CXIX.—*The Complex Salts of Bivalent Platinum with αβγ-Triaminopropane.*

By Frederick George Mann.

It has already been shown by the present author (J., 1926, 2681; 1927, 1224) that chloroplatinic acid co-ordinates with triamino-propane trihydrochloride to give tetrachloro(triaminopropane-γ-monohydrochloride)platinum,

$$[Cl_4PtNH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2, HCl], H_2O,$$

a compound whose resolution into optically active forms proves that the platinum is co-ordinated only to the α- and β-amino-groups, leaving the γ-amino-group free to form a hydrochloride. It is now found that if potassium chloroplatinite is treated with triamino-propane trihydrochloride, *dichloro(triaminopropane-monohydro-chloride)platinum monohydrate*,

$$[Cl_2PtNH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2, HCl], H_2O,$$

is formed similarly. This compound, like the tetrachloro-compound, might exist in two forms, one in which co-ordination occurs through the α- and β-amino-groups, giving a γ-monohydrochloride (I),
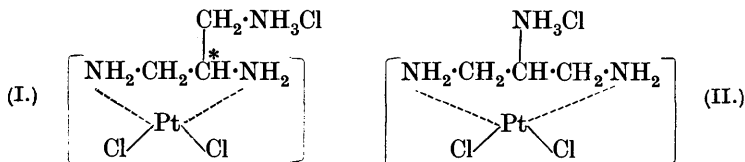

and the other in which co-ordination occurs through the α- and γ-amino-groups, giving a β-monohydrochloride (II). These iso-merides differ fundamentally in that (I) is dissymmetric, having the β-carbon atom (marked *) asymmetric, whereas (II) is symmetric. The resolution of this compound into optically active forms, described in the present paper, proves it to have the former constitution, being, like the tetrachloro-compound, a γ-monohydrochloride. It is therefore the second known compound in which asymmetry of a carbon atom is induced by the operation of auxiliary valencies.

The properties of dichloro(triaminopropane-γ-monohydrochloride)-platinum resemble closely those of the tetrachloro-compound; *e.g.*, the two optically active forms are both anhydrous, and the racemic product is a monohydrate. The most characteristic salt is again the *γ-monohydrogen oxalate*,
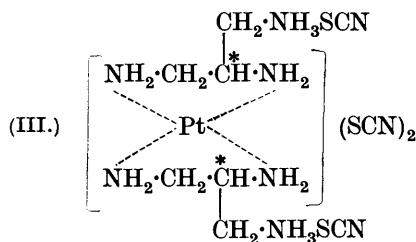
$$[Cl_2PtNH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2, (CO_2H)_2],$$
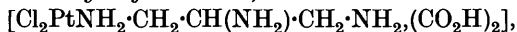
which is rapidly precipitated when the monohydrochloride is treated in solution with oxalic acid. Furthermore, if the monohydro-chloride is treated with ammonia, the latter withdraws the hydrogen chloride, and the amino-group liberated immediately co-ordinates with the platinum, expelling a chlorine atom from the complex and giving *monochlorotriaminopropaneplatinous monochloride*,

$$[ClPtNH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2]Cl.$$
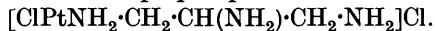
Treatment of potassium chloroplatinite with an excess of tri-aminopropane base instead of the trihydrochloride gives rise, however, to two entirely different types of complex salt. Co-ordination in these circumstances is rapid, giving a colourless solution : if this is now concentrated, acidified with acetic acid, and treated with potassium thiocyanate, the white crystalline *bis(tri-*

aminopropane-monothiocyanate)platinous dithiocyanate (III) is produced.   In this compound each molecule of the base is co-ordinated

$$\text{(III.)} \quad \left[\begin{array}{c} \overset{\displaystyle CH_2 \cdot NH_3 SCN}{\underset{\displaystyle}{\overset{\displaystyle|}{\overset{\displaystyle *}{}}}} \\ NH_2 \cdot CH_2 \cdot \overset{*}{C}H \cdot NH_2 \\ > Pt < \\ N\overset{\displaystyle *}{H}_2 \cdot CH_2 \cdot \overset{*}{C}H \cdot NH_2 \\ | \\ CH_2 \cdot NH_3 SCN \end{array} \right] (SCN)_2$$

to the metal by only two of its three amino-groups, leaving the third free for normal salt formation as a thiocyanate : the 4-co-ordination platinous atom, being thus saturated, also forms a dithiocyanate, and the compound in solution furnishes, in all, four thiocyanate ions. This compound is therefore of precisely the same type as the cupric compound already described (*loc. cit.*).   The work of Mills and Gotts (J., 1926, 3121) has shown that in such cupric compounds the four co-ordination valencies are directed to the apices of a tetrahedron, and the very close resemblance in type and properties between these cupric and platinous compounds would show that the latter also probably have the tetrahedral configuration.   Experimental evidence for this is unfortunately difficult to obtain.   It will be seen that the platinous compound (III) has two asymmetric carbon atoms, and should therefore exist in racemic and *meso*-forms by virtue of these carbon atoms alone : in both forms, however, the complex itself, if tetrahedrally arranged, is dissymmetric and should be capable of further resolution into optically active forms.   Mere resolution of the compound, therefore, gives no evidence as to the configuration of the platinous complex itself.   Such evidence could only be obtained by separating the racemic and the *meso*-forms, and then resolving the latter form : this " secondary " activity could not be due to the asymmetric carbon atoms, and would thus prove the tetrahedral configuration of the platinous complex.   Actually the platinous thiocyanate, like the cupric compound, is a crystalline compound of sharp melting point, and is obviously a single chemical individual : no evidence of the existence of two forms, racemic and *meso*, could be obtained.

If now the colourless solution obtained by treating potassium chloroplatinite with the free base is concentrated and then, without the addition of acid, is treated with potassium iodide solution, *bis(triaminopropane)platinous di-iodide*,

$$[Pt\{NH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2\}_2]I_2,$$
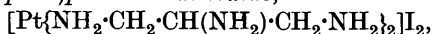
is precipitated.   This would appear to be a novel type of compound

in which the bivalent platinum atom has a co-ordination number of 6 instead of its usual number of 4. There remains a second possibility, *viz.*, that this compound is of precisely the same type as the thiocyanate (III), but that, in the absence of acid, the two γ-amino-groups exist free, being neither co-ordinated to the metal nor neutralised by acid. This is, however, unlikely, since on crystallisation from aqueous solution each free amino-group would almost undoubtedly add on a molecule of water to give a substituted ammonium hydroxide, as in the cupric ethylenediaminobisacetyl-acetone ethylenediamine hydrate described by Morgan and Smith (J., 1926, 918). The existence of two free γ-amino-groups was, however, completely disproved by treating the di-iodide in aqueous solution with an excess of free picric acid : a *dipicrate* alone was obtained, showing that all six amino-groups are co-ordinated to the platinum atom. Had the two γ-amino-groups been free, the di-iodide should have given a tetrapicrate, since, in addition to the dipicrate of the complex, each free amino-group would also unite with picric acid.

These are the first compounds to be described in which a bivalent platinum atom has a co-ordination number of 6. They serve to illustrate one respect in which the stability of the complex salts with simple molecules, *e.g.*, ammonia and water, differs from that of complex salts with polyamine molecules, *e.g.*, triaminopropane. The stability of the simple ammines is determined primarily by the electronic structure of the metal when thus co-ordinated, *e.g.*, cobalt of atomic number 27 requires 9 electrons to complete its outer shell and in $[(NH_3)_6Co]Cl_3$ these 9 are obtained $(+ 12 - 3)$ and an extremely stable salt results. Platinum of atomic number 78 requires 8 electrons to complete its outer shell. In the platinic series, *e.g.*, $[(NH_3)_6Pt]Cl_4$, these are again acquired, giving a very stable salt, whereas in the platinous series, *e.g.*, $[(NH_3)_4Pt]Cl_2$, only 6 are obtained ; since, however, a small deficiency of electrons is more readily tolerated than an excess, these tetramminoplatinous salts are stable, although less so than the hexamminoplatinic salts. The stability of the complex salts of the polyamines is dependent, however, on an additional factor, *viz.*, the comparative ease with which the polyamine molecule, for purely structural reasons, can arrange itself about a complex that may be a square, a tetrahedron, or an octahedron. There is considerable evidence to show that triaminopropane adjusts itself readily and very stably to the 6-co-ordination octahedron (Mann and Pope, *Proc. Roy. Soc.*, 1925, *A*, **107**, 80; J., 1926, 2675). The great stability of the bis(triamino-propane)-cobaltic and -rhodium trihalides is to be expected, since the metallic atoms here have completed their electronic outer shells

in the usual way. But in the case of nickel, the tetrammino-nickelous dihalides, $e.g.$, $[(NH_3)_4Ni]Cl_2$, in which the metal has a deficiency of 2 electrons, are far more stable than the hexammino-nickelous dihalides, $e.g.$, $[(NH_3)_6Ni]Cl_2$, in which the metal has a surplus of 2 electrons. Yet nickel combines with triaminopropane to give always the very stable bis(triaminopropane)nickelous salts, $e.g.$, $[\{NH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2\}_2Ni]I_2$, in which the metal has a co-ordination number of 6, and no triaminopropane salt in which the nickel has a co-ordination number of 4 has yet been isolated. Triaminopropane thus adjusts itself so much more stably around the 6-co-ordination octahedron than around a tetrahedron or a square that a metallic atom, normally of co-ordination number 4, will sometimes increase the latter to 6 in order to accommodate itself to the triamine, although for purely electronic reasons such an arrange-ment would be regarded as unstable. A further example of this is provided by the bis(triaminopropane)platinous dihalides now described, in which the bivalent platinum has increased its co-ordination number to 6 in order to provide the octahedron necessary for stable co-ordination with triaminopropane, although the metallic atom has thereby acquired an excess of 2 electrons.

When triaminopropane co-ordinates by means of only two of its three amino-groups, the above considerations no longer hold, and stable 4-co-ordination derivatives, $e.g.$, of platinum and copper, result.

Ammonium chloropalladite co-ordinates with triaminopropane trihydrochloride to give $dichloro(triaminopropane$-$monohydro$-$chloride)palladium$, $[Cl_2PdNH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2, HCl]$. This salt proved to be unstable in hot aqueous solution, and therefore no attempts were made to resolve it into optically active forms.

EXPERIMENTAL.

All rotations given in this paper have been measured at 15° in a 4-dm. polarimeter tube by means of the mercury green line ($\lambda =$ 5461).

$Dichloro(triaminopropane$-γ-$monohydrochloride)platinum$ $Mono$-$hydrate$.—Potassium chloroplatinite (16 g.) and triaminopropane trihydrochloride (16 g.) were dissolved in turn in water (240 c.c.), and the solution was boiled under reflux for 2 hours, the deep red colour changing to orange. The solution was concentrated until crystals appeared, then filtered and chilled. The crude product (11·8 g.), when recrystallised from hot water, gave the above $mono$-$hydrate$ in pale yellow crystals, which darken at 280° and melt at 290—291° (decomp.) (Found : C, 8·9; H, 3·4; N, 9·9; Pt, 47·6; H_2O, 4·4. $C_3H_{12}N_3Cl_3Pt,H_2O$ requires C, 8·8; H, 3·4; N, 10·25; Pt, 47·6; H_2O, 4·4%).

d-*Dichloro(triaminopropane-mono*-d-*bromocamphor*-π-*sulphonate*)-*platinum Monohydrate*,

$[Cl_2PtNH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2, C_{10}H_{14}OBr \cdot SO_3H], H_2O$.
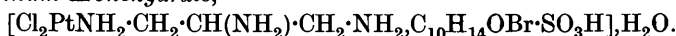
—Hot aqueous solutions of dichloro(triaminopropane-monohydrochloride)platinum monohydrate (12 g.) and silver d-bromocamphorsulphonate (13·2 g.) were mixed, boiled for 5 minutes, and filtered. The filtrate, when concentrated and cooled, deposited orange-yellow crystals, which, after five recrystallisations from water, gave the above optically pure d-*base* d-*sulphonate* (Found : C, 22·8; H, 4·2; Pt, 28·4. $C_{13}H_{28}O_5N_3Cl_2BrSPt$ requires C, 22·8; H, 4·1; Pt, 28·5%). A 0·5773% aqueous solution had α = + 1·76°, whence [α] = + 76·2°, [M] = + 522°.

d-*Dichloro(triaminopropane-monohydrochloride)platinum*.—A solution of the above optically pure d-base d-sulphonate in the minimum of hot water was diluted with a hot concentrated solution of calcium chloride, filtered, and chilled. After 24 hours, the anhydrous crystalline d-*monohydrochloride* which had separated was filtered off, washed with alcohol and ether, and dried (Found : Pt, 50·0. $C_3H_{12}N_3Cl_3Pt$ requires Pt, 49·8%). A 1·051% aqueous solution had α = + 2·09°, whence [α] = + 49·7°, [M] = + 195°.

l-*Dichloro(triaminopropane-mono*-l-*bromocamphor*-π-*sulphonate*)-*platinum Monohydrate*.—This separated from a saturated aqueous solution of the racemic monohydrochloride when the latter was diluted with a concentrated solution of ammonium l-bromocamphorsulphonate, and again five recrystallisations from water furnished the optically pure l-*base* l-*sulphonate* (Found : Pt, 28·65%). A 0·5032% aqueous solution had α = − 1·54°, whence [α] = − 76·5°, [M] = − 524°.

l-*Dichloro(triaminopropane-monohydrochloride)platinum* was prepared as pale yellow crystals by treating the l-base l-sulphonate in solution with calcium chloride (Found : Pt, 49·9%). A 1·279% aqueous solution had α = − 2·51°, whence [α] = − 49·1°, [M] = − 192°.

Dichloro(triaminopropane-mono-d-*camphor*-β-*sulphonate)platinum*, $[Cl_2PtNH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2, C_{10}H_{15}O \cdot SO_3H]$, was isolated in a similar way to the bromocamphorsulphonate by the interaction of the monohydrochloride (10 g.) and silver d-camphorsulphonate (8·4 g.).   Two recrystallisations from water gave the d-*camphorsulphonate* as a pale yellow, crystalline powder (Found : C, 26·5; H, 4·7; Pt, 33·1. $C_{13}H_{27}O_4N_3Cl_2SPt$ requires C, 26·6; H, 4·6; Pt, 33·2%).   A 1·294% aqueous solution had α = + 0·54°, whence [α] = + 10°, [M] = + 61°.   The material was now recrystallised three times, and then in a 1·463% solution had α = + 0·58°, whence [α] = 9·9°, [M] = + 58°.   As the average rotation found by

Graham (J., 1912, **101**, 746) for the camphor-β-sulphonate ion is 65·8°, it was obvious that the resolution was proceeding very slowly, and no further experiments were made with this salt.

Dichloro(triaminopropane - hydrogen - oxalate)platinum. — When aqueous solutions of the monohydrochloride and of oxalic acid were mixed, the above *hydrogen oxalate* rapidly separated as an orange crystalline powder, only slightly soluble in cold water. It was recrystallised from hot water and then, since the water of crystallisation was only slowly lost in a desiccator, it was dehydrated by heating at 95° in a vacuum. The anhydrous material had m. p. 216—217° (decomp.) with preliminary darkening (Found : C, 13·2; H, 3·1; Pt, 44·2. $C_5H_{13}O_4N_3Cl_2Pt$ requires C, 13·5; H, 2·9; Pt, 43·8%).

Monochlorotriaminopropaneplatinous   Monochloride. — When aqueous ammonia was added to a concentrated aqueous solution of the monohydrochloride, a yellow crystalline precipitate rapidly separated. This was insoluble in cold water, and dissolved in hot water only with decomposition, since such solutions slowly deposited a white product. It was therefore filtered off, washed with cold water, and dried, and the above *monochloride* was thus obtained in yellow crystals, m. p. 282—283° (decomp.) (Found : C, 10·0; H, 3·15; Pt, 54·8. $C_3H_{11}N_3Cl_2Pt$ requires C, 10·1; H, 3·1; Pt, 54·95%).

Bis(triaminopropane-monothiocyanate)platinous   Dithiocyanate (III).—Triaminopropane trihydrochloride (9·4 g.), dissolved in water (50 c.c.), was treated with 15% sodium hydroxide solution (34·8 c.c.), and this solution of the free base was now added to potassium chloroplatinite (6 g.), also dissolved in water (50 c.c.). When the final solution was heated on a water-bath, the red colour faded and a buff-coloured precipitate separated : this slowly redissolved, and the now colourless solution was concentrated, chilled, filtered from any sodium chloride, acidified with acetic acid, and treated with concentrated potassium thiocyanate solution, also containing acetic acid. The white precipitate which slowly separated was filtered off after 24 hours, and twice recrystallised from hot water, in which it was very soluble. The above *dithiocyanate* was obtained in white crystals, m. p. 177—178° (Found : C, 19·7; H, 4·0; Pt, 32·15; ionised SCN, 38·2. $C_{10}H_{24}N_{10}S_4Pt$ requires C, 19·7; H, 4·0; Pt, 32·1; 4SCN, 38·2%).

Bis(triaminopropane - mono - d - bromocamphorsulphonate)platinous Di-d-bromocamphorsulphonate Trihydrate,
$[Pt\{NH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2, C_{10}H_{14}OBr \cdot SO_3H\}_2](C_{10}H_{14}OBr \cdot SO_3)_2, 3H_2O.$
—Hot aqueous solutions of the thiocyanate (4 g.) and silver *d*-bromo-

camphorsulphonate (11·7 g.; 4 mols.) were mixed. Concentration of the filtered solution gave the white crystalline *bromocamphorsulphonate trihydrate*, which was recrystallised seven times from water (Found : C, 32·9; H, 5·3; Pt, 11·7. $C_{46}H_{80}O_{16}N_6Br_4S_4Pt,3H_2O$ requires C, 33·0; H, 5·2; Pt, 11·7%). A 0·5184% aqueous solution had $\alpha = +1·66°$, whence $[\alpha] = +80·1°$, $[M] = +1340°$. Since the bromocamphorsulphonate ion has $[M] = 347°$ (Pope and Read, J., 1910, **97**, 2201), the rotation was due to the four sulphonate ions alone.

Bis(triaminopropane)platinous Di-iodide.—The preparation was carried out precisely as for the above thiocyanate, but the final concentrated colourless solution was treated directly with saturated potassium iodide solution, without addition of acetic acid. The fine, white precipitate was twice recrystallised from a little hot water, and the above *di-iodide* obtained as fine white crystals, m. p. 266—267° (decomp.) (Found : C, 11·8; H, 3·5; I, 40·9; Pt, 31·2. $C_6H_{22}N_6I_2Pt$ requires C, 11·6; H, 3·6; I, 40·5; Pt, 31·1%).
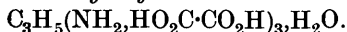
The corresponding *dibromide* was similarly obtained by treating the final colourless solution with saturated sodium bromide solution. After recrystallisation from water, it was obtained in white crystals, m. p. 270—271° (decomp.), far more soluble than the iodide (Found : C, 13·6; H, 4·2; Pt, 36·6. $C_6H_{22}N_6Br_2Pt$ requires C, 13·5; H, 4·2; Pt, 36·6%).

Bis(triaminopropane)platinous Dipicrate,
$$[Pt\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}_2]\{C_6H_2(NO_2)_3\cdot O\}_2.$$
—A dilute solution of the above dibromide was added to a considerable excess of aqueous picric acid solution; the yellow precipitate produced was collected after 2 hours, washed with much cold water, in which it was almost insoluble, and dried. The *dipicrate* was thus obtained as a fine, yellow powder, which deflagrated violently when heated (Found : N, 20·1; Pt, 23·7. $C_{18}H_{26}O_{14}N_{12}Pt$ requires N, 20·3; Pt, 23·5%).

Dichloro(triaminopropane - γ - monohydrochloride)palladium.—Ammonium chloropalladite (3 g.) and triaminopropane trihydrochloride (6·9 g.; 3 mols.) were in turn dissolved in water (50 c.c.) and the clear solution was boiled under reflux for 4 hours, the colour fading to a pale golden-brown. The solution was filtered and allowed to cool in a closed vessel; fine, yellowish-brown crystals were deposited over-night. These were recrystallised as rapidly as possible from a little hot water, and the above *monohydrochloride* obtained in minute, golden-brown crystals, m. p. 279—280° (decomp.) (Found : C, 11·9; H, 4·0; N, 14·1; Pd, 35·3. $C_3H_{12}N_3Cl_3Pd$ requires C, 11·9; H, 4·0; N, 13·9; Pd, 35·2%).

Triaminopropane Trihydrogen Trioxalate Monohydrate,
$$C_3H_5(NH_2,HO_2C \cdot CO_2H)_3,H_2O.$$
—When aqueous solutions of the trihydrochloride and of oxalic acid are mixed, the very characteristic *trihydrogen trioxalate* rapidly separates in white needles, m. p. 173—174° (decomp.) after recrystallisation from hot water. The oxalate is only slightly soluble in cold water, but is freely soluble in hot water (Found : C, 28·8; H, 5·1. $C_9H_{17}O_{12}N_3,H_2O$ requires C, 28·6; H, 5·1%).