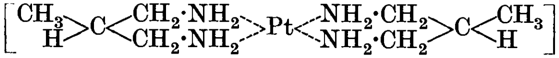
CLXIV.—*The Complex Salts of β-Methyltrimethylenediamine with Bivalent Platinum.*

By Frederick George Mann.

Bivalent platinum, of co-ordination number 4, forms complex salts which usually have the uniplanar configuration : there is, however, some evidence that certain such salts have the tetrahedral configuration. For instance, considerations of structure alone make it highly probable that ββ′β″-triaminotriethylamineplatinous di-iodide, $[PtN(CH_2{\cdot}CH_2{\cdot}NH_2)_3]I_2$ (Mann and Pope, *Proc. Roy. Soc.*, 1925, *A*, **109**, 457), has the tetrahedral, rather than the uniplanar, configuration. Bis(triaminopropane-monothiocyanate)platinous dithiocyanate, $[Pt\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HSCN\}_2](SCN)_2$, is identical in type with the corresponding cupric salt (Mann, this vol., p. 890) : since the tetrammino-cupric complex is known to have the tetrahedral configuration, it is again highly probable that the platinous salt also has the same configuration. Attempts were made to obtain more decisive evidence by a further study of the salts of the bis(β-methyltrimethylenediamine)platinous complex,



$$\left[\begin{matrix}CH_3\\H\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2{\cdot}NH_2\\CH_2{\cdot}NH_2\end{matrix}\!>\!Pt\!<\!\begin{matrix}NH_2{\cdot}CH_2\\NH_2{\cdot}CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CH_3\\H\end{matrix}\right]''$$

(Mann, J., 1927, 2917). If this complex has the uniplanar configuration, its salts should show *cis-trans* isomerism according as the two methyl groups are on the same or opposite sides of the common plane of the two rings : if it has the tetrahedral configuration, the two ring systems are at right angles to each other, and the molecular dissymmetry thus produced should render its salts capable of resolution into optically active forms.

The six salts of this complex which have been isolated showed no sign of *cis-trans* isomerism, although they were all highly crystalline compounds in which such isomerism should have been readily detected : moreover, their widely differing solubilities make it extremely unlikely that a more soluble isomeride remained in solution in each case, and so avoided identification. The camphorsulphonate, bromocamphorsulphonate, and tartrate, on the other hand, could not be resolved into optically active forms. Such salts, like those of the corresponding nickelous complex (Mann, *loc. cit.*), thus provide no evidence as to the configuration of the metallic complex. If the complex is uniplanar, this may be due to one isomeride being relatively so stable that it is formed to the almost complete exclusion of the other : if the complex is tetrahedral, the absence of evidence may be due to very rapid racemisation of the salts in solution.

EXPERIMENTAL.

All rotations have been measured at 15° in a 4-dcm. polarimeter tube, using the mercury green line ($\lambda = 5461$).

Bis(β-methyltrimethylenediamine)platinous Dichloride, $[Pt\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}_2]Cl_2$.—A solution of β-methyltrimethylenediamine dihydrochloride (12 g.; 3 mols.) in 10% aqueous sodium hydroxide (58 c.c.) was added to a solution of potassium chloroplatinite (10 g.) in water (150 c.c.), and the whole boiled gently under reflux. The red colour of the chloroplatinite rapidly faded, and long, colourless needles separated; these slowly redissolved, giving a colourless solution. The latter, when concentrated on the water-bath, can be used for the preparation of most salts of the complex.

The dichloride was obtained when the colourless solution was allowed to cool and crystallise : it separated in long, colourless, uniform needles, m. p. 266—267° (decomp.).

The *dibromide*, obtained by treating the colourless solution with saturated sodium bromide solution, was recrystallised from water, and separated in colourless needles, m. p. 266—268° (decomp.) (Found: C, 18·0; H, 4·55; Pt, 36·6. $C_8H_{24}N_4Br_2Pt$ requires C, 18·1; H, 4·55; Pt, 36·7%).

The *di-iodide*, similarly obtained by precipitation with potassium iodide, when recrystallised from hot water gave colourless, crystalline leaflets, m. p. 263—264° (decomp.) with preliminary darkening (Found: C, 15·4; H, 3·9; Pt, 31·2. $C_8H_{24}N_4I_2Pt$ requires C, 15·4; H, 3·9; Pt, 31·2%). The di-iodide, owing to its very slight solubility in cold water, is the best form in which to isolate the complex from the colourless solution obtained in the original preparation.

The *dinitrate*, obtained from the original solution by treatment with sodium nitrate, separates on recrystallisation from hot water in large, dense, colourless crystals, which are only slightly soluble in cold water. On heating, it deflagrates violently (Found : C, 19·2; H, 4·9; Pt, 39·1. $C_8H_{24}O_6N_6Pt$ requires C, 19·4; H, 4·9; Pt, 39·4%).

The *di*-d-*camphor*-β-*sulphonate monohydrate*,

$$[Pt\{CH_3{\cdot}CH(CH_2{\cdot}NH_2)_2\}_2](C_{10}H_{15}O{\cdot}SO_3)_2,H_2O,$$

was obtained by treating the di-iodide in hot aqueous solution with the calculated quantity of silver *d*-camphorsulphonate. The solution, when boiled, filtered, and concentrated, gave the *sulphonate* in fine, colourless crystals, moderately easily soluble in cold water. These were recrystallised three times from water, and then had m. p. 279—281° (decomp.) (Found : C, 39·6; H, 6·6; Pt, 23·2. $C_{28}H_{56}O_9N_4S_2Pt$ requires C, 39·5; H, 6·6; Pt, 22·9%). A 1·467% aqueous solution had $\alpha = +0{\cdot}90°$, $[\alpha] = +15°$, $[M] = +130°$: neither the rotation nor the decomposition point was changed by further recrystallisation from water. Since Graham (J., 1912, **101**, 746) has found the camphorsulphonate ion at similar concentration to have an average value of $[M] = 66°$, the rotation of the above salt must have been due to the sulphonate ions alone : this was confirmed by converting the dicamphorsulphonate into the dibromide, which was inactive.

The *di*-d-α-*bromocamphor*-π-*sulphonate* was prepared by mixing very dilute hot aqueous solutions of the di-iodide and of the calculated quantity of silver *d*-bromocamphorsulphonate : from the filtered, cooled mixture, the very sparingly soluble *di*-d-*bromocamphorsulphonate* separated rapidly in long colourless needles, which on heating decomposed slowly between 278° and 285° (Found : C, 34·0; H, 5·25; Pt, 19·7. $C_{28}H_{52}O_8N_4Br_2S_2Pt$ requires C, 33·9; H, 5·3; Pt, 19·7%). After three recrystallisations of the salt from water, a 0·8453% solution had $\alpha = +2{\cdot}34°$, $[\alpha] = +69{\cdot}2°$, and $[M] = +686°$. Since the bromocamphorsulphonate ion has $[M] = 347°$, the rotation of the complex salt is again due solely to the sulphonate ions.

The *ditartrate* was obtained by adding freshly prepared, finely powdered silver tartrate to a hot solution of the di-iodide; after boiling for ½ hour, the solution was filtered and concentrated. The concentrated aqueous solution of the tartrate, however, would not crystallise, but remained as a thick syrup. The latter was therefore taken up in a little water and fractionally precipitated with alcohol; this precipitation was repeated twice and the final syrup redissolved in water and converted into dibromide. The latter, however, was inactive.

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[*Received, March 24th*, 1928.]