CCCLII.—*The Configuration of the Bistriaminopropane Metallic Complexes.*

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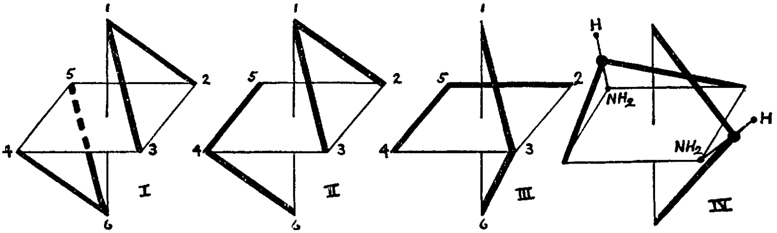
We have previously described (*Proc. Roy. Soc.*, 1925, **107**, *A*, 80) a method by which αβγ-triaminopropane, $NH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2$, can be prepared expeditiously and in high yield, and we have shown furthermore that this triamine co-ordinates with cobalt and rhodium to give complex compounds of the type of bistriaminopropanecobaltic chloride, $[Co\{NH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2\}_2]Cl_3$, a compound in which two molecules of the aliphatic triamine have replaced the six molecules of ammonia in hexamminocobaltic chloride, $[Co(NH_3)_6]Cl_3$. On the basis of Werner's octahedral configuration of the hexamminocobaltic complex, it will be seen that the bistriaminopropanecobaltic complex should exist in three distinct isomeric forms. In the first two forms (I and II, where the position of the triamine molecules is indicated by the thick lines), each molecule of the triamine is bent at an angle of 60° about the central carbon atom, so that the three amino-groups become attached to the three corners of a triangular octahedron face : in the third form (III), the triamine molecule is bent at an angle of 90° about the central carbon atom, the three amino-groups being thus attached to the three corners of the square cross-section of the octahedron. The first isomeride has the two molecules of the triamine occupying the 2, 1, 3 : 4, 6, 5 positions (I), and the complex possesses therefore a plane of symmetry, and is not resolvable into optically active forms. The second isomeride has the triamine molecules in the 2, 1, 3 : 5, 4, 6 positions (II) and is therefore dissymmetric and should be capable of resolution into optically active forms. In the third isomeride—of completely different type from the former two—the triamine molecules occupy the 1, 3, 6 : 4, 5, 2 positions (III). This form would appear to have a plane of symmetry through the square cross-section 1, 3, 6, 5, of the octahedron.



Further consideration shows, however, that actually the triaminopropane molecules would not be placed symmetrically to the two cube planes of symmetry of the regular octahedron, because the central co-ordinating amino-group should give a lateral displacement to the central carbon atom, thus preventing the triamine molecule from coinciding with the cube plane of symmetry. This is shown in (IV), where the actual positions occupied by the central carbon atom and by the hydrogen atom and the amino-group attached to it are depicted. This lateral displacement of the central carbon atom by the β-amino-group would destroy the symmetry of the third isomeride, which should therefore also be resolvable into optically active forms. In the first isomeric form (I), this lateral displacement of the central carbon atom (at the 1 and 6 positions, respectively) occurs in the plane of symmetry, which is thus not affected.

Triaminopropane has now been co-ordinated with tervalent cobalt, tervalent rhodium, and bivalent nickel. The simple salts of the complexes so formed are in all cases highly crystalline, stable compounds, in which no trace of the above isomerism could be detected by macroscopic examination. It is therefore highly probable that one of the three isomerides is very much more stable than the other two, and is always formed to the almost complete exclusion of these. A somewhat similar case has recently been described by Morgan and Main Smith (J., 1925, **127**, 2030), who have co-ordinated ethylenediaminobisacetylacetone with cobalt to give diamminoethylenediaminobisacetylacetonecobaltic monochloride. Here the substituted ethylenediamine occupies four of the six co-ordination positions, and the complex so formed should exist in one symmetric and in two dissymmetric isomeric forms. The latter two were in this case actually isolated, but each passed rapidly into the symmetric and therefore more stable form : moreover, the presence of the latter stable form in the laboratory at once prevented further preparation and isolation of the dissymmetric and optically active isomerides.

Spatial considerations would indicate that triaminopropane, when co-ordinated to the three corners of a triangular face of the octahedron, should give a more stable arrangement than when co-ordinated to the three corners of a square cross-section. Isomerides I and II are therefore probably far more stable than III, and of these two the first, as the symmetric form, is in turn more stable than the second. We therefore consider it highly probable that all the complex salts of this triamine which we have prepared consist almost exclusively of the isomeride having the configuration I, the two molecules of the triamine occupying the 2, 1, 3 and the 4, 6, 5 positions, respectively.

The only evidence of the existence of isomeric forms that we have been able to obtain is that bistriaminopropanecobaltic *d*-camphor-β-sulphonate, after repeated crystallisation, does furnish a very faintly active chloride. The more soluble fractions, however, when reconverted into the iodide, give a *l*-camphorsulphonate which, after fractional crystallisation, furnishes a completely inactive chloride. This would suggest that the symmetric cobalt complex of configuration I may contain a very small proportion of a dissymmetric isomeride, probably of configuration II, but that this second isomeride is very easily either converted into the symmetric form or eliminated by fractional crystallisation.

Fractional crystallisation of the *d*-α-bromocamphor-π-sulphonate gave a completely inactive chloride. Werner found that the camphor- and bromocamphor-sulphonates of the metallic complexes frequently separated in mixed crystals, and to resolve, for example, the tris-αα′-dipyridylferrous complex and the trisethylenediaminerhodium complex, he had recourse to fractional crystallisation of their chlorotartrates (*Ber.*, 1912, **45**, 433, 1228), and in the case of the trisethylenediaminechromium complex, to fractional crystallisation of the camphor-α-nitronate (*ibid.*, p. 865). No crystalline chlorotartrate of the bistriaminopropanecobaltic complex could, however, be prepared, whilst fractional crystallisation of the camphor-α-nitronate gave no resolution.

The stability of the bistriaminopropane metallic complex is further shown by the fact that it is formed even when the metal is treated with only one molecule of the base, half the available metal thus not entering into combination with the amine under these conditions. Thus monochloropentamminocobaltic chloride, when treated with one molecule of the base, gives bistriaminopropanecobaltic chloride, and not triamminomonotriaminopropanecobaltic chloride, whilst nickel succinimide under similar conditions also gives solely the bistriaminopropanenickel salt.

EXPERIMENTAL.

In the formulæ of the following co-ordination compounds, the symbol " ptn " is used to denote one molecule of triaminopropane.

Improved Preparation of Bistriaminopropanecobaltic Chloride, [Co ptn$_2$]Cl$_3$.—A solution of triaminopropane trihydrochloride (20 g.) in 15% aqueous sodium hydroxide (71·4 c.c.) is added to a mixture of water (50 c.c.) and monochloropentamminocobaltic chloride (10 g.) or the equivalent quantity of monoaquopentamminocobaltic chloride. The whole is warmed on a water-bath for 3 hours, ammonia being freely evolved, and is then concentrated to small bulk, made just acid with hydrochloric acid, and filtered. The filtrate can be used for the preparation of most salts of the complex. Further evaporation gives the crystalline bistriaminopropanecobaltic chloride, whilst treatment with potassium thiocyanate solution gives the *thiocyanate*, [Co ptn$_2$](SCN)$_3$, which on recrystallisation from water is obtained in pale brown prisms, m. p. 286—288° (decomp.) (Found : C, 26·3; H, 5·4. $C_9H_{22}N_9S_3Co$ requires C, 26·3; H, 5·4%). The bistriaminopropanecobaltic complex is isolated in best yield by precipitation with potassium iodide as the far less soluble iodide, which we have already described (*loc. cit.*).

Bistriaminopropanecobaltic d-*camphor*-β-*sulphonate*,

$$[\mathrm{Co\ ptn_2}](C_{10}H_{15}O\cdot SO_3)_3,$$

is of interest since it furnishes the only evidence so far obtained that the cobalt complex may contain a very small proportion of a dissymmetric isomeride. Aqueous solutions of the iodide of the complex and of the requisite amount of silver *d*-camphor-β-sulphonate were boiled together, the silver iodide was filtered off, and the solution evaporated to small bulk. The solution could not be induced to crystallise and finally gave a thick syrup. This was dried in a vacuum, and the product recrystallised four times from absolute alcohol. The *camphor*-β-*sulphonate* was thus obtained in orange-yellow crystals containing a molecule of alcohol of crystallisation {Found : $C_2H_5\cdot OH$, 4·85. [Co ptn$_2$]($C_{10}H_{15}SO_4)_3,C_2H_5\cdot OH$ requires $C_2H_5\cdot OH$, 4·7%. Found for the alcohol-free material: C, 46·2; H, 7·45. $C_{36}H_{67}O_{12}N_6S_3Co$ requires C, 46·4; H, 7·3%}. The alcohol-free material, which is markedly hygroscopic, shrinks at about 265° and finally melts at 285—286° (decomp.). A 2·960% aqueous solution had $\alpha + 1{\cdot}03°$ ($l = 2$), whence $[\alpha] = + 17{\cdot}4°$ and $[M] = + 162°$.*

Some of this material was dissolved in a minimum of water and a considerable excess of concentrated pure calcium chloride solution added. To the clear mixture was added a large quantity of alcohol;

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* All rotations given in this paper are for the mercury yellow line ($\lambda = 5780$).

the precipitated bistriaminopropanecobaltic chloride, after being washed with warm alcohol and dried, was pure (Found: C, 20·8; H, 6·5. Calc. for $C_6H_{22}N_6Cl_3Co$: C, 20·9; H, 6·45%). For rotation measurements, only a short length of the very dilute orange-coloured solution could be used, otherwise the high absorption of light rendered accurate measurement impossible. A 3·088% solution of the chloride gave $\alpha + 0{\cdot}22°$ ($l = 2$), whence $[\alpha] = + 3{\cdot}6°$. The *d*-camphorsulphonate, when recrystallised from alcohol nine times, possessed the same melting point as above, and in 3·072% aqueous solution gave $\alpha + 1{\cdot}10°$ ($l = 2$), whence $[\alpha] = + 17{\cdot}9°$ and $[M] = + 166°$. The chloride obtained from this product was also faintly active, since a 5·452% aqueous solution gave $\alpha + 0{\cdot}29°$ ($l = 2$), whence $[\alpha] = + 2{\cdot}7°$. The *d*-camphorsulphonate remaining in the alcoholic mother-liquor from the nine recrystallisations was now recovered and converted into the iodide, and the latter was once recrystallised from water and then converted as before into the *l*-camphor-β-sulphonate. The latter was recrystallised four times from alcohol; the alcohol-free material began to shrink at about 265° and melted at 287—288° (decomp.). A 2·965% aqueous solution gave $\alpha - 1{\cdot}03°$ ($l = 2$), whence $[\alpha] = - 17{\cdot}4°$ and $[M] = - 162°$. This material gave, however, a completely inactive chloride.

These results were repeated, and once again the *d*-camphorsulphonate prepared from fresh iodide gave a faintly dextrorotatory chloride, but the *l*-camphorsulphonate, obtained by working up the mother-liquors *via* the iodide, gave an inactive chloride.

These results would indicate that the bistriaminopropanecobaltic complex does actually contain a very small proportion of a dissymmetric isomeride, probably having the configuration (II), and it is to the presence of this isomeride that the faint dextrorotation of the above chloride is due. This dissymmetric compound would be less stable and more soluble than its symmetric isomeride, and it is either converted into the latter or is left in solution when the *d*-camphorsulphonate residues are converted into the iodide, the latter recrystallised, and converted into the *l*-camphorsulphonate.

Bistriaminopropanecobaltic d-α-*Bromocamphor*-π-*sulphonate*, $[Co\,ptn_2](C_{10}H_{14}SO_4Br)_3$.—This was obtained in the usual way by the interaction of the iodide of the complex and the silver salt of the sulphonic acid. The concentrated aqueous solution of the sulphonate must be allowed to cool very slowly to obtain a crystalline deposit. The latter was recrystallised four times from water and was then obtained as a *pentahydrate* (Found: C, 34·3; H, 6·0. $C_{36}H_{64}O_{12}N_6Br_3S_3Co,5H_2O$ requires C, 34·4; H, 5·9%). The pentahydrate, when confined over calcium chloride at atmospheric pressure for several days, gives a *dihydrate*, which is stable under these conditions (Found : C, 35·7; H, 5·6; H_2O, 3·1. $C_{36}H_{64}O_{12}N_6Br_3S_3Co,2H_2O$ requires C, 35·9; H, 5·7; $2H_2O$, 3·0%). A 3·305% aqueous solution of the anhydrous sulphonate gave $\alpha + 4{\cdot}98°$ ($l = 2$), whence $[\alpha] = + 75{\cdot}3°$ and $[M] = + 880°$. The anhydrous sulphonate melts at 266—267° (decomp.). When the final crop of the sulphonate was mixed in strong aqueous solution with calcium chloride and the whole diluted with alcohol, the precipitated chloride of the complex was quite inactive.

Bistriaminopropanecobaltic d-*Camphor-α-nitronate*, $[Co\ ptn_2](C_{10}H_{14}O{\cdot}NO_2)_3$.—A solution of the chloride of the complex (7·0 g.) in water (80 c.c.) was mixed with a solution of ammonium nitrocamphor (14 g.) in water (100 c.c.). The pale yellow product which rapidly separated was recrystallised five times from water, and, when dry, was obtained in yellow, crystalline scales, m. p. 242—245° (decomp.) (Found : C, 52·2; H, 7·7. $C_{36}H_{64}O_9N_9Co$ requires C, 52·3; H, 7·8%). An aqueous solution of the fifth crop of the camphornitronate gave an inactive bromide of the complex.

Attempts were made to prepare the chlorotartrate of the cobalt complex by shaking an aqueous solution of the chloride with silver tartrate (1 mol.). The filtered solution was evaporated to small bulk and finally in a vacuum over sulphuric acid. A small crop of the chloride itself then separated, but no further crystalline product could be isolated.

Bistriaminopropanenickelous Iodide, $[Ni\ ptn_2]I_2$.—Triaminopropane trihydrochloride (11·4 g.) dissolved in warm 33% aqueous sodium hydroxide (16·4 c.c.) was added to a hot solution of nickel succinimide (6·0 g.) in alcohol (180 c.c.). The solution, which rapidly became reddish-blue, was evaporated to small bulk with the occasional addition of water until no alcohol remained. It was then added to saturated aqueous potassium iodide solution : the red precipitate, on recrystallisation from hot water, gave *bistriaminopropanenickelous iodide* as pale red, crystalline scales, which, when heated, darken at about 290° but do not melt below 300° (Found : C, 14·8; H, 4·6; I, 51·8; Ni, 11·9. $C_6H_{22}N_6I_2Ni$ requires C, 14·7; H, 4·5; I, 51·7; Ni, 12·0%).

Bistriaminopropanenickelous Sulphate Pentahydrate, $[Ni\ ptn_2]SO_4,5H_2O$.—Hot aqueous solutions of the iodide (9·0 g.) and silver sulphate (5·7 g.) were mixed, filtered, and evaporated to very small bulk. On cooling, the hydrated *sulphate* separated as deep red crystals (Found : C, 16·9; H, 7·6; SO_4, 23·0; H_2O, 21·2. $C_6H_{22}O_4N_6SNi,5H_2O$

requires C, 17·0; H, 7·6; SO_4, 22·7; $5H_2O$, 21·3%). The sulphate loses its water of crystallisation readily at 90° in a vacuum, and the anhydrous sulphate does not melt below 300°. The filtrate from the recrystallisation of the sulphate was diluted with alcohol until a faint turbidity appeared; a further crop of the pentahydrate then separated slowly in large, deep red crystals (Found: SO_4, 22·7%).

Many attempts were made to prepare triamminotriaminopropanecobaltic chloride, $[Co(NH_3)_3ptn]Cl_3$, by treating roseo- and purpureocobalt chloride with one molecular proportion of the base: these experiments always gave, however, the bistriaminopropanecobaltic salts, the remainder of the metal separating as the hydroxide. Similar experiments were made with nickel succinimide with the object of preparing salts in which the metal would show a coordination number of 4, such as aquotriaminopropanenickel chloride, $[NiH_2O\,ptn]Cl_2$, or of 6, such as triamminotriaminopropanenickel chloride, $[Ni(NH_3)_3\,ptn]Cl_2$: these experiments also always gave the bistriaminopropanenickel salts and a residue of a simple basic nickel salt.

Triaminopropane Dihydrochloride Monohydriodide, $C_3H_5(NH_2)_3,2HCl,HI$.—This mixed salt of the triamine is here placed on record. When a highly concentrated aqueous solution of triaminopropane trihydrochloride is treated with saturated potassium iodide solution, the *dihydrochloride monohydriodide* slowly separates. It crystallises from water in fine, white crystals, m. p. 303—304° (decomp.), which are very soluble in water (Found: C, 12·7; H, 4·9; N, 14·3; 2Cl + I, 68·4. $C_3H_{14}N_3Cl_2I$ requires C, 12·4; H, 4·9; N, 14·5; 2Cl + I, 68·2%). ββ′β″-Triaminotriethylamine trihydrochloride under similar conditions gives the monohydrochloride dihydriodide of the base (Mann and Pope, *Proc. Roy. Soc.*, 1925, **109**, *A*, 449).

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