332. *The Behaviour of Chelate Groupings Attached to Platinum and to Palladium.*

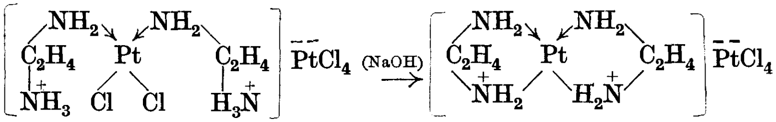
By H. D. K. DREW.

DICKINSON has shown that the anions of crystalline K_2PdCl_4 and K_2PtCl_4 are planar, and Cox (this vol., pp. 1015, 1912) that the kation of $[Pt(NH_3)_4]Cl_2$ is likewise planar. If, however, it be assumed from this that the kations of pallado- and plato-tetrammines, generally, are planar in form, it must follow that those tetrammines which contain a chelate group are all *cis*-compounds; for chelate groups admittedly cannot span *trans*-positions in a planar formula. It is shown in the present paper that, whereas in the degradation of pallado-tetrammines containing chelate groups *cis*-elimination of groupings takes place exclusively (this vol., p. 1902), in the degradation of plato-tetrammines containing the same groups *trans*-elimination occurs. Either, therefore, the tetrammines cannot be all of planar structure, or Werner's principle of the *trans*-elimination of groups is not valid. In either event it must follow that something more than a stereochemical reason is required to account for the fact that only certain of the possible combinations of groupings are set free in any particular case. The theory already advanced (this vol., pp. 1006, 1903) is independent of any stereochemical assumption as to the forms of the tetrammines and is the only theory which accounts for the whole of the facts.

Jörgensen (1889) prepared from potassium chloroplatinite and ethylenediamine the yellow compound, Pt en Cl_2, which is a β-diammine because with ammonia it gives a β-tetrammine, $[Pt(NH_3)_2\,en]Cl_2$, identical with that prepared from β-$Pt(NH_3)_2Cl_2$ and ethylenediamine. Similarly, with ethylenediamine Pt en Cl_2 gives $[Pt\,en_2]Cl_2$, which is likewise of β-structure. It is now found that, when treated with hydrochloric acid, the latter tetrammine eliminates an α-pair of linkings giving the *dihydrochloride*,

$PtCl_2(NH_2{\cdot}C_2H_4{\cdot}NH_3Cl)_2$ (I), which forms a red *plato-salt*, $[PtCl_2(NH_2{\cdot}C_2H_4{\cdot}NH_3)_2]PtCl_4$ (II). This is confirmed by the behaviour of $[Pt(NH_3)_2\,en]Cl_2$, which similarly gives the *monohydrochloride*, $PtCl_2(NH_3)(NH_2{\cdot}C_2H_4{\cdot}NH_3Cl)$, forming a lilac *plato-salt*, $[PtCl_2(NH_3)(NH_2{\cdot}C_2H_4{\cdot}NH_3)]_2PtCl_4$.

When the dihydrochloride (I) is treated with cold dilute caustic soda the chelate loops close up again, with loss of two molecules of hydrogen chloride, forming the β-tetrammine, $[Pt\,en_2]Cl_2$ (above) which gives a violet plato-salt, $[Pt\,en_2]PtCl_4$ (III). Similarly, the red plato-salt when brought into contact with dilute alkali closes up again, without dissolving, into the above violet plato-salt :



(II.) (III.)

The red plato-salt (II) is clearly a substitution product of $(NH_4)_2PtCl_4$, two hydrogen atoms of the latter having been replaced by the bivalent grouping $PtCl_2(NH_2{\cdot}C_2H_4{-})_2$, and therefore the positive charges are associated with the nitrogen atoms, as is further shown by the marked solubility of the salt in warm water. During the closure shown in the scheme above, the anionic grouping $PtCl_4''$ remains unaltered, and therefore the chlorine atoms removed are those of the $PtCl_2$ grouping of the kation. Thus, unless a rearrangement of charges takes place during the closure, it must follow that the positive charges of the kations of the plato-salts are located upon nitrogen atoms in α-positions. A similar argument applies to the tetrammine itself.

EXPERIMENTAL.

β-Pt en Cl_2 was prep. by the action of cold aq. ethylenediamine upon K_2PtCl_4 aq., the yellow ppt. being filtered off before the deposition upon it of a reddish impurity had begun. The product before recrystn. consisted of yellow rectangular needles (A) which gave a feeble red coloration with phenoxtellurine dibisulphate; when cryst. from H_2O or from dil. HCl aq., it consisted of similar needles (B) of lighter shade, which no longer gave a coloration with phenoxtellurine dibisulphate and were somewhat less sol. in boiling H_2O (1 g. dissolves in about 115 c.c.) (Found : in A, Pt, 59·85; in B, C, 7·55; H, 2·55; N, 8·7; Pt, 59·75. Calc. : C, 7·35; H, 2·45; N, 8·6; Pt, 59·85%). The obs. mol. wt. of B in boiling H_2O (M, 300—400) indicated that the compound was monomeric, but the elevation of b. p. was only about 0·01°.

β-$[Pt\,en_2]Cl_2$ was prep. by the action (4 weeks at room temp. or 1 hr. at 100°) of aq. ethylenediamine upon the above diammine, both specimens (A and B) of the latter giving the same product. The tetrammine forms colourless, massive, rhomboidal prisms or long needles from H_2O, from which it crystallises readily; it is anhydrous (Found : Pt, 50·0, 50·7. Calc. : Pt, 50·5%). The action of ethylenediamine aq. upon α-Pt$(NH_3)_2Cl_2$ invariably gave this tetrammine, whether carried out at room temp. or with heating; even when only 1 mol. of ethylenediamine was used, NH_3 was still displaced (Found: Pt, 50·1; 50·55%). The tetrammine forms a plato-salt (III) consisting of lilac-violet, rectangular needles or plates, comparatively sparingly sol. in boiling 5*N*-HCl; it is not blackened when heated to 260° (Found: Pt, 59·55, 60·0. Calc.: Pt, 59·85%).

Action of Hydrochloric Acid upon β-[Pt en$_2$]Cl$_2$.—When the tetrammine was dissolved in a little H_2O, and the solution mixed with much conc. HCl and heated at 100° during 6—9 hrs., the cooled solution deposited a pale-yellow ppt. consisting mainly of (I) (yield *ca.* 45% of theoretical), together with β-Pt en Cl_2 (yield 14%). These two substances were readily separated, only the former being sol. in cold H_2O (Found in the β-Pt en Cl_2: Pt, 59·6, 60·0, 60·0. Calc.: Pt, 59·85%). Evidence has been obtained that the small proportion of β-Pt en Cl_2 is the result of a secondary reaction involving closure of an open chain. [Pt(en H)$_2$Cl$_2$]Cl$_2$ (I) formed minute pale cream-yellow needles, readily recryst. from dil. HCl (Found: C, 10·6; H, 3·95; Pt, 43·1, 42·75. $C_4H_{18}N_4Cl_4Pt$ requires C, 10·45; H, 3·9; Pt, 42·5%). The *dihydrochloride*, which gives no coloration with phenoxtellurine dibisulphate, changes again into β-[Pt en$_2$]Cl$_2$ when treated with a little NaOH aq. or ethylenediamine, but not when treated with ethylenediamine dissolved in dil. HCl. It gives a red *plato-salt* (II), stout, hexagonal needles or complex prisms, readily sol. in hot dil. HCl and even in hot H_2O (Found: C, 6·75; H, 2·6; Pt, 54·1, 53·7. $C_4H_{18}N_4Cl_6Pt_2$ requires C, 6·6; H, 2·5; Pt, 53·8%). When this plato-salt is moistened with cold dil. NaOH it at once changes into the violet salt (III).

Action of Aqueous Ammonia upon β-Pt en Cl_2.—A number of expts. under different conditions were carried out on both specimens (A and B) of the diammine. These are briefly summarised below.

(*a*) The diammine (A) dissolved in excess of conc. NH_3 aq. in 3—5 days at room temp. or in 1 hr. when warmed. On evaptn., the liquid left a cryst. residue of the mixed tetrammine.

β-Diamminoethylenediaminoplatinous chloride, prep. in this manner, separated from aq. EtOH in thin, colourless rectangular or hexagonal leaflets of pearly lustre (Found: Pt, 54·65, 53·8, 54·4, 54·6, 54·4, 54·58. $C_2H_{14}N_4Cl_2Pt$ requires Pt, 54·2%). It gave a *plato-salt*, forming lustrous, pale lilac-blue, woolly bundles of slender pointed needles, unaltered when recryst. from dil. HCl (Found: C, 4·1; H, 2·3; Pt, 62·0, 62·2. $C_2H_{14}N_4Cl_4Pt_2$ requires C, 3·8; H, 2·2; Pt, 62·35%). There was some evidence that the above mixed tetrammine forms a dihydrate when cryst. from H_2O alone.

(*b*) When the diammine (B) was treated in the above manner, it dissolved more slowly (about 10 days at room temp.). The mixed tetrammine was then obtained, after recrystn. from aq. EtOH, in large, colourless, square-ended or hexagonal prismatic needles, or in cubic crystals, not having a pearly lustre (Found: C, 6·8; H, 3·95; Pt, 54·1, 54·6%). Some evidence that a monohydrate exists was also obtained. The mixed tetrammine, thus prep., gave a purplish-violet plato-salt crystallising in short, dense, flat, rectangular prisms, retaining this form on recrystn. from dil. HCl; this salt blackened without melting on being heated to 200—240° (Found: C, 4·3; H, 2·4; Pt, 62·35%).

Action of Aqueous Ethylenediamine on β-Pt$(NH_3)_2Cl_2$.—The β-plato-diammine dissolved in excess of aq. ethylenediamine in about a week at room temp., the mixed tetrammine obtained being then of nacreous appearance and similar to that under (*a*) above (Found : Pt, 53·95%). It gave a plato-salt also similar to that under (*a*) (Found : Pt, 62·2%). When, however, the β-plato-diammine was dissolved in hot NH_3 aq., the mixed tetrammine and its plato-salt approximated more closely in appearance to those obtained under (*b*).

The differences between the two ' forms ' of mixed tetrammine, and of their plato-salts, obtained in the foregoing expts. were so slight as to suggest that the substances are really identical in the ordinary sense of the term. Their solubilities did not appear to be independent. The ' forms ' in each case seemed to be related much as are the two forms of a dimorphous substance, except that they did not appear to be interchangeable. The absence of the latter property might be due to an impurity in one of them ; but this hypothesis is not entirely satisfactory and crystallographic work is being carried out to decide the point. Similar remarks apply to the two specimens (A and B) of the β-plato-diammine.

Action of Hydrochloric Acid on β-[Pt en $(NH_3)_2]Cl_2$.—When the mixed tetrammine was dissolved in a little cold H_2O and heated for 8 hrs. at 100° with a large excess of conc. HCl, a test sample of the liquid gave no ppt. with K_2PtCl_4. On cooling, a cryst. yellow ppt. of the *monohydrochloride* (below) in an almost pure state was obtained ; a second crop, which separated later from the mother-liquor, was found to consist of the same substance contaminated with β-Pt en Cl_2 (yield, 4%). The total yield of the monohydrochloride was 50%.

[Pt(en H)$(NH_3)Cl_2]Cl$ was a yellow cryst. powder, fairly readily sol. in cold H_2O ; it was crystallised from 5*N*-HCl and dried over solid KOH and P_2O_5 (Found : Pt, 51·65. $C_2H_{12}N_3Cl_3Pt$ requires Pt, 51·4%). It gave no coloration with phenoxtellurine dibisulphate and was blackened by NaOH aq. The substance gave a *plato-salt*, which formed very thin, silky, lilac-pink, square plates, readily sol. in boiling H_2O and giving a brilliant red coloration with phenoxtellurine dibisulphate (Found: C, 4·9 ; H, 2·4 ; Pt, 57·1. $C_2H_{12}N_3Cl_5Pt_2$ requires C, 4·7; H, 2·35; Pt, 57·1%).

Summary.

(1) The ethylenediamino-group cannot span the α-positions in the case of platinum, but can do so with palladium.

(2) In the case of platinum, this chelate group can be opened and closed again by suitable reactions in a manner which agrees with the theory given in former papers. In the case of palladium, the behaviour of the chelate group has already been shown to be entirely different, but still in accord with the theory.

(3) Werner's theory of *trans*-elimination of the ammine groups of tetrammines cannot hold for both platinum and palladium.

(4) It is deduced that the positive charges of plato-tetrammines, and of their plato-salts, probably reside upon the α-pairs of nitrogen atoms and not upon platinum.

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