36. *The Structure of β-(*cis-*)Diamminoplatinous Chloride : Evidence based on the Preparation of the Palladochloride.*

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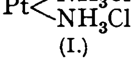
β-(*cis*-)Diamminoplatinous chloride gives, with potassium palladochloride, the salt $[Pt(NH_3)_2]PdCl_4$, from which the generators can be re-formed by treatment with an excess of aqueous potassium chloride. Hitherto, the occurrence of a salt of this type has been regarded as impossible, owing to the apparent lack of ionisation of the chlorine atoms of β-diamminoplatinous chloride. The salt may be compared with Magnus's salt, or with its analogue, $[Pt(NH_3)_4]PdCl_4$, and its preparation shows that β-diamminoplatinous chloride possesses potentially ionisable chlorine atoms, the structure *cis*-$Pt(NH_3Cl)_2$ being thus supported. The palladi-salt, $[Pt(NH_3)_2Cl]_2PdCl_6$, has also been prepared, in a nearly homogeneous state. The α- and the γ-form of diamminoplatinous chloride did not react with palladous chloride or potassium palladochloride under the conditions tried; nor did a number of other α- and β-platinammines.

The structure (I), advocated for β-diamminoplatinous chloride by Drew, Pinkard, Wardlaw, and Cox (J., 1932, 993), has been criticised on the ground that there was little evidence of the tendency towards ionisation of the chlorine atoms which would be expected if they were associated with the nitrogen atoms. This point is met by the assumption of a partial control of the valency electrons of nitrogen by the neighbouring unsaturated platinum atom (*loc. cit.*, p. 998), but it seemed probable that in certain circumstances the ions might become manifest. The object of the present work was to see whether β-diamminoplatinous chloride could simulate the behaviour of an admittedly ionised substance, such as $[Pt(NH_3)_4]Cl_2$ or $[Pt(NH_3)_3Cl]Cl$. These substances react with platinous and palladous chlorides or their salts in a well-known manner, of which the formation of Magnus's salt is an example :



$$Pt<\begin{matrix}NH_3Cl\\NH_3Cl\end{matrix}$$

(I.)

$$[Pt(NH_3)_2Cl]_2PdCl_6$$

(II.)

$$[Pt(NH_3)_2]PdCl_4$$

(III.)

$$[Pt(NH_3)_4]Cl_2 + K_2PtCl_4 = [Pt(NH_3)_4]PtCl_4 + 2KCl.$$

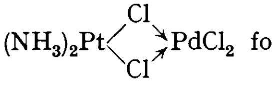
Similarly, the triammine gives $[Pt(NH_3)_3Cl]_2PtCl_4$; and the corresponding mixed pallado-plato-salts, *e.g.*, $[Pt(NH_3)_4]PdCl_4$, are readily prepared (Drew, Pinkard, Preston, and Wardlaw, J., 1932, 1896).

On treating palladous chloride in hydrochloric acid with an aqueous solution of β-diamminoplatinous chloride during some days, we obtained small jet-black plates of *bis-*(β-*chlorodiamminoplatinous*) *palladichloride* (II), probably formed by the oxidation in presence of hydrochloric acid of the corresponding palladochloride, $[Pt(NH_3)_2Cl]_2PdCl_4$, a small proportion of which appeared to be associated with it. The palladichloride is decomposed by hot water or hydrochloric acid, or by aqueous potassium chloride, into the original β-platodiammine chloride and chloropalladic acid (or the potassium salt) or its decomposition products. In the circumstances attending the preparation of (II), therefore, β-diamminoplatinous chloride behaves in the same manner as the triammine $[Pt(NH_3)_3Cl]Cl$.

However, when the palladichloride (II) was redissolved by heating in the original mother-liquor, a new salt separated on cooling. This was obtained quite pure and was shown to be β-*diamminoplatinous palladochloride* (III). It formed greyish-black, metallic-looking needles, having a bronzed reflex. With aqueous potassium chloride it was decomposed into its generators, and a similar action took place with hydrochloric acid.

The above reactions with palladous chloride in hydrochloric acid were repeated a number of times under different conditions. They are difficult to carry out, owing to the well-known tendency towards oxidation of the β-platodiammine compounds in the presence of this acid and also to the simultaneous production of both palladous and palladic compounds. It was found, however, that the action of the β-platodiammine on potassium palladochloride gave (III) without complication, the preparation of this substance being thus greatly simplified. In the production of (III), therefore, the β-platodiammine behaves like a platotetrammine, the reaction being reversible :

$$[Pt(NH_3)_2]Cl_2 + K_2PdCl_4 \rightleftharpoons [Pt(NH_3)_2]PdCl_4 + 2KCl.$$

The foregoing reactions of β-diamminoplatinous chloride show that it can behave as if it had either of the formulæ $[Pt(NH_3)_2]Cl_2$ and $[Pt(NH_3)_2Cl]Cl$. Formula (I), which represents the chlorine atoms as being potentially ionisable from the nitrogen atoms, is compatible with both of the above formulæ, either both chlorine atoms or one becoming ionised. An alternative hypothesis would be to regard the chlorine atoms as ionisable from platinum, against which must be set the failure of α-diamminoplatinous chloride and its γ-isomeride to react with palladous chloride, and also their failure to give the reactions (see below) which characterise the β-isomeride. Formulæ showing chlorine co-ordinated with palladium, as  $(NH_3)_2Pt{<}\begin{matrix}Cl\\Cl\end{matrix}{\rightarrow}PdCl_2$ for (III), appear unlikely, since other β-platodiammines and their α-isomerides should then react in the same way and this is not the case.

It has already been shown (Drew and Wyatt, J., 1934, 56; Saenger and Wardlaw, *ibid.*, p. 182) that β-$Pt(NH_3)_2Cl_2$ has the nitrogen atoms disposed in *cis*-positions about platinum, and that this β-diammine differs from the α- and γ-isomerides in its behaviour in forming (1) Cossa's ammonium salt with hydrochloric acid, (2) the greenish-black diamminodichloroplatosulphuric acid with concentrated sulphuric acid (Drew, J., 1934, 1793), and (3) the purplish-black complex with phenoxtellurine dibisulphate (Drew, *loc. cit.*). The reactions described in the present paper have the same implication, but on account of their simplicity they present the issue in a clearer light.

Finally, it has been pointed out (Drew and Tress, J., 1933, 38; 1935, 1212) that among the β-platodiammine dichlorides there are to be found two types : (*a*) those (*e.g.*, β-$Pt\,etn_2Cl_2$ and $Pt\,enCl_2$) which do not give the reactions with hydrochloric acid, sulphuric acid, and phenoxtellurine dibisulphate, and presumably have the chlorine atoms attached to platinum, and (*b*) the much smaller class which show the three reactions to a greater or less extent, and, in at least a proportion of their molecules, have the chlorine atoms attached to nitrogen. Of the latter class, β-$Pt(NH_3)_2Cl_2$ is the only member so far described which shows each of the reactions in a very pronounced manner, and its character must, therefore, be regarded as somewhat exceptional. A number of β-diammines of the first type were tried, and all failed to react with palladous chloride; several other α-diammines likewise failed to react.

EXPERIMENTAL.

Bis-(β*-chlorodiamminoplatinous*) *Palladichloride* (II).—Palladous chloride (5—7 parts by wt.) was dissolved in just sufficient warm concentrated hydrochloric acid, and to the solution was added a saturated solution of β-$Pt(NH_3)_2Cl_2$ (1 part) in boiling water. The mixture was heated to boiling and allowed to cool, with stirring. Part of the β-dichloride separated unchanged, but after about ½ hour voluminous black plates began to separate; after 1—5 days' standing, according to the concentrations used, the whole of the separated material consisted of (II). The above conditions gave a maximum yield, but others may be employed allowing different periods of reaction. If the solutions are too dilute, the reaction occurs over a very protracted period and may be incomplete, and if too much β-diammine is used, part of it is gradually oxidised to β-diamminoplatinous tetrachloride, which forms a troublesome impurity. The following is an example of a favourable mixture : 0·9 g. of palladous chloride in 2·25 c.c. of concentrated hydrochloric acid; 0·15 g. of β-$Pt(NH_3)_2Cl_2$ in 10·5 c.c. of water. When the change was complete, the product was filtered off, washed with 15% hydrochloric acid and then with water, and dried over phosphoric oxide (additional washing with alcohol and ether gave the same result). [The palladous chloride used in the above reactions was obtained by dissolving the metal in concentrated nitric acid, evaporating to dryness, and then evaporating three times with concentrated hydrochloric acid, brownish-black prisms being left.] The *palladichloride* (II) consisted of microscopic jet-black plates, grey or black in bulk, and black when powdered; when contaminated with the β-diammine it appeared greenish-black; if the period of reaction was longer than 7 days, contamination with (III) was liable to occur. When warmed on the water-bath with dilute hydrochloric acid or aqueous potassium chloride, it was decomposed quantitatively into β-$Pt(NH_3)_2Cl_2$ and probably a mixture of pallado- and palladi-chloric acids (or their potassium salts), with partial loss of chlorine; the filtrates from β-$Pt(NH_3)_2Cl_2$ showed chemiluminescence with an alkaline solution of 5-aminophthalaz-1 : 4-dione. When warmed with water, it dissolved and was decomposed in the same manner, a little β-$Pt(NH_3)_2Cl_2$ first separating on cooling, and then long metallic-looking needles of (III) produced by recombination of the remaining constituents. Little or no production of β-$Pt(NH_3)_2Cl_4$ appeared to occur in these decomposition reactions. Numerous analyses of different preparations of (II) were carried out, of which the following may be quoted :

	Pd + Pt.	Pd.	Pt.	N.	Cl.
Found (1st sample), %	57·6	12·3	45·5	7·8	29·9
Found (2nd sample), %	57·9	13·15	46·05	7·5	32·25
$H_{12}N_4Cl_8PdPt_2$ requires	58·5	12·55	45·95	6·6	33·45

(The determination of Pd + Pt was independent of the separate determinations of Pd and of Pt.) The results for the two samples give the ratios of atoms: N : Cl : Pd : Pt = 4·8 : 7·2 : 1·0 : 2 and 4·5 : 7·7 : 0·9 : 2, respectively, showing that the substance was substantially (II), probably contaminated with a little $[Pt(NH_3)_2Cl]_2PdCl_4$.

β*-Diamminoplatinous Palladochloride* (III).—The second of the following methods of preparation gave a rather better result, since all chance of contamination with β-$Pt(NH_3)_2Cl_4$ was absent : (1) The preparation of (II) was carried out, but the precipitate, instead of being filtered off, was redissolved in the mother-liquor by heating for about ½ min.; on standing, the solution deposited (III) in clusters of needles, which were washed and dried as in the case of (II). (2) A saturated solution of potassium palladochloride (about 6 parts by wt.) in cold water was treated with a solution of β-$Pt(NH_3)_2Cl_2$ (1 part) in boiling water, and the mixture allowed to cool : after some days, long lustrous needles of (III) were produced, which were washed and dried as before. The change was first apparent after about 20 minutes, but reaction was never complete in less than 4 days; with dilute solutions the change was not completed even after long standing. The *palladochloride* (III) formed clusters of greyish-black needles with dark copper-like bronze; when warmed with water or dilute hydrochloric acid, it broke up into β-$Pt(NH_3)_2Cl_2$ and H_2PdCl_4, the latter being partly hydroxylated when water was used; partial recombination to (III) took place on standing. With warm aqueous potassium chloride, reversal of the reaction described under the second method of preparation occurred. The analyses were as follows :

	Pd + Pt.	Pd.	Pt.	N.	Cl.
Found (preptn. 1, two samples), % ...	63·0, 62·95	21·85	40·15, 40·8	6·3	31·25, 30·4
Found (preptn. 2), %	63·0	21·85	40·7	5·9	30·1
$H_6N_2Cl_4PdPt$ requires	63·15	22·35	40·8	5·85	29·75

Methods of Analysis.—Pd + Pt was determined by the micro-muffle method. The separate determination of platinum was made by weighing the β-$Pt(NH_3)_2Cl_2$ produced on decomposition of the sample (20—40 mg.) with aqueous potassium chloride (0·5—0·8 c.c.); the separate determination of palladium was made by precipitating the above filtrate from β-$Pt(NH_3)_2Cl_2$ with an excess of a 1% solution of α-dimethylglyoxime in 95% alcohol, the precipitate being thoroughly washed with water to remove any potassium chloride. It was found that the dimethylglyoxime method of precipitating palladium was inaccurate if water or hydrochloric acid was used to decompose either of the substances (II) and (III); but the results were trustworthy in neutral solution, as was shown by comparative trials with potassium palladochloride. Precipitation of the palladium as $[Pt(NH_3)_4]PdCl_4$ gave low results.

We noticed during the present work that potassium palladichloride (but not the palladochloride) produced a momentary chemiluminescence when added to an alkaline solution of 5-aminophthalaz-1 : 4-dione; none of the diamminoplatinous chlorides produced a luminescence in this way; but substance (II) did so, showing that it contains palladic palladium. Potassium platinichloride and both the red and the green form of $Pt\,etn_4Br_3$ (J., 1935, 1245) gave the above chemiluminescence.

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