311. Some New Types of Chelated Platinammines.

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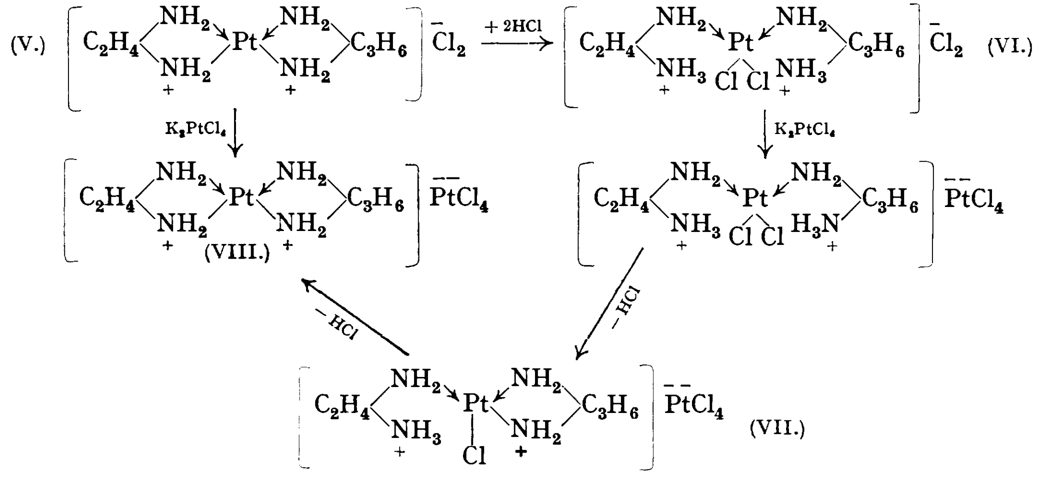
This paper describes platinammines containing the following diamines, in which the hydrocarbon chain increases regularly by CH_2 as the series is ascended: ethylenediamine (en); trimethylenediamine (tr); tetramethylenediamine (te); pentamethylenediamine (pe). The α-positions are defined as those occupied by the nitrogen atoms in α-$Pt(NH_3)_2Cl_2$; the β-positions as those occupied in β-$Pt(NH_3)_2Cl_2$. We wished to find whether it was possible to insert large chelate loops across the β-positions of the bivalent platinum atom; and also whether the α-positions, never yet shown to be bridged, could be spanned by sufficiently large groups. The results proved that with en and tr the chelate loops span the β-positions, giving sparingly soluble β-diammines of normal type; but that on passing to te and pe a sudden change in the character of the products occurs, only ill-defined insoluble substances being obtained. It appears, therefore, that te and pe are unable to form loops at a single platinum atom, presumably because this would involve the setting up of highly strained seven- and eight-membered rings; hence, these diamines probably act as bridges between pairs of platinum atoms, giving chain-like structures of high molecular weight. The formation of five- and six-membered rings containing a platinum atom is, however, feasible, and therefore en and tr are able to give normal monomeric compounds. In none of the cases examined were we able to isolate a platinammine having a chelate group stretched across the α-positions of a single platinum atom, and therefore it must be concluded that such an arrangement is not to be brought about by increasing the apparent length of a diamine chain.

The mixed and unmixed trimethylenediaminoplatinammines have been studied at length, and as a result it is now for the first time possible to present a complete scheme, verified by experiment at each stage, for the degradation of a chelate platotetrammine through the triammine to the diammine.

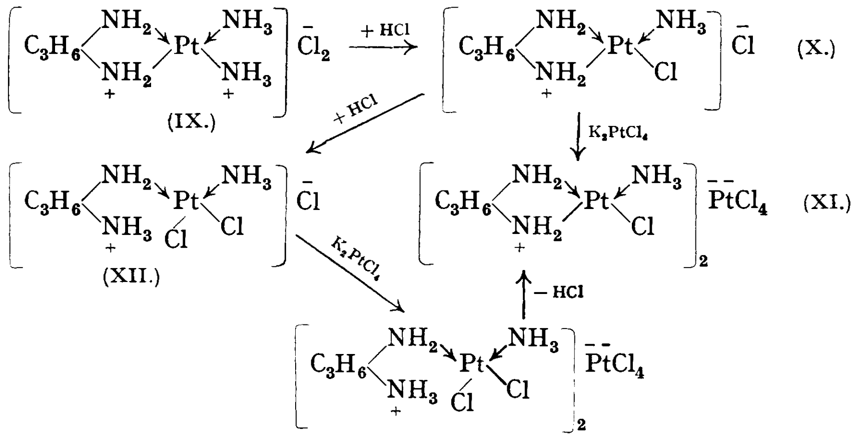
Trimethylenediaminoplatinous chloride, $Pt\,tr\,Cl_2$ (I), is a yellow substance which must have a β-structure with respect to the disposition of the nitrogen atoms, both because it was prepared from tr and aqueous potassium chloroplatinite, a method which gives β-diammines in all known cases, and because of the nature of its interaction with ammonia, as explained below. With further diamine, (I) gave the colourless tetrammine, *bistrimethylenediaminoplatinous chloride*, $[Pt\,tr_2]Cl_2$ (II), which must likewise be of β-structure. Decomposition of (II) with hydrochloric acid opened both chelate loops, showing by analogy with other tetrammines that elimination occurs at α-positions, and produced the colourless *dihydrochloride* of an α-diammine, $[PtCl_2(tr\ H)_2]Cl_2$ (III). Simultaneously, however, about one-fourth of (II) was converted into (I). The structure of (III) is verified by its interaction with potassium chloroplatinite to give a solution of the unstable plato-salt, which lost 2 mols. of hydrogen chloride and became transformed into the flesh-pink *plato-salt*, $[Pt\ tr_2]PtCl_4$ (IV), identical with that obtained directly from (II).

The behaviour of (II) towards hydrochloric acid was confirmed by a comparison with the colourless mixed dichelate β-tetrammine, *ethylenediaminotrimethylenediaminoplatinous chloride*, $[Pt\ en\ tr]Cl_2$, (V). This substance was the same whether prepared from (II) and ethylenediamine or from ethylenediaminoplatinous chloride and trimethylenediamine, showing that the principle of the equivalence of the two pairs of β-positions about a platinum atom holds also for chelate groups. With hydrochloric acid, (V) gave the colourless *dihydrochloride* of a mixed α-diammine, $[PtCl_2(en\ H)(tr\ H)]Cl_2$, (VI), showing that again both chelate loops had been opened. The structure of (VI) was verified by preparing a solution of its unstable plato-salt, which on evaporation lost 2 mols. of hydrogen chloride in succession, giving (i) the pinkish-brown *plato-salt* of the *monohydrochloride* of a triammine, $[PtCl(en\ H)(tr)]PtCl_4$ *or*, less probably, $[PtCl(en)(tr\ H)]PtCl_4$, (VII); and (ii) the pink *plato-salt*, $[Pt\ en\ tr]PtCl_4$, (VIII), identical with that prepared directly from (V).



At the same time, however, about one-fourth of the initial substance (V) was converted into a mixture of $Pt\ tr\ Cl_2$ and $Pt\ en\ Cl_2$, the former predominating (3 mols.: 1 mol.).

When $Pt\ tr\ Cl_2$ (I) was treated with ammonia it gave the colourless mixed tetrammine, *diamminotrimethylenediaminoplatinous chloride*, $[Pt(NH_3)_2tr]Cl_2$, (IX), which was shown to be of β-structure by preparing it also from the β-diammino-chloride and trimethylenediamine, whereas the action of the latter base upon the α-diammino-chloride caused the complete displacement of ammonia and the production of (II). The regulated degradation of (IX) by means of 6*N*-hydrochloric acid at 100° proceeded in two stages. (i) An ammonia molecule was first removed, giving rise to the colourless mixed triammine, *amminotrimethylenediaminoplatinous chloride*, $[PtCl(NH_3)tr]Cl$, (X), which was shown to possess only one ionised chlorine atom by preparing from it the pinkish-brown *plato-salt*, (XI). The triammine (X) is of much interest, since it is the only known triammine containing a chelate group; moreover, its isolation verifies what has hitherto been only a probable hypothesis, *viz.*, that the diammines are produced from the tetrammines and hydrochloric acid by way of the triammines. (ii) More prolonged action then caused the opening of the chelate loop, with the production of the yellow *monohydrochloride* of a mixed α-diammine, $[PtCl_2(NH_3)(trH)]Cl$ (XII), also obtained by the direct action of hydrochloric acid on (X). The structure of (XII) was verified by preparing a solution of its unstable plato-salt, evaporation of which caused the loss of 2 mols. of hydrogen chloride, with transformation into the plato-salt (XI), identical with that produced directly from (X) and potassium chloroplatinite.



At the same time, about one-fourth of (IX) was converted into Pt tr Cl_2; and a similar proportion of (X) was transformed into this β-diammine in the more direct experiment.

There can be no doubt that in (III), (VI), and (XII), and in their plato-salts, the positive charges of the kations are associated with the nitrogen atoms, because these compounds are derivatives of ammonium chloride and of ammonium chloroplatinite respectively. It is almost equally certain from the above reactions that in the triammines and tetrammines themselves the charges are located upon the nitrogen atoms as in the graphic formulæ above. The main reaction of hydrochloric acid upon the tetrammines takes place, therefore, at the charged nitrogen atoms (*i.e.*, in the α-positions), first one and then the second nitrogen uniting with hydrogen and becoming detached from platinum, whilst retaining the positive charge; the entering chlorine atoms replace the nitrogen atoms of the α-positions.

The production of β-diammines from the tetrammines in the three cases given here cannot yet be accounted for. The only other recorded cases of this kind of reaction among platinammines are those in which Pt en Cl_2 results from [Pt en_2]Cl_2 and from [$Pt(NH_3)_2$en]Cl_2 (Drew, J., 1932, 2330), where the behaviour was attributed to a secondary reaction involving closure of an open chain. This explanation, although it agrees with the fact that only chelate tetrammines show this exceptional behaviour, can no longer be regarded as valid in view of the fresh fact that the intermediate triammine (X) gave with hydrochloric acid both (XII) and Pt tr Cl_2, whereas (XII) was stable to hydrochloric acid under the same conditions and so cannot be a stage in the production of the Pt tr Cl_2. It must be accepted that with chelate plato-tetrammines and -triammines a proportion of β-elimination can occur.

The lemon-yellow *plati-diammines* Pt en Cl_4 and Pt tr Cl_4 and the colourless *plati-tetrammines* of the formula $[PtCl_2X_4]Cl_2$, where the four co-ordination positions (X_4) were filled by $4NH_3$, $2NH_3$ + tr, 2en, en + tr, or 2tr, were prepared from the corresponding plato-ammines by boiling their solutions in hydrochloric acid with hydrogen peroxide for a few moments. The first of these ($X_4 = 4NH_3$), which has been variously described in a yellow and a white form (Gmelin–Kraut, " Handbuch der anorganische Chemie," 1915, Vol. 5, Part 3, p. 669), appeared to exist in only one form, colourless when pure; it was much less soluble in water than the chelated plati-ammines, the last three of which separated as hydrates from water. The brownish-red plato-salt, $[PtCl_2(NH_3)_4]PtCl_4$, was similarly less soluble than the yellow or brown *chloroplatinites* of the chelated plati-tetrammines. The chelated plati-ammines were also obtained from solutions of the plato-ammines in dilute hydrochloric acid by oxidation in air, and for this reason air was excluded as much as possible in experiments where such oxidation might occur.

An unexpected change took place when Pt en Cl_4 was treated with hot aqueous

$[Pt(NH_3)_4]Cl_2$, a well-defined red crystalline substance (XIII) being precipitated; it proved to be identical with the substance formulated as Pt en Cl_3 by Tschugajeff and Tschernjajeff (*Z. anorg. Chem.*, 1929, **182**, 159), who obtained it by oxidising Pt en Cl_2 with ammonium persulphate and aqueous hydrochloric acid. We found that (XIII) could be oxidised to Pt en Cl_4 by means of hydrogen peroxide in presence of hydrochloric acid, and reduced to Pt en Cl_2 by means of aqueous potassium oxalate. The following equilibria were assumed: the first in order to explain the repeated separation of (XIII) from the mother-liquor in its preparation, and the second to explain the reduction of (XIII) to Pt en Cl_2 by means of $Pt(NH_3)_4Cl_2$ and the partial oxidation of Pt en Cl_2 to (XIII), here written as (Pt en $Cl_3)_2$, by means of aqueous $[PtCl_2(NH_3)_4]Cl_2$:

$$2\text{Pt en Cl}_4 + \text{Pt(NH}_3)_4\text{Cl}_2 \rightleftharpoons \text{Pt(NH}_3)_4\text{Cl}_4 + (\text{Pt en Cl}_3)_2$$
$$2\text{Pt en Cl}_2 + \text{Pt(NH}_3)_4\text{Cl}_4 \rightleftharpoons \text{Pt(NH}_3)_4\text{Cl}_2 + (\text{Pt en Cl}_3)_2$$

(XIII) is too sparingly soluble to allow of a determination of its molecular weight, so that whether it is a derivative of tervalent platinum or is a dimeride containing platinic platinum remains undetermined; in any case, it is clearly an analogue of the two salts which have previously been formulated as $[Pt(NH_3)\,py\,Cl_3]_2$ and $[Pd(NH_3)_2Cl_3]_2$ (J., 1932, 1013, 1898). For comparison, we prepared the unstable buff-coloured *bisethylenediaminoplatinous chloroplatinate*, $[Pt\,en_2]PtCl_6$, and also the buff-coloured *dichlorobisethylenediaminoplatinic chloroplatinite*, $[PtCl_2en_2]PtCl_4$, which were quite different.

When Pt tr Cl_4 was similarly treated with tetramminoplatinous chloride, the latter was oxidised to tetramminoplatinic chloride and only Pt tr Cl_2 was obtained along with it.

α-$Pt(NH_3)_2Cl_2$ differs from its β-isomeride in giving no coloration with phenoxtellurine dibisulphate and in failing to react directly with hot hydrochloric acid, whereas the β-salt yields a deep purple phenoxtellurine complex and with hydrochloric acid readily gives Cossa's ammonium salt. We have already shown that only the β-forms of Pt en Cl_2 and Pt tr Cl_2 exist, and that the nitrogen atoms in these substances have undoubtedly the same stereochemical relationship as those in β-$Pt(NH_3)_2Cl_2$. There may, nevertheless, be a structural difference between the chelated β-plato-diammines and β-$Pt(NH_3)_2Cl_2$, and this possibility is to some extent supported by the fact that the chelated β-diammines give no phenoxtellurine compounds. To obtain further evidence, we tried to prepare the analogues of Cossa's salts from the above chelated β-plato-diammines, but were unsuccessful; instead, on treatment with *N*-hydrochloric acid, β-Pt tr Cl_2, which should have given either the intermediate hydrochloride $[PtCl_2\,(trH)]Cl$ or the Cossa's salt $PtCl_3(tr\,H)$, was unchanged except in so far as it suffered atmospheric oxidation to *trimethylenediaminoplatinic chloride*, Pt tr Cl_4; similarly, the ethylenediamino-analogue was merely oxidised. With 6*N*-hydrochloric acid, however, a proportion of each plato-diammine was transformed into the simple chloroplatinite, *e.g.*, $[tr\,H_2]PtCl_4$, part of the rest remaining unchanged and part undergoing oxidation. There thus remains a possibility that the β-plato-diammines may act as tautomeric substances, those with chelate groups having a greater tendency to assume a form in which the chlorine atoms are linked directly to platinum.

In the formulæ in this paper we make no assumption with regard to the spatial distribution of the bonds to platinum, preferring to leave this question until further evidence is available. In all cases, the pairs of α-positions are written in the same horizontal line above or below the platinum atom, those of β-positions in the same vertical line on either side of that atom. If plane formulæ be adopted for the tetrammines, the pairs of α-positions will, of course, be at the ends of the two diagonals. The experimental evidence shows that the links between platinum and the four nitrogen atoms of a plato-tetrammine cannot all be of the same kind. In the formulæ given, two kinds of nitrogen–platinum links are distinguished according as the nitrogen atom (*a*) bears a full charge, $\overset{+}{N}$–Pt, owing to its association with the anion, or (*b*) shares its lone pair of electrons to an unknown extent with the platinum, this being denoted by N ⟶ Pt (cf. Sidgwick) in order to avoid the use of a new symbol which could not yet be defined exactly.

EXPERIMENTAL.

All substances were dried over phosphoric oxide in a vacuum before analysis.

Trimethylenediamine was prepared almost quantitatively by Gabriel's method. Potassium phthalimide was condensed with trimethylene bromide in nitrobenzene for 1—2 hours at 170—180°, and the solvent removed in steam; $\alpha\gamma$-diphthalimidopropane separated as colourless, oblique, hexagonal columns, pure enough for hydrolysis without recrystallisation.

β-*Trimethylenediaminoplatinous chloride* (I) was prepared from aqueous potassium chloroplatinite and the diamine at room temperature (2—3 hours). It separated from dilute hydrochloric acid as yellow rectangular needles, sparingly soluble in boiling water (1 g. in *ca.* 110 c.c.) (Found: N, 8·2; Pt, 57·4. $C_3H_{10}N_2Cl_2Pt$ requires N, 8·2; Pt, 57·4%). It crystallised unchanged from hot aqueous potassium chloroplatinite and tetramminoplatinous chloride, and gave no coloration when ground with phenoxtellurine dibisulphate.

Trimethylenediaminoplatinic chloride was prepared by boiling the foregoing compound in dilute hydrochloric acid with hydrogen peroxide. It separated as lemon-yellow polyhedra which dissolved sparingly in boiling water (1 g. in *ca.* 140 c.c.) and crystallised very slowly on cooling (Found: Pt, 47·4. $C_3H_{10}N_2Cl_4Pt$ requires Cl, 34·5; Pt, 47·5%). It was reduced by tetramminoplatinous chloride in boiling aqueous solution to the above platinous salt (Found: Pt, 57·2%), tetramminoplatinic chloride being obtained from the mother-liquor.

β-*Bistrimethylenediaminoplatinous chloride* (II) was prepared from (I), or from α-diamminoplatinous chloride, and aqueous trimethylenediamine at room temperature and at 100° (Found: Pt, 47·1. $C_6H_{20}N_4Cl_2Pt$ requires Pt, 47·1%). It separated from aqueous alcohol as colourless columns, sometimes with gabled ends, very soluble in cold water. It formed a *plato-salt* (IV) of flesh-pink rectangular needles, sparingly soluble in boiling water (Found: Pt, 57·2. $C_6H_{20}N_4Cl_4Pt_2$ requires Pt, 57·4%).

Bistrimethylenediaminoplatinic chloride was prepared from a concentrated hydrochloric acid solution of (II) by boiling it with hydrogen peroxide or exposing it to air. It separated from aqueous alcohol and concentrated hydrochloric acid as colourless rhombic needles, and from water as colourless rhombic plates which, when dried for analysis at 140°, changed into hygroscopic white pseudomorphs. It dissolved in cold water (Found: C, 14·6; H, 4·2; N, 11·8; Pt, 40·0. $C_6H_{20}N_4Cl_4Pt$ requires C, 14·8; H, 4·2; N, 11·5; Pt, 40·2%). It formed a *plato-salt* of orange cubes, soluble in boiling water, which was also obtained from bistrimethylenediaminoplatinous chloroplatinite and concentrated hydrochloric acid in air (Found: Pt, 52·1. $C_6H_{20}N_4Cl_6Pt_2$ requires Pt, 52·0%).

The α-*dihydrochloride* (III) of (II) was prepared by heating (II) (0·414 g.) in 6*N*-hydrochloric acid (4 c.c.) at 100° for 7 hours in a closed vessel, filtering off (I) (0·07 g.; Found: Pt, 57·3%), evaporating the filtrate over phosphoric oxide in a vacuum, and recrystallising the product from alcohol containing 6*N*-hydrochloric acid. It separated from concentrated hydrochloric acid as colourless plates, soluble in cold water (Found: Pt, 40·0. $C_6H_{22}N_4Cl_4Pt$ requires Pt, 40·1%). Its solution in aqueous potassium chloroplatinite on evaporation at 80° became strongly acid and deposited the chloroplatinite (IV).

β-*Ethylenediaminotrimethylenediaminoplatinous chloride* (V) was prepared from (I) and aqueous ethylenediamine, or from Pt en Cl_2 and aqueous trimethylenediamine at room temperature and at 100°. It separated from aqueous alcohol as colourless rectangular plates, very soluble in cold water (Found: Pt, 48·6. $C_5H_{18}N_4Cl_2Pt$ requires Pt, 48·8%). It formed a *plato-salt* (VIII) of pink rectangular needles, sparingly soluble in boiling water (Found: Pt, 58·5. $C_5H_{18}N_4Cl_4Pt_2$ requires C, 9·0; H, 2·7; Pt, 58·6%).

Ethylenediaminotrimethylenediaminoplatinic chloride was prepared by boiling [Pt en tr]Cl_2 in concentrated hydrochloric acid with hydrogen peroxide. It separated from the concentrated acid as colourless hexagonal tables which, when dried at 140° for analysis, changed to hygroscopic white pseudomorphs (Found: Pt, 41·1. $C_5H_{18}N_4Cl_4Pt$ requires Pt, 41·4%); it dissolved in cold water, and formed a *plato-salt* of orange cubes, soluble in boiling water (Found: Pt, 52·8. $C_5H_{18}N_4Cl_6Pt_2$ requires Pt, 52·9%).

The α-*dihydrochloride* (VI) of (V) was prepared from the latter in the same way as the dihydrochloride (III); after separation of Pt en Cl_2 and Pt tr Cl_2 [0·09 g. Found: C, 9·9; H, 2·9; Pt, 57·9. Calc. for the mixture 1(Pt en Cl_2) + 3(Pt tr Cl_2): C, 9·8; H, 2·8; Pt 58·0%], and working up the filtrate as before, the salt was obtained as colourless plates, soluble in cold water (Found: Pt, 41·0. $C_5H_{20}N_4Cl_4Pt$ requires Pt, 41·3%). With aqueous potassium chloroplatinite, after evaporation at 80° and cooling, it deposited pinkish-brown plates of the *chloroplatinite* (VII), soluble in hot water (Found: C, 8·8; H, 2·8; Pt, 55·9. $C_5H_{19}N_4Cl_5Pt_2$

requires C, 8·5; H, 2·7; Pt, 55·6%); the strongly acid mother-liquor, on further evaporation, deposited [Pt en tr]Pt Cl_4 described above (Found: C, 9·0; H, 2·9; Pt, 59·0%).

β-*Diamminotrimethylenediaminoplatinous chloride* (IX) was prepared from (I) and aqueous ammonia at room temperature or at 100°. It was also formed, together with [Pt tr_2]Cl_2, from β-Pt$(NH_3)_2Cl_2$ (1 mol.) and the aqueous base (2 mols.), analyses of the plato-salts of the crude mixtures showing that at room temperature about 20% and at 100° about 50% of the ammonia was displaced by trimethylenediamine. It separated from aqueous alcohol as colourless rectangular needles, very soluble in cold water (Found: Pt, 52·2. $C_3H_{16}N_4Cl_2Pt$ requires Pt, 52·2%). It formed a *plato-salt*, pink rectangular needles, sparingly soluble in boiling water (Found: Pt, 61·0. $C_3H_{16}N_4Cl_4Pt_2$ requires Pt, 61·0%).

Diamminotrimethylenediaminoplatinic chloride was prepared by oxidising (IX) in the usual way with hydrogen peroxide or air. It separated from concentrated hydrochloric acid and aqueous alcohol as colourless rhombic columns or needles, and from water as rhombic plates (Found: N, 12·7; Cl, 32·5; Pt, 43·9. $C_3H_{16}N_4Cl_4Pt$ requires N, 12·6; Cl, 31·8; Pt, 43·8%). It dissolved in cold water, and formed a *plato-salt* of brown rectangular plates, soluble in boiling water, which was also obtained from [Pt$(NH_3)_2$tr]PtCl_4, potassium chloroplatinite and concentrated hydrochloric acid in air (Found: N, 8·0; Pt, 55·0. $C_3H_{16}N_4Cl_6Pt_2$ requires N, 7·9; Pt, 54·9%).

β-*Amminotrimethylenediaminoplatinous chloride* (X) was prepared from [Pt$(NH_3)_2$tr]Cl_2 (IX) (0·374 g.) and 6*N*-hydrochloric acid (1·5 c.c.) by 2 hours' heating in the same process as that used for (III) (p. 1339). It separated from aqueous alcohol as colourless rectangular needles, soluble in cold water (Found: N, 11·8; Pt, 54·6. $C_3H_{13}N_3Cl_2Pt$ requires N, 11·8; Pt, 54·6%), and formed a *plato-salt* (XI) of pinkish-brown rectangular plates, sometimes pointed, soluble in hot water (Found: C, 7·2; H, 2·7; Pt, 59·7. $C_6H_{26}N_6Cl_6Pt_3$ requires C, 7·3; H, 2·7; Pt, 59·7%). During the preparation, Pt tr Cl_2 (0·017 g. Found: Pt, 57·5%) was removed.

The α-*monohydrochloride* (XII) of the foregoing salt (X) resulted if the heating was prolonged for 8 hours and 5 c.c. of 6*N*-acid were used; it was similarly obtained from (X) by 5 hours' heating (in both cases, further heating produced no change). It crystallised from concentrated hydrochloric acid as yellow, square and octagonal plates, soluble in cold water (Found: C, 9·4; H, 3·7; Pt, 49·9. $C_3H_{14}N_3Cl_3Pt$ requires C, 9·1; H, 3·6; Pt, 49·6%); it reacted with aqueous potassium chloroplatinite, under conditions previously described (p. 1339), to yield [PtCl(NH_3)tr]$_2$PtCl_4 described above (Found: C, 7·0; H, 2·7; Pt, 59·6). In both methods of preparation, from (IX) or (X), Pt tr Cl_2 was removed (Found: Pt, 57·6, 57·2% respectively).

Tetramminoplatinic chloride, prepared by boiling the plato-tetrammine in concentrated hydrochloric acid with hydrogen peroxide, separated as colourless rhombic tables, soluble in boiling water (Found: H, 2·9; N, 13·4; Pt, 48·2. Calc. for $H_{12}N_4Cl_4Pt$: H, 3·0; N, 13·8; Pt, 48·2%). It was also obtained, though of a slightly yellow colour, by oxidising the plato-tetrammine with various plati-tetrammines, *e.g.*, [Pt$Cl_2(NH_3)_2$tr]Cl_2, in cold aqueous solution. It formed a plato-salt of brownish-red rhombic columns, sparingly soluble in boiling water (Found: Pt, 58·3. Calc. for $H_{12}N_4Cl_6Pt_2$: Pt, 58·2%).

Ethylenediaminoplatinic chloride was prepared by oxidising the platinous chloride by hydrogen peroxide under the usual conditions (p. 1339). It formed lemon-yellow rhombic and hexagonal plates, which dissolved sparingly in boiling water (1 g. in about 350 c.c.) and separated very slowly on cooling (Found: C, 6·3; H, 2·1; Pt, 49·2. Calc. for $C_2H_8N_2Cl_4Pt$: C, 6·0; H, 2·0; Cl, 35·7; Pt, 49·2%).

Pt en Cl_3 or (Pt en Cl_3)$_2$ (XIII) was prepared by boiling aqueous solutions of the foregoing compound and tetramminoplatinous chloride; further crops separated repeatedly from the mother-liquor after filtration and boiling and tetramminoplatinic chloride was obtained from the final filtrate. It was also formed by boiling the latter with Pt en Cl_2 in aqueous solution, separating as red rhombic or hexagonal plates, sparingly soluble in boiling water (1 g. in 300 c.c.) (Found: C, 6·8; H, 2·3; N, 8·1; Pt, 54·3. Calc. for $C_2H_8N_2Cl_3Pt$: C, 6·6; H, 2·2; N, 7·7; Pt, 54·0%). It gave a scarlet coloration when ground with phenoxtellurine dibisulphate, and crystallised unchanged from aqueous potassium chloroplatinite. With silver nitrate solution the supercooled aqueous solution formed only an opalescence in the cold, but gave a white precipitate on boiling. It was oxidised by boiling hydrogen peroxide and hydrochloric acid, and also by Pt$(NH_3)_4Cl_4$, to Pt en Cl_4 (Found: Pt, 48·6%), and was reduced by potassium oxalate with a trace of potassium formate, and also by Pt$(NH_3)_4Cl_2$, to Pt en Cl_2

(Found : Pt, 59·1. Calc. : Pt, 59·8%). It was quite different from the buff plato-plati-salts [Pt en_2]$PtCl_6$ (Found : Pt, 54·7%) and [$PtCl_2en_2$]$PtCl_4$ (Found : Pt, 54·1%) which were precipitated from aqueous solutions of the corresponding chlorides.

Action of Hydrochloric Acid on β-Ethylenediamino- and -Trimethylenediamino-platinous Chlorides.—The first salt (Found : C, 7·6; H, 2·7; Pt, 59·7. Calc. : C, 7·4; H, 2·5; Pt, 59·8%) separated in part unchanged from 6*N*-hydrochloric acid after 5 hours' boiling; on evaporation, the mother-liquor gave (i) Pt en Cl_4 described above (Found : Cl, 35·7; Pt, 48·9%), (ii) yellow plates of (en H_2)$PtCl_6$, soluble in hot water (Found : Pt, 41·3. Calc. : Pt, 41·5%), and (iii) red needles, probably of (en H_2)$PtCl_4$, soluble in cold water. Similarly, the second salt was mainly unchanged, but gave (i) Pt tr Cl_4 (Found : Cl, 34·3; Pt, 47·2%), (ii) yellow plates of (tr H_2)$PtCl_6$, soluble in hot water (Found : N, 6·0; Pt, 40·4. Calc. : N, 5·8; Pt, 40·3%), and (iii) red needles, probably of (tr H_2)$PtCl_4$, soluble in cold water.

The latter salt also separated mainly unchanged from *N*-hydrochloric acid after 50 hours' heating at 100°, Pt tr Cl_4 (Found : Pt, 47·9%) being obtained from the mother-liquid.

Action of Tetra- and Penta-methylenediamines on Aqueous Potassium Chloroplatinite.—In this reaction, the first diamine at room temperature (8 hours) gave a pale yellow, microcrystalline *substance*, hygroscopic when dried, and practically insoluble in boiling water, hydrochloric acid, and organic solvents. It could not be purified [Found : C, 14·1; H, 3·9; Pt, 52·4. $Pt(C_4H_{12}N_2)Cl_2$ requires C, 13·5; H, 3·4; Pt, 55·1], and formed white gels with aqueous tri- or tetra-methylenediamine.

The second diamine, after 12 hours, gave a similar cream-yellow *substance* [Found : C, 17·0; H, 4·3; Pt, 49·3. $Pt(C_5H_{14}N_2)Cl_2$ requires C, 16·3; H, 3·8; Pt, 53·0%].

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