CCCLIII.—*The Complex Salts of $\alpha\beta\gamma$-Triaminopropane with Copper and Platinum.*

By FREDERICK GEORGE MANN.

MOST complex salts of bivalent copper can be grouped into two classes, *viz.*, those in which the metal shows a co-ordination number of 4, such as tetramminocupric chloride, $[Cu(NH_3)_4]Cl_2$, and bis-ethylenediaminecupric chloride, $[Cu(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2]Cl_2$; and those in which it shows a co-ordination number of 6, such as hexamminocupric chloride, $[Cu(NH_3)_6]Cl_2$, and trisethylenediaminecupric chloride, $[Cu(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_3]Cl_2$. Salts of the latter class are, however, considerably less stable than those of the former class, and usually revert readily, for instance, on attempted recrystallisation from water, to the corresponding compounds in which the copper has a co-ordination number of 4. It has been shown in the previous paper (p. 2676) that the bistriaminopropane metallic complex salts possess great stability, and that bistriaminopropanenickel iodide, $[Ni\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2]I_2$, for instance, shows no perceptible tendency to revert to a compound in which the nickel shows a co-ordination number of 4 : in fact, no such compounds have yet been isolated. It was therefore considered probable that a compound of the type of bistriaminopropanecupric chloride, $[Cu\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_2]Cl_2$, would also be sufficiently stable to allow of its isolation and purification, and attempts were made to prepare such a compound in the hope that it might show the isomerism which the corresponding cobalt, rhodium, and nickel salts had failed to reveal.

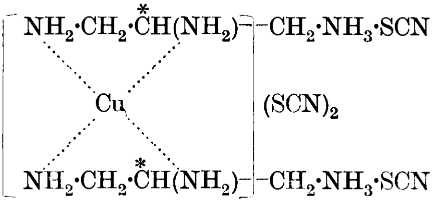
When triaminopropane was added to an aqueous solution of a cupric salt, co-ordination at once occurred with the production of the usual characteristically deep violet colour. From such a solution, however, no complex salt of triaminopropane and copper, in which the latter shows a co-ordination number of 6, could be obtained. Instead, two complex salts of unexpected and novel types, in both of which the metal shows a co-ordination number of 4, were isolated. If copper, whilst showing a co-ordination number of 4, is to be completely saturated with a triamine, three atoms of the metal should unite with four molecules of the base : a complex of this type has now been isolated, for when potassium iodide was added to the above violet solution, *tetratriaminopropanetricupric hexaiodide* (I) slowly separated. This hexaiodide, and the corresponding *hexathiocyanate*, which has also been prepared, are quite

(I.) $[Cu_3\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_4]I_6$.
(II.) $[Cu\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HSCN\}_2](SCN)_2$.
(III.) $[Cu\{NH_2{\cdot}CH_2{\cdot}CH(NH_2,HSCN){\cdot}CH_2{\cdot}NH_2\}_2](SCN)_2$.

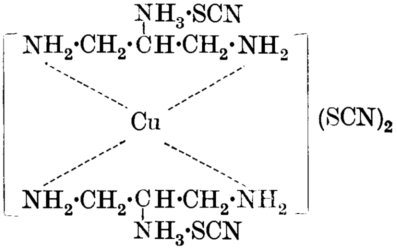
insoluble in cold water, as would be expected in view of their high molecular weight, and slowly decompose when boiled with water.

If, however, an aqueous solution of potassium thiocyanate acidified with acetic acid is added to the original violet copper solution, there separates a highly crystalline, stable compound, which can be obtained pure by recrystallisation from hot water. This compound is *bis(triaminopropanemonothiocyanate)cupric thiocyanate* (II), in which the copper is linked to two molecules of the triamine but, as it still has a co-ordination number of 4, to only two amino-groups in each molecule of the triamine, the third amino-group in each case forming a salt with thiocyanic acid.† The complex itself is here bivalent, but since the thiocyanate radicals joined to the unco-ordinated amino-groups are also ionised, the compound in solution gives four thiocyanate ions. Two possibilities arise here. The copper may be co-ordinated to the αβ-diamino-groups, leaving the γ-amino-group free to form the thiocyanate salt, as in (II), or the copper may co-ordinate with the αγ-diamino-groups, leaving the β-amino-group free to form the thiocyanate, as in (III).

In the former compound (II), the triamine is acting, for co-ordination purposes, as a substituted ethylenediamine, and gives with the copper a five-membered ring (IV), whilst in the latter compound (III), the triamine is acting as a substituted trimethylenediamine, and thus gives with the metal a six-membered ring (V). For this reason, it is to be expected that the compound (II) would prove rather more stable than (III). On the other hand, consideration of the constitutional formulæ of the two compounds shows that the latter, having the αγ-diamino co-ordination linking, possesses far greater symmetry than the former and might therefore be of at least equal stability. Thus if the copper is co-ordinated through the αβ-diamino-groups of the triamine molecule, the γ-amino-groups, which form the thiocyanate salts, are not actually part of the metallic complex, and the compound (II) may be written in full as (IV). The two carbon atoms marked * are now



(IV.)



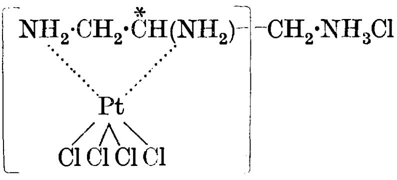
(V.)

† This compound may be compared with triglycerylcupric sulphate, $[Cu\{HO\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH\}_3]SO_4$, where only two of the three hydroxy-groups in the trihydroxypropane molecule are co-ordinated to the metal.

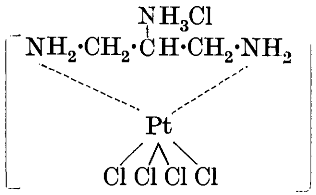
asymmetric, since they are linked on one side to an aminomethyl group ($-CH_2{\cdot}NH_2\cdots$) and on the other to a methylene-ammonium radical ($-CH_2{\cdot}NH_3-$). The compound should therefore be capable of existing in dextro-, lævo-, racemic, and meso-forms. Moreover, if the four co-ordination valencies of the copper atom are directed to the apices of a regular tetrahedron, the copper atom is itself asymmetric, and the dextro-, lævo-, and meso-compounds should each exist in two forms, in which the copper has the *d*- and the *l*-configuration, respectively.

The compound having the $\alpha\gamma$-diamino co-ordination linking (V) has, on the other hand, a highly symmetric complex containing no asymmetric carbon or copper atoms, and might therefore, in spite of its six-membered ring, prove even more stable than that shown in (II). The constitution of the compound would be decided by its resolution into optically active forms, but in view of the intense violet colour of its solutions, no such attempts have yet been made.

This co-ordination of a metallic atom to two of the three amino-groups of triaminopropane is not limited to copper. It has been shown by Curtius and Hesse (*J. pr. Chem.*, 1900, **62**, 232) that triaminopropane trihydrochloride gives a chloroplatinate of composition $C_3H_5(NH_2)_3,3HCl,PtCl_4$. If the chloroplatinate is boiled in aqueous solution with an excess of the trihydrochloride of the base, a crystalline, canary-yellow compound, having the composition $C_3H_5(NH_2)_3,HCl,PtCl_4$, separates with a molecule of water of crystallisation, which may be easily driven off. This suggests that here again the metal has co-ordinated with two of the three amino-groups, leaving the third free to form a hydrochloride, and that the compound is actually *tetrachloro(triaminopropane monohydrochloride) platinum*, $[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HCl]$, having the constitution (VI) or (VII). Here the complex itself, consisting of quadrivalent platinum co-ordinated to two basic and four acidic groups, is neutral and non-ionic, but the unco-ordinated amino-group, by uniting with hydrogen chloride to give a substituted ammonium chloride, furnishes one chloride ion. This is



(VI.)



(VII.)

confirmed by the fact that when the compound is treated with chloroplatinic acid, this unco-ordinated amine-hydrochloride group reacts normally to give a chloroplatinate of the composition

$$\{[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH(NH_2)\text{-}]\text{-}CH_2{\cdot}NH_2\}_2,H_2PtCl_6.$$

Here again, if the platinum in the parent compound is co-ordinated to the αβ-diamino-groups, as shown in (VI), the carbon atom marked * becomes asymmetric, although the complex itself may possess a plane of symmetry.† If, on the other hand, the metal is linked to the αγ-diamino-groups, as in (VII), no asymmetric carbon atom exists. This platinum compound is thus simpler in type than the previous copper compound, and its resolution into optically active forms should decide whether in this type of complex salt the metal is co-ordinated to the αβ- or the αγ-diamino-groups. Such attempts are now being made.

EXPERIMENTAL.

Tetratriaminopropanetricupric Hexaiodide (I).—A solution of triaminopropane trihydrochloride monohydrate (19·0 g.) in 15% aqueous sodium hydroxide (64·0 c.c.) was added to one of hydrated cupric sulphate (10·0 g.) in water (50 c.c.); to the deep violet solution, after 2 hours, cold saturated potassium iodide solution was added. After 12 hours, the precipitate was filtered off, washed with water until the wash liquors were colourless, and dried. *Tetratriaminopropanetricupric hexaiodide* was thus obtained as a fine, slate-blue powder, m. p. 236—237° (decomp.) (Found: C, 11·0; H, 3·4; N, 12·7; I, 57·8; Cu, 14·4. $C_{12}H_{44}N_{12}I_6Cu_3$ requires C, 11·0; H, 3·4; N, 12·8; I, 58·2; Cu, 14·6%). Warming the original solution before the addition of the potassium iodide resulted in the hexaiodide giving slightly low values for iodine, due presumably to hydrolysis.

When a solution of potassium thiocyanate, freshly prepared in cold water, was added to the original solution, slow precipitation occurred and continued for several hours. The first crop consisted of *tetratriaminopropanetricupric hexathiocyanate*,

$$[Cu_3\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_4](SCN)_6,$$

mixed with the dithiocyanate described below: it was washed with water to remove the soluble dithiocyanate. The second crop contained much less dithiocyanate and required less washing to

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† Lateral displacement of the central carbon atom in the propane molecule by the β-amino-group (discussed in the previous paper) might destroy this plane of symmetry and render the complex itself dissymmetric.

give the pure *hexathiocyanate*. The latter was thus obtained in small, deep violet crystals, m. p. 184—185° (decomp.) (Found: C, 24·3; H, 4·9; N, 27·8; S, 21·7; Cu, 21·1. $C_{18}H_{44}N_{18}S_6Cu_3$ requires C, 24·1; H, 4·95; N, 28·2; S, 21·5; Cu, 21·3%).

Bis(*triaminopropanemonothiocyanate*)*cupric Thiocyanate* (II).—A concentrated aqueous solution of potassium thiocyanate diluted with a small quantity of acetic acid was added to the original violet copper solution; deep violet crystals rapidly separated. After some time, these were filtered off, washed, and recrystallised from water, the *thiocyanate* being thus obtained in long needles or prisms, m. p. 174—175° (decomp.). For analysis, the ionised thiocyanate was estimated by precipitation with silver nitrate (*a*) in cold aqueous solution containing a few drops of dilute nitric acid, which destroyed the complex salt, (*b*) in cold neutral solution, in which the complex was stable [Found in different preparations: C, 25·2, 25·2; H, 5·1, 5·1; N, 29·4; S, 26·8; Cu, 13·4, 13·4; SCN (*a*) 48·8, (*b*) 49·3. $C_{10}H_{24}N_{10}S_4Cu$ requires C, 25·2; H, 5·1; N, 29·4; S, 26·9; Cu, 13·4; 4SCN, 48·8%].

If the potassium thiocyanate solution used in the preparation has previously been kept for several days or heated on the water-bath for a few hours, it becomes sufficiently acid by partial hydrolysis to precipitate the above thiocyanate, without any addition of acetic acid. The salt separates under these conditions more slowly than when the potassium thiocyanate contains acetic acid, and may form crystals 1—2 cm. in length.

Bis(*triaminopropanemonohydrobromide*)*cupric Bromide Dihydrate*, $[Cu\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2,HBr\}_2]Br_2,2H_2O$.—A warm, aqueous solution of the thiocyanate was treated with silver nitrate (4 mols.) and the filtered solution was evaporated to very small bulk, and, when cool, diluted with a saturated aqueous solution of sodium bromide. The crystalline bromide which separated was too soluble in water to be recrystallised. Its aqueous solution was therefore diluted with alcohol until faintly turbid and then filtered. On keeping over-night, it deposited the *bromide* in deep violet crystals (Found: C, 12·2; H, 4·7; N, 13·7; Br, 53·5; H_2O, 6·3. $C_6H_{28}O_2N_6Br_4Cu$ requires C, 12·0; H, 4·7; N, 14·0; Br, 53·3; $2H_2O$, 6·0%).

Tetrachloro(*triaminopropanemonohydrochloride*)*platinum Monohydrate*, $[Cl_4PtNH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2,HCl]H_2O$.—An aqueous solution containing triaminopropane trihydrochloride (2 mols.) and chloroplatinic acid was boiled under reflux for 3 hours, the orange-red colour becoming pale yellow, then heated on the water-bath for 3 hours with the occasional addition of water, and finally evaporated to small bulk; fine, yellow crystals separated on cooling.

These, when recrystallised from a little water, gave *tetrachloro(triaminopropanemonohydrochloride)platinum monohydrate* as fine, canary-yellow crystals, which lost water of crystallisation in a vacuum at 110° (Found in different preparations: C, 7·6, 7·5; H, 2·9, 2·9; Pt, 40·6, 40·6; Cl, 37·0, 37·1; H_2O, 3·85. $C_3H_{14}ON_3Cl_5Pt$ requires C, 7·5; H, 2·9; Pt, 40·6; Cl, 36·9; H_2O, 3·75%). The hydrate darkened at about 255° and melted at 272—273° (decomp.), whilst the anhydrous material darkened in the same way and melted at 273—274° (decomp.): the dehydration had not therefore changed the essential nature of the compound. The molecule of water of crystallisation may be attached to the complex itself or to the free amine-hydrochloride group.

Tetrachloro(triaminopropanemonohydrochloride)platinum Chloroplatinate Monohydrate,

$$\{[Cl_4PtNH_2\cdot CH_2\cdot CH(NH_2)\cdot]\cdot CH_2\cdot NH_2,HCl\}_2PtCl_4,H_2O.$$

—A cold concentrated aqueous solution of the above monohydrochloride was added to a strong solution of chloroplatinic acid which had previously been nearly neutralised with sodium carbonate. A fine precipitate slowly separated and when recrystallised from a little hot water gave the *chloroplatinate* as a fine yellow-orange coloured powder, which did not melt below 290°: the original solution slowly gave a further crop of the chloroplatinate as fine needles (Found: C, 5·5; H, 2·1; Cl, 38·9; Pt, 45·7. $C_6H_{26}ON_6Cl_{14}Pt_3$ requires C, 5·6; H, 2·05; Cl, 38·8; Pt, 45·7%).

Tetrabromo(triaminopropanemonohydrochloride)platinum Monohydrate, $[Br_4PtNH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2,HCl]H_2O$.—An aqueous solution of the original tetrachloro-compound was mixed with a saturated aqueous solution of potassium bromide, and after 24 hours the yellowish-red crystals which had separated were collected and recrystallised from a little water, in which they were very soluble. *Tetrabromo(triaminopropanemonohydrochloride)platinum monohydrate* was thus obtained in fine, orange crystals, which darkened at about 245° and melted at 262—263° (decomp.) [Found: C, 5·4; H, 2·1; (4Br + Cl), 53·8; Pt, 29·8. $C_3H_{14}ON_3ClBr_4Pt$ requires C, 5·5; H, 2·1; (4Br + Cl), 53·9; Pt, 29·6%].

Tetrachloro(triaminopropanemonohydrochloride)platinum gave in aqueous solution an unexpected reaction with potassium thiocyanate, since the mixed solutions slowly deposited potassium platinithiocyanate, $K_2Pt(SCN)_6$ (Found, for the recrystallised material: C, 11·7; N, 13·2. Calc. for $C_6N_6S_6K_2Pt$: C, 11·6; N, 13·5%). Ammonium thiocyanate solution similarly gave ammonium platinithiocyanate, $(NH_4)_2Pt(SCN)_6$ (Found: Pt, 33·8. Calc. for $C_6H_8N_8S_6Pt$: Pt, 33·7%).

Potassium and ammonium chloride solutions did not give precipitates of the corresponding chloroplatinates even after several days : these solutions on keeping would not, however, develop the acid properties of the thiocyanate solutions.

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

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