251. *The Structure of some Ammines of Platinous Chloride.*

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DURING recent years chemical and physical evidence has accumulated which indicates quite clearly that platinum with a covalency of four may have a planar configuration. The isolation of three compounds $[Pt(NH_3)(NH_2OH)py\,NO_2]_2[PtCl_4]$ by Tschernjaev (*Ann. Inst. Platine,* 1928, **6**, 55) supports this idea on the chemical side, whilst the physical evidence from *X*-ray investigations of $[Pt(NH_3)_4]Cl_2,H_2O$ and Magnus's salt $[Pt(NH_3)_4][PtCl_4]$ (J., 1932, 1912, 2527) discloses that in these complex salts the platinum atom and the four chlorine atoms or the four co-ordinated nitrogen atoms occupy one plane. Moreover, the *X*-ray diagram for Cleve's salt $[Pt(NH_3)_3Cl]_2[PtCl_4]$ resembles so closely the diagram for Magnus's salt that it seems certain that the ion $[Pt(NH_3)_3Cl]^{\cdot}$ has the same planar configuration as $[Pt(NH_3)_4]^{\cdot\cdot}$. The assumption, therefore, that in the mixed tetrammines and triammines of platinous chloride a planar structure is present, is not without substantial experimental support.

To study further the ammines of platinous chloride, we prepared two mixed *triammines* from α-[Pt py_2 Cl_2] and α-[Pt $py(NH_3)Cl_2$], adding the additional molecule of ammonia by Tschugaev's method (J., 1915, **107**, 1247). We found that they were decomposed much more easily than the mixed tetrammines of similar type; *e.g.*, they underwent decomposition with 3*N*-hydrochloric acid in two days, at room temperature, and gave a 90% yield of the diammine from which they were originally prepared, no other diammine being produced. In both cases the last-added molecule of ammonia had been removed by the hydrochloric acid, and removed so easily that it appeared most unlikely that any configurational change had taken place. It seems reasonable to conclude, therefore, that the α-diammines so produced have a planar structure. We next attempted to isolate the β-triammine from β-Pt py_2Cl_2 by addition of a molecule of ammonia by Tschugaev's method (*loc. cit.*). Here we succeeded only in obtaining solutions of the triammine mixed with the tetrammine $[Pt(NH_3)_2py_2]Cl_2$. These solutions, when decomposed with acid of the same concentration, gave one diammine only, *viz.*, α-$[Pt(NH_3)py\,Cl_2]$, from which it will be seen that the ammine group removed is not that last added but one of those present in the original diammine. We next investigated the mixed *tetrammines* of the types $[PtA_2A'_2]Cl_2$ and $[PtAA'A''_2]Cl_2$, where A, A', A" are ammonia, pyridine, and hydroxylamine. The results obtained, on decomposing these tetrammines with hydrochloric acid, can be summarised as follows :—

(*a*) In a tetrammine containing one hydroxylamine group, this group is always eliminated, and at the same time the group in the α-position to it :

$$\alpha\text{-}PtNH_3(NH_2OH)Cl_2 \xrightarrow{py} [Pt(NH_3)(NH_2OH)py_2]Cl_2 \xrightarrow{HCl} \alpha\text{-}Pt\,py_2Cl_2$$

(*b*) A tetrammine containing two hydroxylamine groups in the α-position to one another loses both these groups, but the diammine so produced is sometimes accompanied by very small amounts of α-$[Pt(NH_2OH)_2Cl_2]$:

$$\alpha\text{-}Pt(NH_2OH)_2Cl_2 \xrightarrow{NH_3} [Pt(NH_2OH)_2(NH_3)_2]Cl_2 \xrightarrow{HCl} \alpha\text{-}Pt(NH_3)_2Cl_2$$

(*c*) A tetrammine containing two hydroxylamine groups in the β-position to one another gives exclusively a mixed α-diammine of the type $[Pt(NH_2OH)(A \text{ or } A')Cl_2]$:

$$\beta\text{-}Pt(NH_3)_2Cl_2 \xrightarrow{NH_2OH} \beta\text{-}[Pt(NH_3)_2(NH_2OH)_2]Cl_2 \xrightarrow{HCl} \alpha\text{-}PtNH_3(NH_2OH)Cl_2$$

(*d*) A tetrammine containing three hydroxylamine groups gives a mixed α-diammine of the type $[PtA'(NH_2OH)Cl_2]$ and some α-$[Pt(NH_2OH)_2Cl_2]$:

$$\alpha\text{-}Pt(NH_2OH)pyCl_2 \xrightarrow{NH_2OH} [Pt(NH_2OH)_3py]Cl_2 \xrightarrow{HCl} \alpha\text{-}Pt(NH_2OH)py\,Cl_2 + \alpha\text{-}Pt(NH_2OH)_2Cl_2$$

The relative weakness of the link Pt–NH_2OH in (*a*) and (*b*) operates in conjunction with the tendency to eliminate groups from α-positions. As a result the hydroxylamine groups are almost completely eliminated, giving one diammine as the main product. The same tendency operates in (*d*), but not to such a marked extent.

In (*c*) it is very significant that where the tendency to elimination of groups in α-positions is opposed by the tendency to preferential elimination of hydroxylamine, the former overrides the latter completely. This elimination of α-groups is a remarkable feature of both the triammines and the tetrammines of platinous chloride.

Werner assumed that α- were *trans*-positions and β- were *cis*-positions in the case of the ammines of platinous chloride. This idea explains in a consistent way the results we have obtained with the triammines and tetrammines. The only point that remains undecided is the formula for the β-$Pt(NH_3)_2Cl_2$ and similarly constituted substances. The α-$Pt(NH_3)_2Cl_2$ and similarly constituted diammines seem undoubtedly to be planar substances, with the ammine groups in *trans*-positions. Although a *cis*-planar structure for the β-$Pt(NH_3)_2Cl_2$ and allied diammines explains the reactions dealt with in this paper, yet the structure is by no means settled. The action of ethylenediamine on the mixed α-diammines, α-$PtAA'\,Cl_2$, where A and $A' = NH_3$, py, or NH_2OH, and on α-$Pt(NH_2OH)_2Cl_2$ has been studied. It was found that in every case complete replacement of the ammine groups of the diammines took place, the sole product being $[Pt(en)_2]Cl_2$. This strongly supports the idea that α-diammines have a *trans*-planar configuration. If they had either of the alternative configurations (*cis*-planar or tetrahedral), the ethylenediamine could easily replace the chlorines without necessarily disturbing the ammine groups, whereas, since the ethylenediamine molecule is not long enough to span the *trans*-positions, it can only react with a *trans*-planar diammine as described above. Werner's hypothesis of *trans*-elimination of groups from tetrammines and triammines of platinous chloride still lacks a theoretical basis. We suggested some time ago that a pairing of valencies takes place (J., 1932, 1004). This has received substantial support from recent *X*-ray investigations carried out in these laboratories.

The failure to isolate the triammine in the case of the β-Pt py_2Cl_2 appears to us to be due to the following causes. The reaction between this compound and aqueous potassium cyanate at 80° gives a solution containing the triammine sought for, with the tetrammine β-$[Pt(NH_3)_2py_2]Cl_2$. The solubilities of the triammine and tetrammine are, however, so similar as to frustrate attempts to separate them by fractional crystallisation. Furthermore, the method of fractional crystallisation of the plato-salts and subsequent regeneration of the triammine from its plato-salt by the precipitation of green salt of Magnus with the theoretical amount of $[Pt(NH_3)_4]Cl_2$ (cf. Tschugaev, *loc. cit.*) fails for a noteworthy reason. The addition of potassium chloroplatinite to the solution containing the triammine precipitates the buff-coloured plato-salt of the triammine. This substance rapidly turns pink, and this pink substance can be fractionated into $[Pt(NH_3)_2py_2][PtCl_4]$ and $[Pt\ py_4][PtCl_4]$ by means of hot water. It seems, then, that the triammine plato-salt β-$[Pt\ py_2(NH_3)Cl]_2[PtCl_4]$ readily undergoes an intramolecular change :

$$\underset{\text{buff}}{2[Pt(NH_3)py_2Cl]_2[PtCl_4]} \longrightarrow \underset{\text{cerise}}{2[Pt(NH_3)_2py_2][PtCl_4]} + \underset{\text{pink}}{[Pt\ py_4][PtCl_4]}$$

analogous to that already recorded (J., 1932, 2527) in the case of the simple triammine $[Pt(NH_3)_3Cl]_2[PtCl_4]$ and Magnus's salt $[Pt(NH_3)_4][PtCl_4]$.

Attempts to prepare a triammine $[Pt(NH_3)(NH_2OH)py\ Cl]Cl$ by the above method from α-$[Pt(NH_2OH)py\ Cl_2]$ failed, the diammine undergoing decomposition.

The action of ammonia on α-$Pt(NH_2OH)_2Cl_2$ was carefully studied in view of the conflicting statements made by Alexander (*Annalen*, 1893, **246**, 239) and by Tschugaev and Tschernjaev (J., 1918, **113**, 891). We find that a small quantity of ammonia (*d* 0·880) gives with α-$Pt(NH_2OH)_2Cl_2$ in the cold the tetrammine $[Pt(NH_2OH)_2(NH_3)_2](OH)_2$. With dilute ammonia, a yellow-brown precipitate of varying composition is obtained, which appears to contain some of the tetrammine $[Pt(NH_2OH)_2(NH_3)_2]Cl_2$. We have been unable to obtain the compound $Pt(NH_2OH)Cl(OH)$ reported by Tschugaev and Tschernjaev (*loc. cit.*).

EXPERIMENTAL.

Diammines.—The α- and β-forms of $PtCl_2(NH_3)_2$, $PtCl_2\ py_2$, and α-$[PtCl_2(NH_3)py]$ were prepared as previously described (J., 1932, 999, 1013); α-$PtCl_2(NH_2OH)_2$ and α-$PtCl_2(NH_3)(NH_2OH)$ as in J., 1918, **113**, 884.

α-Hydroxylaminopyridinoplatinous chloride was isolated by decomposing, with 3*N*-hydrochloric acid (2 c.c.) at 80°, the colourless solution produced by warming at 90° β-$PtCl_2py_2$ (0·35 g.), hydroxylamine hydrochloride (0·30 g.), water (5 c.c.), and 2·5*N*-sodium hydroxide (0·5 c.c.). The product was recrystallised from chloroform and dried over phosphoric oxide (Found : Pt, 51·8. $C_5H_8ON_2Cl_2Pt$ requires Pt, 51·6%).

Triammines.—*α-Chloroamminodipyridinoplatinous chloride.* α-$PtCl_2py_2$ (0·5 g.) was boiled with aqueous potassium cyanate (0·25 g.; 10 c.c.) for ¾ hour, cooled, and neutralised with hydrochloric acid. The filtrate contained α-$[Pt(NH_3)_2py_2]Cl_2$. The residue, dried at 60° and treated with chloroform to remove unchanged diammine, was recrystallised twice from hot water. The white needles obtained were dried over phosphoric anhydride in a vacuum, and proved to be the desired *salt* (Found : Pt, 44·1, 44·2. $C_{10}H_{13}N_3Cl_2Pt$ requires Pt, 44·2%). The triammine gave with potassium chloroplatinite a chamois *plato-salt* which was recrystallised from hot water (Found : Pt, 51·1, 50·8. $C_{20}H_{26}N_6Cl_6Pt_3$ requires 51·0%). The aqueous solution of this salt gave with the theoretical quantity of $[Pt(NH_3)_4]Cl_2$, a precipitate of green $[Pt(NH_3)_4][PtCl_4]$, and the triammine was recovered from the filtrate. When the triammine was warmed with 3*N*-hydrochloric acid, it gave α-$PtCl_2py_2$ only (Found : Pt, 45·8. Calc. : Pt, 46·0%).

α-Chlorodiamminopyridinoplatinous chloride. When α-$PtCl_2(NH_3)py$ (0·5 g.) was boiled with aqueous potassium cyanate (0·3 g.; 10 c.c.), a white flocculent precipitate separated from the colourless solution on cooling. This proved to be the *carbonate* of the α-chlorodiamminopyridino-complex, which, on recrystallisation from hot water, gave fine white needles [Found : Pt, 52·3. $(C_5H_{11}N_3ClPt)_2CO_3$ requires Pt, 52·2%]; warmed with 3*N*-hydrochloric acid, it decomposed immediately to the original salt, with evolution of carbon dioxide. With aqueous potassium chloroplatinite, acidulated with hydrochloric acid, it gave the *plato-salt* of the triammine (Found: Pt, 56·9. $C_{10}H_{22}N_6Cl_6Pt_3$ requires Pt, 57·2%), from which the triammine was obtained as before by treatment with the theoretical quantity of aqueous $[Pt(NH_3)_4]Cl_2$.

The filtrate from the above carbonate was carefully neutralised with 3*N*-hydrochloric acid, and the diammine which separated removed. On concentrating the filtrate over solid potassium hydroxide in a vacuum the triammino-*chloride* separated, and was recrystallised from hot water (Found: Pt, 51·2. $C_5H_{11}N_3Cl_2Pt$ requires Pt, 51·5%). With aqueous potassium chloroplatinite, the chamois *plato-salt*, soluble in hot water, was obtained (Found: Pt, 56·9. $C_{10}H_{22}N_6Cl_6Pt_3$ requires Pt, 57·2%). With 3*N*-hydrochloric acid, the triammine readily decomposed, even in the cold, giving a 92% yield of the characteristic crystals of α-$PtCl_2(NH_3)$py (Found: Pt, 54·0. Calc.: Pt, 53·9%). The small amount of the oxidised product, $[PtCl_3(NH_3)py]_x$, produced in the decomposition was removed by recrystallisation from water before the yield was weighed.

β-*Chloroamminodipyridinoplatinous chloroplatinite.* β-$PtCl_2py_2$ (0·5 g.) was warmed with aqueous potassium cyanate (0·25 g.; 10 c.c.) at 80° till a clear solution was obtained; this was cooled, neutralised with hydrochloric acid, and the precipitated diammine removed. Addition of potassium chloroplatinite solution to the filtrate gave a buff precipitate, which rapidly turned pink. Attempts were made to isolate the buff substance by rapid filtration, but some change always took place; the best samples were dried over phosphoric oxide {Found: Pt, 51·4, 51·7. $[PtCl(NH_3)py_2]_2[PtCl_4]$ requires Pt, 51·0%. $[Pt(NH_3)_2py_2][PtCl_4]$ requires Pt, 53·9%}. Crystallisation of the buff *plato-salt* from hot water gave a less soluble, cerise plato-salt {Found: Pt, 53·5. Calc. for $[Pt(NH_3)_2py_2][PtCl_4]$: Pt, 53·9%} and a more soluble, pink plato-salt {Found: Pt, 47·3. Calc. for $[Pt\,py_4][PtCl_4]$: Pt, 46·0%}. Solutions of the triammine, prepared as above, on being warmed with 3*N*-hydrochloric acid, gave α-$PtCl_2(NH_3)$py (Found: Pt, 54·0. Calc.: Pt, 53·9%), together with a small amount of oxidised product $[PtCl_3(NH_3)py]_x$.

When β-$PtCl_2py_2$ (0·5 g.) was boiled with aqueous potassium cyanate (0·25 g.; 10 c.c.), the clear solution obtained gave a white solid on cooling. Recrystallisation from aqueous alcohol (80%) gave white needles (Found: Pt, 44·2, 44·1; N, 12·7, 12·8%), insoluble in water and yielding no plato-salt with potassium chloroplatinite. Only after prolonged boiling with silver nitrate is silver chloride obtained. Cold 3*N*-hydrochloric acid immediately decomposes the substance, giving a solution of β-$[Pt(NH_3)_2py_2]Cl_2$, identified (*a*) by its cerise plato-salt (Found: Pt, 53·9. Calc.: Pt, 53·9%) and (*b*) by its decomposition with hydrochloric acid, only $PtCl_2(NH_3)$py being obtained.

Attempts to prepare triammines by the addition of 1 mol. of ammonia (Tschugaev's method) to α-$PtCl_2(NH_3)(NH_2OH)$, α-$PtCl_2(NH_2OH)_2$, or α-$PtCl_2(NH_2OH)$py were unsuccessful. In all cases decomposition to a brown solid occurred.

Tetrammines.—α-*Hydroxylaminoamminodipyridinoplatinous chloride* was obtained as a white solid when a solution of α-$PtCl_2(NH_3)(NH_2OH)$ in aqueous pyridine was concentrated. The product was recrystallised from water and dried over phosphoric oxide (Found: Pt, 41·2. $C_{10}H_{16}ON_4Cl_2Pt$ requires Pt, 41·2%). On warming with 3*N*-hydrochloric acid at 90°, α-$PtCl_2py_2$ alone separated (Found: Pt, 45·9. Calc.: Pt, 46·0%). The pale salmon *plato-salt* was recrystallised from 0·5*N*-hydrochloric acid (Found: Pt, 52·5. $C_{20}H_{32}O_2N_8Cl_4Pt_3$ requires Pt, 52·7%).

α-*Hydroxylaminotripyridinoplatinous chloroplatinite.* A solution of the foregoing tetrammine was prepared by dissolving α-$PtCl_2(NH_2OH)$py in the calculated quantity of warm aqueous pyridine. Neutralisation and addition of potassium chloroplatinite gave a pale rose *plato-salt*, which was recrystallised from 0·5*N*-hydrochloric acid and dried over phosphoric oxide (Found: Pt, 48·4. $C_{15}H_{18}ON_4Cl_4Pt_2$ requires Pt, 48·7%). Excess of pyridine in the original preparation produces $[Pt\,py_4]Cl_2$ (Found: Pt, 33·7. Calc.: Pt, 33·5%). On being warmed with 3*N*-hydrochloric acid, the solution of the tetrammine prepared as above gave only α-$PtCl_2py_2$ (Found: Pt, 45·8. Calc.: Pt, 46·0%).

α-*Dihydroxylaminodipyridinoplatinous chloride.* By the method of Tschugaev and Tschernjaev (*loc. cit.*), this tetrammine was isolated from the reaction between cold aqueous pyridine and α-$PtCl_2(NH_2OH)_2$ (Found: Pt, 40·4. Calc.: Pt, 39·8%). It yielded the required *plato-salt* as microscopic, pale rose prisms (Found: Pt, 51·9. $C_{10}H_{16}O_2N_4Cl_4Pt_2$ requires Pt, 51·6%). With 3*N*-hydrochloric acid at 50° the tetrammine yielded α-$PtCl_2py_2$ (Found: Pt, 46·0. Calc.: Pt, 46·0%), and a small quantity of α-$PtCl_2(NH_2OH)_2$, recognised by its characteristic crystals.

α-$[Pt(NH_3)_2(NH_2OH)_2]Cl_2$ was obtained as a white solid by the method of Tschugaev and Tschernjaev (*loc. cit.*), and gave with hydrochloric acid, as described by these authors, α-$PtCl_2(NH_3)_2$ (Found: Pt, 65·0. Calc.: Pt, 65·0%).

α-Dihydroxylaminoamminopyridinoplatinous chloride. A colourless solution of this tetrammine was prepared by dissolving α-$PtCl_2(NH_3)py$ (0·5 g.) in aqueous hydroxylamine hydrochloride (2·6 g.; 2·9 c.c.) and sodium hydroxide solution (10%; 1·5 c.c.). On acidification with hydrochloric acid and addition of potassium chloroplatinite, a strawberry-red *plato-salt* separated after concentration over phosphoric oxide (Found: Pt, 56·3. $C_5H_{14}O_2N_4Cl_4Pt_2$ requires Pt, 56·2%). 3*N*-Hydrochloric acid at 90° decomposes the tetrammine, yielding α-$PtCl_2(NH_3)py$ (Found: Pt, 53·7. Calc.: Pt, 53·9%).

β-Dihydroxylaminodipyridinoplatinous chloride was obtained in solution by warming β-$PtCl_2py_2$ (0·35 g.) with solutions of hydroxylamine hydrochloride (0·3 g.; 5 c.c.) and sodium hydroxide (10%; 0·5 c.c.) at 80°. The deep rose *plato-salt*, formed as usual, was recrystallised from 0·5*N*-hydrochloric acid and dried over phosphoric oxide (Found: Pt, 51·3. $C_{10}H_{16}O_2N_4Cl_4Pt_2$ requires Pt, 51·6%). Decomposition of the tetrammine with hydrochloric acid gave α-$PtCl_2(NH_2OH)py$ (Found: Pt, 51·8. Calc.: Pt, 51·6%).

β-$[Pt(NH_2OH)_2(NH_3)_2]Cl_2$ and the plato-salt were prepared as previously described (J., 1918, **113**, 890) (Found, for chloride: Pt, 53·4. Calc.: Pt, 53·3%. Found, for chloroplatinite: Pt, 61·9. Calc.: Pt, 61·7%*). On being warmed with hydrochloric acid, the tetrammine gives α-$PtCl_2(NH_3)(NH_2OH)$ (Found: Pt, 61·6. Calc.: Pt, 61·7%).

α-$[Pt(NH_2OH)_3py]Cl_2$ separated as a white solid on dissolving α-$PtCl_2(NH_2OH)py$ (0·5 g.) in a solution of hydroxylamine hydrochloride (2·5 g.; 2·8 c.c.) and sodium hydroxide (10%; 1·4 c.c.) at 90° (Found: Pt, 43·8. Calc. for $C_5H_{14}O_3N_4Cl_2Pt$: Pt, 43·9%); the *chloroplatinite* was lilac (Found: Pt, 55·1. $C_5H_{14}O_3N_4Cl_4Pt_2$ requires Pt, 55·0%). When warmed with *N*-hydrochloric acid at 80°, the tetrammine yielded α-$PtCl_2(NH_2OH)py$ (Found: Pt, 51·8. Calc.: Pt, 51·6%) and α-$PtCl_2(NH_2OH)_2$, identified by its characteristic crystals.

$[Pt(en)_2][PtCl_4],H_2O$ (Found: Pt, 58·0, 58·6, 58·4, 58·4. Calc.: Pt, 58·2%) was formed by the addition of potassium chloroplatinite to the acidified solution produced by the action of aqueous ethylenediamine on α-$PtCl_2(NH_3)py$, α-$PtCl_2(NH_3)(NH_2OH)$, α-$PtCl_2(NH_2OH)py$, or $PtCl_2(NH_2OH)_2$. No other plato-salt was isolated.

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