Diamminoplatinic Tetrachloride.—This substance also crystallises in the tetragonal system, and the molecule has three mutually perpendicular planes of symmetry. Consequently, the two ammonia groups must be *trans* to each other as shown (III), while the four chlorines may be arranged in a plane round the central atom in either of the ways (I) or (II). Here again, the second arrangement is much more satisfactory, *i.e.*, only the valencies which are *trans* to each other are equivalent.

Since this tetrachloride is obtained by direct chlorination of the α -diamminoplatinous dichloride, which in turn can be recovered by reduction of the tetrachloride, it seems highly probable that the dichloride has the planar *trans*-configuration (IV).



β -Diamminoplatinic Tetrachloride.—This substance crystallises in orthorhombic plates; on account of experimental difficulties, it was not possible to determine the molecular symmetry unequivocally. It appears that the molecule has not more than one element of symmetry, *i.e.*, a plane, an axis, or a centre. The usually accepted formulation for this substance is the un-ionised *cis*-structure (V), and this will satisfy the experimental requirements, if there is "trans-pairing" of valencies. With the same proviso, a planar *cis*-configuration with two chlorines ionised off would also be satisfactory, but the symmetry will not admit either of the *trans*-configuration (III), or of a tetrahedral arrangement with two chlorines ionised off. Thus, the β -dichloride obtained by reduction of this tetrachloride almost certainly has a planar *cis*-configuration, with the possibility of its being ionised.

Ammonium Chloropalladite.—This substance was investigated by Dickinson (*J. Amer. Chem. Soc.*, 1922, **44**, 2404), who found that the PdCl_4 ion consisted of four chlorine

atoms in a square round the palladium atom. In view of the results for the other substances described in this paper, we re-examined this salt but could find no evidence of any "pairing." The reason for this is evidently to be sought in the different distribution of shared electrons consequent upon the introduction into the central atom of two extra electrons from the ammonium ions.

The conclusions reached in this paper are in harmony with the majority of previous work on platinous and palladous amines; in particular, they offer an independent demonstration of the reality of the phenomena underlying Werner's hypothesis of "trans-elimination." The fact that corresponding palladous and platinous compounds apparently do not always react in the same way is probably merely a question of degree; our own results have shown that the differentiation of valencies does not occur to the same extent in the two metals.

A suggestion which has been made in the past (*e.g.*, Drew, J., 1932, 2328) is that in the complex ion of the tetrammine, the positive charges are located definitely on two nitrogen atoms. The differentiation of Pt-N or Pd-N bonds which we have described in this paper might, in certain cases, be ascribed to the supposed existence of positive charges on two of the nitrogen atoms only. This idea, however, is immediately invalidated by the fact that we find a differentiation of Pt-Cl bonds in the *neutral* complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$. There is also the objection that localisation of charges in complex ions should, if it exists, be a phenomenon of very general occurrence, *e.g.*, it should be observed in $\text{K}_2[\text{Pt}(\text{SCN})_6]$ or $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$, both of which have been examined by X-rays without any differentiation of valencies being observed. On the other hand, if the differentiation is ascribed to different distribution of electrons in the central atom, it is clear that the phenomenon will be entirely dependent on the nature of the central atom and its state of ionisation.

EXPERIMENTAL.

The X-ray investigations were carried out chiefly by means of single-crystal rotation and oscillation photographs, using $\text{Cu}_{K\alpha}$ radiation. Laue photographs were taken when necessary to confirm the symmetry.

Bisethylenediaminoplatinous Chloride.—Ethylenediaminoplatinous chloride was dissolved in ethylenediamine, and alcohol added. The precipitate was dissolved in the minimum of water, and evaporation over phosphoric oxide yielded colourless anhydrous crystals [Found: Pt, 50.5. Calc. for $\text{Pt}(\text{C}_2\text{H}_8\text{N}_2)_2\text{Cl}_2$: Pt, 50.5%]. They formed triclinic combinations of $a\{100\}$, $b\{010\}$, $c\{001\}$, and $Q\{011\}$, usually elongated in the b direction, sometimes tabular on $a\{100\}$. By a combination of X-ray and goniometric measurements, the elements were found to be $a = 8.37$, $b = 4.95$, $c = 6.86$ Å.U.; $\alpha = 100^\circ 46'$, $\beta = 111^\circ 40'$, $\gamma = 81^\circ 56'$; $a : b : c = 1.692 : 1 : 1.387$. The classification angles are $a(100) : c(001) = 69^\circ 21'$, $a(100) : b(010) = 94^\circ 30'$, $b(010) : q(011) = 30^\circ 53'$, and $q(011) : c(001) = 50^\circ 40'$; with one molecule in the unit cell, d (calc.) = 2.47 g./c.c. (Found: 2.3 approx.).

The pinakoidal symmetry was confirmed by the absence of pyroelectricity when tested by Martin's method (*Min. Mag.*, 1931, 22, 519). (A control experiment with a fragment of tourmaline showed a strong effect.) The space-group is therefore $P\bar{1}$ (C_1) and the complex ion $[\text{Pt} 2en]^{++}$ possesses a centre of symmetry.

The corresponding palladous salt is isomorphous with the above salt and has almost identical cell dimensions. It was prepared in a similar way [Found: Pd, 36.1. Calc. for $\text{Pd}(\text{C}_2\text{H}_8\text{N}_2)_2\text{Cl}_2$: Pd, 35.85%].

Tetramminopalladous Chloride.—The diammino-chloride was dissolved in hot aqueous ammonia, and the solution evaporated to dryness. Colourless prisms of the monohydrate, isomorphous with the corresponding platinum compound, were obtained [Found: Pd, 40.6. Calc. for $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$: Pd, 40.45%]; they are tetragonal combinations of $a\{100\}$ and $o\{111\}$, and from their development they appear to be either ditetragonal bipyramidal (D_{4h}) or trapezohedral (D_4). Laue photographs show full D_{4h} symmetry. Cell dimensions: $a = 14.30$, $c = 4.27$ Å.U. With four molecules to the cell, d (calc.) = 2.01 g./c.c. (Found: 1.94 approx.).

On rotation photographs about the a -axis the odd layer lines are very weak, indicating that the structure approximates to one based on a unit cell with $a = 7.15$ Å.U. and containing only one molecule. From the analysis of suitable oscillation photographs, it is found that the following planes do not reflect: (hkl) for $(h + k)$ odd, and (hhl) for h odd. The former indicates

that the c -face is centred. The space-groups giving these halvings are D_{4h}^5 , C_{4v}^2 , and D_{2d}^5 , and of these, only D_{4h}^5 ($P4/mbm$) is in agreement with the observed external symmetry. With this space-group and four molecules in the (base-centred) cell, the molecular symmetry (and therefore that of the complex ion) is either Q_h or C_4 , *i.e.*, three mutually perpendicular planes or a four-fold axis.

Tetramminoplatinous Chloride.—This was prepared in the same way as, and is isomorphous with, the palladium compound [Found: Pt, 55.1. Calc. for $Pt(NH_3)_4Cl_2 \cdot H_2O$: Pt, 55.4%]. Previous work (J., 1932, 1912) had shown that the symmetry is D_{4h} , and the cell dimensions $a = 7.38$, $c = 4.21$ Å.U. Prolonged exposures have now been found to give very faint intermediate layer lines on the a -axis rotation photographs, so that the cell dimensions are $a = 14.76$, $c = 4.21$ Å.U., corresponding closely with the palladium compound, the space-group and molecular symmetry being apparently the same. The deviation from D_{4h} symmetry in the platinum compound is, however, very small.

α -Diamminoplatinic Tetrachloride.—This compound was prepared by the action of chlorine on an aqueous solution of the corresponding dichloride [Found: Pt, 52.5. Calc. for $Pt(NH_3)_2Cl_4$: Pt, 52.6%]. Lemon-yellow tetragonal crystals, sometimes bipyramids, usually tabular on {001}, showing a positive uniaxial interference figure. The crystal class appears to be D_{4h} or D_4 . Rotation photographs gave $a = 5.72$, $c = 10.37$ Å.U., so, with two molecules in the unit cell, d (calc.) = 3.61 g./c.c. (Found: $3.3 < d < 3.9$).

From the analysis of oscillation photographs, the absent reflexions were found to be (okl) for ($k + l$) odd; the space-group is therefore D_{4h}^{14} ($P4_2/mnm$) and with two molecules in the cell the molecular symmetry is Q_h (three mutually perpendicular planes).

It was found that all (hkl) reflexions for which ($h + k + l$) is odd are either very weak or absent, showing that the lattice is very nearly body-centred. With this structure, each ammonia group is surrounded by eight chlorine atoms belonging to its own or adjoining molecules, and each chlorine is surrounded by four ammonias.

From a microscopic examination it appears that the bromide is isomorphous with the chloride.

β -Diamminoplatinic Tetrachloride.—This was prepared in a similar way to the α -compound [Found: Pt, 52.65. Calc. for $Pt(NH_3)_2Cl_4$: Pt, 52.6%]. It forms lemon-yellow orthorhombic plates, tabular on {010}, bounded by {101} and sometimes {100}. Owing to their thinness, the crystals are usually distorted, and on this account the cell dimensions could only be measured with an accuracy of about 2%, and the space-group was not determined. The cell dimensions are $a = 10.0$, $b = 11.2$, $c = 6.0$ Å.U. With four molecules to the cell, d (calc.) = 3.6 g./c.c. (Found: $3.3 < d < 3.9$).

Reflexions were observed from the planes (101), (111), and (110), so that the lattice is not centred in any way; since the crystals appear to be holohedral, each of the four molecules in the cell thus possesses one element of symmetry, *i.e.*, a plane, an axis, or a centre. A rotation photograph about the [101] axis showed very weak odd layer lines, indicating that the lattice is very nearly (010)-centred.

Microscopic examination suggests that the dibromide dichloride is isomorphous with the tetrachloride, as would be expected if the ammonias are in *cis*-positions.

Ammonium Chloropalladite.—The previous measurements (Dickinson, *loc. cit.*) were confirmed; the rotation photographs showed no intermediate layer lines even with prolonged exposures.

SUMMARY.

An X -ray examination has been made of several platinum and palladium amines.

Further proof of the planar configuration of these compounds has been obtained, and in addition it has been found that the valencies of the metal atom are not all equivalent, but are differentiated into pairs, those of each pair being *trans* to each other. This result supports the suggestion of paired valencies made by Drew, Pinkard, and Wardlaw (J., 1932, 1006), but shows that this suggestion is not incompatible with Werner's hypothesis of *trans*-elimination, which appears to have a definite physical basis.

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