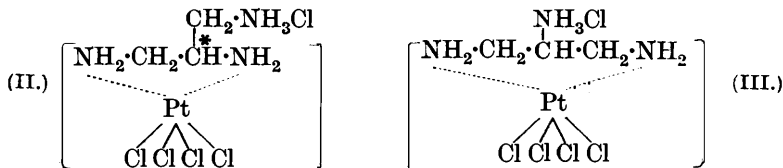


CLXVIII.—*Tetrachloro(triaminopropane- γ -monohydrochloride)platinum, an Optically Active Complex Salt of a New Type.*

By FREDERICK GEORGE MANN.

It has recently been shown by the present author (J., 1926, 2681) that $\alpha\beta\gamma$ -triaminopropane, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{NH}_2$, co-ordinates with platinum and copper to give two complex salts of novel type, in which only two of the three amino-groups in the triaminopropane molecule are joined to the metal, the third being free for normal salt formation with acids. Quadrivalent platinum thus gives tetrachloro(triaminopropane - monohydrochloride)platinum, $\text{Cl}_4\text{Pt}\cdot\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl}$ (I). Here the metallic complex consists of platinum, of co-ordination number 6, linked to four chlorine atoms and to two of the three amino-groups of the base: it is therefore neutral and non-ionic, being, in its co-ordination linkages, of the same general type as tetrachloroethylenediamine-platinum, $[\text{Cl}_4\text{PtNH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2]$. Since, however, the third free amino-group, being unco-ordinated and outside the ring, forms a hydrochloride, the compound in solution furnishes one chlorine ion.

Such a compound may exist in two alternative forms. The platinum may either be co-ordinated to the α - and β -amino-groups, leaving the γ -amino-group free to form the monohydrochloride (II), in which case the triamine is acting for co-ordination purposes as a substituted ethylenediamine, or, alternatively, the platinum may be co-ordinated to the α - and γ -amino-groups, leaving the β -amino-group free to form the hydrochloride (III); in this case the triamine is acting as a substituted trimethylenediamine. A possible method of deciding between these two alternative constitutions was at once suggested by the fact that co-ordination through the α - and β -amino-groups (II) causes the carbon atom marked * to become asymmetric, since it is linked on the one hand to a methylene-amino-group ($\cdot\text{NH}_2\cdot\text{CH}_2\cdot$) and on the other to a methylene-ammonium radical ($\cdot\text{CH}_2\cdot\text{NH}_3^+$). Such a compound should therefore be capable of resolution into optically active forms.

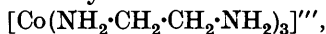


Co-ordination through the $\alpha\gamma$ -diamino-groups (III) gives, however, a symmetrical compound which cannot be so resolved

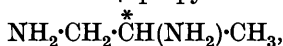
Attempts were therefore made to resolve this compound by converting the hydrochloride of the free amino-group into the corresponding *d*-camphor- β -sulphonate. The latter compound on fractional recrystallisation from water gave finally 1-tetrachloro-(*triaminopropane-mono-d-camphor- β -sulphonate*)platinum, having $[M]_{5461}^{15} = -426^\circ$. This compound on treatment with calcium chloride gave the 1-tetrachloro(*triaminopropane-monohydrochloride*)platinum of $[M]_{5461}^{15} = -502^\circ$. The racemic product was then converted into the *l*-camphor- β -sulphonate, which on recrystallisation furnished similarly *d*-tetrachloro(*triaminopropane-mono-l-camphor- β -sulphonate*)platinum, having $[M]_{5461}^{15} = +424^\circ$, which was in turn converted into the *d*-tetrachloro(*triaminopropane-monohydrochloride*)platinum of $[M]_{5461}^{15} = +501^\circ$. The two optically active monohydrochlorides differ further from the racemic compound in that they crystallise in the anhydrous form, whilst the racemic compound has one molecule of water, which is not readily removed (Mann, *loc. cit.*).

It follows from these results that the platinum compound has the constitution (II), *i.e.*, that the triaminopropane co-ordinates with platinum more readily through the α - and β -amino-groups to form a five-membered ring compound having an asymmetric element, than through the α - and γ -amino-groups, whereby a six-membered ring compound of high symmetry would have been formed.

It should be emphasised that not only is this platinum compound of entirely novel type, but the cause of its optical activity also is novel. All optically active complex salts hitherto recorded have owed their activity to one (or both) of two factors. Either the complex itself has been dissymmetric, and therefore capable of resolution, *e.g.*, the trisethylenediaminecobaltic complex,



or, alternatively, the complex has contained a constituent dissymmetric molecule which has been resolved before the preparation of the complex salt. Thus *d*- $\alpha\beta$ -propylenediamine,



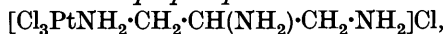
gives a *d*-trispropylenediaminecobaltic complex,



the activity of which is due to the active nature of the constituent amine molecules: here, however, the complex also is itself dissymmetric, and a secondary activity can be manifested by the complex as a whole. In the platinum compound under discussion, however, asymmetry of the central (or β) carbon atom is induced by the mode of co-ordination of the triaminopropane molecule and by the consequent orientation of the co-ordination linkages: the asymmetry of this element therefore does not arise until the co-

ordination compound itself is formed. This is the first case to be recorded in which the asymmetry of a carbon atom arises from the operation of auxiliary valencies.

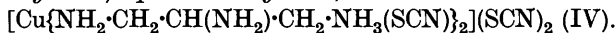
Attempts have been made to replace the four co-ordinated chlorine atoms in tetrachloro(triaminopropane-monohydrochloride)-platinum with further basic groups by treating the compound in solution with ammonia and with ethylenediamine. The action of such bases is, however, solely to withdraw the hydrogen chloride from the free amino-group: the latter at once co-ordinates with the platinum, expelling a chlorine atom from the complex, and the insoluble *trichlorotriaminopropaneplatinic monochloride*,



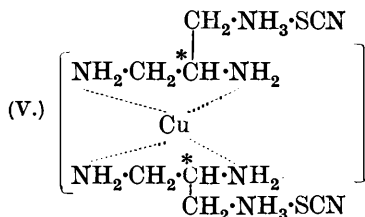
is thus formed.

Tetrachloro(triaminopropane-monohydrochloride)platinum gives a characteristic reaction when treated in solution with oxalic acid, since the very slightly soluble *tetrachloro(triaminopropane-hydrogen-oxalate)platinum*, $[\text{Cl}_4\text{PtNH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{NH}_2(\text{CO}_2\text{H})_2]$, is rapidly precipitated. When this compound is boiled for several hours in aqueous solution, both the unco-ordinated amino-group and the oxalic acid enter the complex, displacing three chlorine atoms, thus furnishing *monochloromonoxalatotriaminopropaneplatinic monochloride*, $[\text{Cl}(\text{CO}\cdot\text{O})_2\text{PtNH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{NH}_2]\text{Cl}$.

It has also been shown (Mann, *loc. cit.*) that copper co-ordinates with triaminopropane to give salts such as *bis(triaminopropane-monothiocyanate)cupric dithiocyanate*,



Here the copper atom is linked to two molecules of the base, but, since it has a co-ordination number of 4, to only two amino-groups in each molecule of the triamine. The metal is thus fully co-ordinated, and the complex therefore bivalent; the two unco-ordinated amino-groups, however, as in the platinum compound, are neutralised by normal salt formation, and in solution thus furnish two additional ions. It would follow by analogy that the $\alpha\beta$ -diamino-linkage probably obtains also in this copper compound, which



would then have the constitution (V), the carbon atoms marked * being asymmetric. Such a compound should exist in racemic,

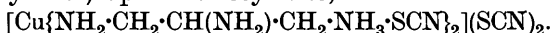
dextro-, lævo-, and *meso*-forms, and if the four co-ordination linkages of the copper are directed to the corners of a regular tetrahedron (Mills and Gotts, J., 1926, 3121), the dextro-, lævo-, and *meso*-forms should each exist in two forms, in which the copper has the *d*- and the *l*-configuration respectively. In view of the intensely deep violet colour of these copper compounds, no attempts at resolution have yet been made.

Further work is now being carried out to determine the mode of co-ordination of triaminopropane with various noble metals, such as iridium and palladium, and with certain bivalent metals such as zinc, cadmium, and mercury, and to determine further whether such compounds are capable of resolution into optically active forms.

The various types of complex salts furnished by triaminopropane may be conveniently summarised here (Mann and Pope, *Proc. Roy. Soc.*, 1925, *A*, 107, 80; J., 1926, 2675; Mann, J., 1926, 2682):—

1. Metals of co-ordination number 4 :

A. Triaminopropane acting as a diamine : Bis(triaminopropane- γ -monothiocyanate)cupric dithiocyanate,

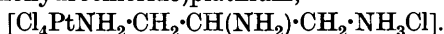


B. Triaminopropane acting as a triamine : Tetratriaminopropane-tricupric hexathiocyanate,



2. Metals of co-ordination number 6 :

A. Triaminopropane acting as a diamine : Tetrachloro(triaminopropane- γ -monohydrochloride)platinum,



B. Triaminopropane acting as a triamine : (a) Triacido-triammine type. Trichlorotriaminopropaneplatonic monochloride,



(b) Hexamine type. Bistriaminopropanecobaltic trichloride,



and the corresponding nickel and rhodium salts.

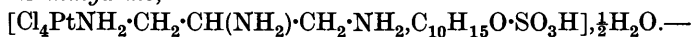
EXPERIMENTAL.

All rotations given in this paper have been measured at 15° in a 4-dcm. polarimeter tube, and, unless otherwise stated, are for the mercury green line ($\lambda = 5461$).

Preparation of Tetrachloro(triaminopropane-monohydrochloride)-platinum Monohydrate.—The following quantitative directions supplement the general directions already given (Mann, *loc. cit.*, p. 2686). A solution of triaminopropane trihydrochloride monohydrate (22 g.) in water (200 c.c.) is added to 100 c.c. of a solution

of chloroplatinic acid containing 10% of metallic platinum. The clear mixture is boiled under reflux for 3 hours, and the pale yellow solution so obtained twice evaporated to small bulk on the water-bath with intermediate addition of water. The solution is finally concentrated until crystals appear, and on cooling, tetrachloro-(triaminopropane-monohydrochloride)platinum monohydrate rapidly separates (20.3 g.). This material, after two recrystallisations from water, is pure, and darkens at 255—260° and melts at 272—273° (decomp.).

1. *Tetrachloro (triaminopropane-mono-d-camphor- β -sulphonate) platinum Semihydrate,*



Hot aqueous solutions of tetrachloro(triaminopropane-monohydrochloride)platinum monohydrate (20 g.) and silver *d*-camphor- β -sulphonate (10.4 g.) were mixed, boiled for 5 minutes, and filtered. The filtrate was evaporated to small bulk on the water-bath, fine, crystalline scales steadily separating; finally the product formed a semi-solid mush, which was at once chilled and filtered. The solid product so obtained was then recrystallised repeatedly from hot water to separate the *l*-base *d*-sulphonate from the more soluble *d*-base *d*-sulphonate. Recrystallisation was best carried out by drying each fraction thoroughly in a vacuum over sulphuric acid, and then adding the powdered product quickly with stirring to a small quantity of almost boiling water. A clear solution was thus rapidly obtained, and on filtering and cooling gave an ample crop of the sulphonate. The latter always retained half a molecule of water of crystallisation even after long exposure to sulphuric acid in a vacuum. After six recrystallisations from water, the *l*-base *d*-sulphonate was obtained as a pale lemon-yellow powder, which in 1.349% aqueous solution had $\alpha = -3.44^\circ$, whence $[\alpha] = -63.7^\circ$ and $[M] = -426^\circ$: it darkened at 260° and melted to a tar between 270° and 285° (Found: Pt, 29.3. $\text{C}_{26}\text{H}_{56}\text{O}_9\text{N}_6\text{Cl}_8\text{S}_2\text{Pt}_2$ requires Pt, 29.25%). This sulphonate does not readily undergo racemisation at the ordinary temperature, since cold aqueous solutions retained their activity unchanged for a week.

A dextrorotatory product also could be separated in the above experiments, for when the cold aqueous mother-liquor from the second fraction was diluted considerably with alcohol and kept over-night, a crop of the camphorsulphonate separated which, in 1.572% solution, had $\alpha = +3.08^\circ$, whence $[\alpha] = +49.0^\circ$ and $[M] = +323^\circ$. This was thus evidently an optically impure *d*-base *d*-sulphonate, and attempts were made to purify it by repeated dissolution in water and reprecipitation with alcohol. These experiments did not, however, give satisfactory results, and

the optically pure dextro-salt was finally obtained by recrystallisation of the *l*-camphorsulphonate, as described below.

l-Tetrachloro(triaminopropane-mono-hydrochloride) platinum. — The sixth fraction of the *l*-tetrachloro(triaminopropane-mono-*d*-camphor- β -sulphonate)platinum, having $[M] = -426^\circ$, was dissolved in a little hot water and the solution was chilled, filtered, and diluted with concentrated aqueous calcium chloride solution. After 4 hours the fine, crystalline mono-hydrochloride which had separated was collected, well washed with alcohol and ether, and dried. The pure anhydrous *l*-mono-hydrochloride thus obtained retained its original crystalline form during the processes of filtering and drying; it had evidently, therefore, separated originally in the anhydrous form, and not lost water of crystallisation whilst being dried. It darkened at $260-265^\circ$ and melted at $277-278^\circ$ (decomp.) (Found: Pt, 42.2. $C_3H_{12}N_3Cl_5Pt$ requires Pt, 42.2%). A 1.407% aqueous solution had $\alpha_{3780}^{15} = -5.24^\circ$, whence $[\alpha]_{3780}^{15} = -93.1^\circ$, $[M]_{3780}^{15} = -431^\circ$, and $\alpha_{5461}^{15} = -6.10^\circ$, whence $[\alpha]_{5461}^{15} = -108.4^\circ$, $[M]_{5461}^{15} = -502^\circ$.

Certain observations made in the course of the above work point strongly to the fact that the resolution is successful only if the camphorsulphonate crystallises at a low temperature, and that at higher temperatures it is probably the racemate, or even a product containing an excess of the opposite enantiomorph, which separates. Thus, in the initial preparation, the first crop of crude *d*-camphorsulphonate was obtained by evaporating the solution on the water-bath and then filtering off the solid product which separated. Since the *l*-base *d*-sulphonate is less soluble (in cold water) than the *d*-base *d*-sulphonate, the filtrate from this first crude product should have contained an excess of the *d*-base *d*-sulphonate. Actually it contained an excess of the *l*-base, and when treated with calcium chloride gave a markedly lævorotatory hydrochloride which, in 1.672% aqueous solution, had $\alpha = -0.78^\circ$, whence $[\alpha] = -11.7^\circ$. When the first crop of crude *d*-camphorsulphonate was subjected to its first recrystallisation, the second fraction obtained now separated after the solution had been chilled; it possessed, of course, an increased lævorotation, and the mother-liquor now contained an excess of the *d*-base, and when treated with calcium chloride gave a feebly dextrorotatory hydrochloride. All the successive fractions also separated after their solutions had been chilled, and the resolution thus proceeded smoothly to completion. It was further observed that if the initial filtrate from the first crop of crude *d*-camphorsulphonate was kept, in the course of 24 hours long, pale lemon-yellow needles of the almost optically pure *l*-base *d*-sulphonate separated, and after several days became contain-

ated with orange-coloured prisms, presumably those of the *d*-base *d*-sulphonate. In some preparations of the *d*-camphorsulphonate, these long, pale lemon-yellow needles were filtered off before the separation of the orange prisms; they were washed with a little water, and placed over sulphuric acid in a vacuum; they then rapidly lost their crystalline form on partial dehydration, and gave the semihydrate of the almost optically pure *l*-base *d*-sulphonate. Two such samples gave the following rotations respectively: (a) a 1.008% aqueous solution had $\alpha = -2.53^\circ$, whence $[\alpha] = -62.7^\circ$ and $[M] = -419^\circ$; (b) a 1.184% solution had $\alpha = -2.93^\circ$, $[\alpha] = -61.9^\circ$, $[M] = -413^\circ$. These were united and converted into the hydrochloride as before by the action of calcium chloride solution. A crop of the anhydrous and optically pure *l*-hydrochloride was thus obtained (Found: Pt, 42.2%). A 1.328% aqueous solution had $\alpha = -5.72^\circ$, $[\alpha] = -108^\circ$, and $[M] = -498^\circ$.

d-Tetrachloro(triaminopropane-mono-*l*-camphor- β -sulphonate)platinum Semihydrate.—This was prepared in precisely the same way as the *l*-base *d*-sulphonate, the racemic hydrochloride being treated in solution with silver *l*-camphor- β -sulphonate. The product was recrystallised as before six times from water, and the final crop had in 1.366% aqueous solution, $\alpha = +3.47^\circ$, whence $[\alpha] = +63.5^\circ$ and $[M] = +424^\circ$ (Found: Pt, 29.15%).

Once again an optically impure crop of the opposite enantiomorph could be obtained by precipitation with alcohol. The filtrate from the second fraction of the *l*-sulphonate, when diluted considerably with alcohol, deposited a crop of the sulphonate which, when separated and dried, had, in 1.218% aqueous solution, $\alpha = -2.59^\circ$, whence $[\alpha] = -53.1^\circ$ and $[M] = -355^\circ$. No further attempts to complete the resolution of this crop by solution in water and reprecipitation with alcohol were made.

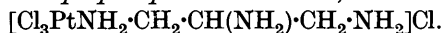
d-Tetrachloro(triaminopropane-mono-hydrochloride)platinum.—The optically pure, sixth fraction of the *d*-base *l*-sulphonate, having $[M] = +424^\circ$, was treated as before in cold aqueous solution with calcium chloride, and the *d*-tetrachloro(triaminopropane-mono-hydrochloride)platinum separated in fine crystals, which were filtered off, washed with alcohol and ether, and dried. These crystals, like the *l*-hydrochloride, were anhydrous (Found: Pt, 42.1%), and darkened at 260—265° and melted at 277—278° (decomp.). A 1.555% aqueous solution had $\alpha_{5780}^{15^\circ} = +5.80^\circ$, whence $[\alpha]_{5780}^{15^\circ} = +93.2^\circ$, $[M]_{5780}^{15^\circ} = +431^\circ$, and $\alpha_{5461}^{15^\circ} = +6.73^\circ$, whence $[\alpha]_{5461}^{15^\circ} = +108^\circ$, $[M]_{5461}^{15^\circ} = +501^\circ$.

As before, the initial filtrate from the first crude crop of the *l*-camphorsulphonate slowly deposited a small quantity of the almost optically pure *d*-base *l*-sulphonate in long, pale lemon-yellow

needles. These, after being washed and dried, had in 1.232% aqueous solution $\alpha = +3.11^\circ$, whence $[\alpha] = +63.1^\circ$ and $[M] = +421^\circ$. There was not sufficient of this material, however, for conversion into the *d*-hydrochloride.

Tetrachloro(triaminopropane-mono-d- α -bromocamphor- π -sulphonate)platinum, $[\text{Cl}_4\text{PtNH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{C}_{10}\text{H}_{14}\text{OBr}\cdot\text{SO}_3\text{H}]$.—The bromocamphorsulphonate was obtained by mixing hot aqueous solutions of the monohydrochloride (10 g.) and of silver *d*-bromocamphorsulphonate (6.8 g.). The mixed solution, when boiled, filtered, concentrated, and chilled, gave the bromocamphorsulphonate in fine, canary-yellow crystals. These, after being once recrystallised from water and dried, melted at $271\text{--}273^\circ$ (decomp.) (Found: C, 21.0; H, 3.6; Pt, 26.6. $\text{C}_{13}\text{H}_{26}\text{O}_4\text{N}_3\text{Cl}_4\text{BrSPt}$ requires C, 21.15; H, 3.55; Pt, 26.5%). The sulphonate in 1.916% aqueous solution had $\alpha = +3.52^\circ$, $[\alpha] = +45.9^\circ$, and $[M] = +339^\circ$. This material was now recrystallised three more times from water and, in 1.320% solution, then had $\alpha = +2.48^\circ$, $[\alpha] = +47.0^\circ$, $[M] = +346^\circ$. Since ammonium *d*-bromocamphor- π -sulphonate has $[M]_{5461}^{22^\circ} = +347^\circ$ (Pope and Read, J., 1910, 97, 2201), it was obvious that the activity of the platinum compound was due to the bromocamphorsulphonate ion alone, and that no apparent resolution was being effected.

Trichlorotriaminopropaneplatonic Chloride,



—A cold aqueous solution of tetrachloro(triaminopropane-mono-hydrochloride)platinum was treated with an excess of ammonia solution (*d* 0.966). The fine, yellow, crystalline precipitate which soon appeared was very sparingly soluble in cold water; when boiled with hot water, it slowly dissolved, but the production of a red colour showed considerable reduction to a platinous salt. This ready reduction of co-ordinated platonic to platinous compounds has already been noted by Werner (*Vierteljahrs. Naturfors. Ges. Zurich*, 1917, 62, 553). The compound was therefore filtered off, and thoroughly washed with cold water, alcohol, and ether, and *trichlorotriaminopropaneplatonic chloride* was thus obtained in fine, yellow crystals which began to darken at about 210° and melted at $242\text{--}243^\circ$ (decomp.) (Found: C, 8.4; H, 2.8; N, 10.1; Pt, 45.9. $\text{C}_3\text{H}_{11}\text{N}_3\text{Cl}_4\text{Pt}$ requires C, 8.45; H, 2.6; N, 9.9; Pt, 45.8%). The same compound was also obtained when the original monohydrochloride was treated in solution with either one or two molecules of ethylenediamine hydrate.

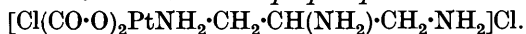
Tetrachloro(triaminopropane-hydrogen-oxalate)platinum,



—This compound rapidly separated when an aqueous solution of the

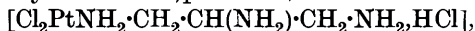
monohydrochloride was treated with a solution of oxalic acid: it is only slightly soluble in cold water, and when filtered off, washed with water, alcohol, and ether, was obtained as a fine, pale yellow powder, m. p. 248—251° (decomp.) (Found: N, 8.4; Cl, 27.7; Pt, 37.6. $C_5H_{13}O_4N_3Cl_4Pt$ requires N, 8.1; Cl, 27.5; Pt, 37.8%).

Monochloromono-oxalatotriaminopropaneplatinic Chloride,



—Solutions of tetrachloro(triaminopropane-monohydrochloride)-platinum (9.9 g.) and hydrated oxalic acid (5.2 g.; 2 mols.), each in 125 c.c. of water, were mixed, and the solution was heated to dissolve the precipitated hydrogen oxalate salt. The clear solution was boiled under reflux for 10 hours, and on filtering and cooling deposited fine, yellow crystals. These were twice recrystallised from hot water, in which they were freely soluble, and the *monochloromono-oxalatotriaminopropaneplatinic chloride* was thus obtained as a pale brownish-yellow, microcrystalline powder, which decomposed with foaming between 200° and 210° and was then slowly transformed to a dry, black mass (Found: N, 9.6; Cl, 16.2; Pt, 43.85. $C_5H_{11}O_4N_3Cl_2Pt$ requires N, 9.5; Cl, 16.0; Pt, 44.0%).

Many attempts were made to reduce the monohydrochloride to a compound of bivalent platinum of the type of dichloro(triaminopropane-monohydrochloride)platinum,



a compound which should also have been susceptible to resolution into optically active forms. The yellow monohydrochloride, when treated in hot aqueous solution with sulphur dioxide, slowly underwent reduction with the production of a colourless solution. From this solution various products were obtained, but all on attempted recrystallisation from water underwent decomposition with the evolution of sulphur dioxide, and no well-defined, stable compound could be isolated.

The author is greatly indebted to Professor Sir William Pope, F.R.S., for supplies of platinum and of *l*-camphor, without which this investigation could not have been carried out.

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