# LXII.—*The Complex Salts of ββ′β″-Triaminotriethylamine with Nickel and Palladium.*

By FREDERICK GEORGE MANN and WILLIAM JACKSON POPE.

WE have already shown (*Proc. Roy. Soc.*, 1925, **A**, **109**, 444) that ββ′β″-triaminotriethylamine may act as a tetra-acidic or a triacidic base, according as the tertiary nitrogen atom exerts or does not exert its basicity. The compound thus gives a tri- and a tetra-hydrochloride, and also two platinichlorides,

$$2N(CH_2{\cdot}CH_2{\cdot}NH_2)_3,6HCl,3PtCl_4,10H_2O \quad (I)$$

and $2N(CH_2{\cdot}CH_2{\cdot}NH_2)_3,8HCl,4PtCl_4,20H_2O$ (II), two aurichlorides and two rhodiochlorides. When, however, the base co-ordinates with metals, it acts solely as a tetramine, and two new types of complex salts were described : thus bivalent platinum of co-ordination number 4 furnishes triaminotriethylamineplatinous iodide, $[Pt\ tren]I_2$ (III), whilst quadrivalent platinum of co-ordination number 6 gives dichlorotriaminotriethylamineplatinic chloride, $[Pt\ tren\ Cl_2]Cl_2$ (IV). In these formulæ, the symbol " tren " denotes one molecule of the base.

The complex compounds which the base furnishes with nickel have now been prepared, and fall into two distinct classes. It is known that bivalent nickel may show a co-ordination number of 4 or 6, furnishing, for example, tetramminonickel sulphate (V) and hexamminonickel iodide (VI).

(V.) $[Ni(NH_3)_4]SO_4$ (VI.) $[Ni(NH_3)_6]I_2$
(VII.) $[Ni\ tren]SO_4$ (VIII.) $[Ni_2tren_3]I_4$

Triaminotriethylamine similarly gives triaminotriethylaminenickelous sulphate (VII) and tristriaminotriethylaminebisnickelous tetraiodide (VIII) : these two compounds are of the same general type as (V) and (VI) in that the metal shows a co-ordination number of 4 and 6 respectively, although in the latter class three molecules of the tetramine distributed between two atoms of nickel are required if the metal is to show a co-ordination number of 6.

Each of these two classes of complex nickel compounds possesses distinct points of interest. We have pointed out (*loc. cit.*, p. 446) that in compounds of the type of triaminotriethylamineplatinous iodide (III), it might be expected that less strain on the amine molecule would result if two molecules of the base shared two atoms of the metal, thus giving a compound of the type $[Pt_2tren_2]I_4$. The same applies to triaminotriethylaminenickelous sulphate (VII), a compound which by virtue of its high solubility in water lends itself to further investigation. Molecular weight determinations show, however, that the sulphate has the normal composition denoted by formula (VII), and that one molecule of the base can actually satisfy one atom of the metal; conductivity measurements point to the same conclusion.

With regard to the compound of co-ordination number 6, tristriaminotriethylaminebisnickelous tetraiodide (VIII), it is difficult to see how this complex, composed of three molecules of the base arranged around the two nickel octahedra, can be other than dissymmetric; all attempts to resolve the tetraiodide, however, proved fruitless, possibly owing to the rapid racemisation of the active complex.

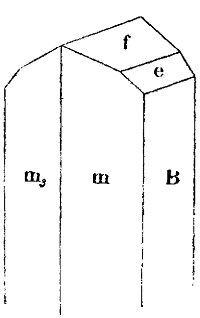
The base has also been co-ordinated with bivalent palladium to give triaminotriethylaminepalladious iodide, a compound precisely similar to the platinous iodide (III).

Triaminotriethylamine thus furnishes three distinct types of complex compound, one with bivalent metals of co-ordination number 4, *e.g.*, compounds (III) and (VII), and two with metals of co-ordination number 6, *e.g.*, compounds (IV) and (VIII). These are the first complex compounds to have been prepared with a tetramine; they are, moreover, the first compounds to be described in which an aliphatic tertiary nitrogen atom occupies a co-ordination position.

## EXPERIMENTAL.

*Preparation of Triaminotriethylaminenickelous Thiocyanate and Tristriaminotriethylaminebisnickelous Tetraiodide.*—Nickel succinimide, $[Ni(N{:}C_2O_2{:}C_2H_4)_2 2H_2O],6H_2O$ (Tschugaev, *Ber.*, 1906, **39**, 3197) forms an excellent starting point for the preparation of the co-ordinated derivatives of the metal, since the succinimide residues are easily replaced by aliphatic amines. A mixture of triaminotriethylamine trihydrochloride (32·5 g.) and 33% aqueous caustic soda solution (40·0 c.c.) is therefore warmed on the water-bath until sodium chloride alone remains undissolved. The mixture is poured into a hot solution of nickel succinimide (25·0 g.) in alcohol (750 c.c.). The green solution changes rapidly to blue and is boiled gently for 30 minutes. It is cooled, the precipitated sodium chloride filtered off, and the solution then evaporated gently on the water-bath with the occasional addition of water until it is free from alcohol and of about 60 c.c. in volume. The solution, now of a deep blue, contains a mixture of the two complex ions $[Ni\ tren]^{\cdot\cdot}$ and $[Ni_2tren_3]^{\cdot\cdot\cdot\cdot}$; these can be isolated readily as the thiocyanate and tetraiodide, respectively. If the solution is poured into a warm strong solution of potassium thiocyanate, the thiocyanate separates as a pale blue powder or deep blue crystals according to the concentration of the nickel solution; if the original solution is poured into hot strong potassium iodide, the tetraiodide separates as a reddish-violet powder or deep violet crystals. These two compounds and their derivatives will be described in turn.

*Triaminotriethylaminenickelous thiocyanate*, [Ni tren]$(SCN)_2$. The thiocyanate crystallises with great facility from hot aqueous solution in long, very beautiful, deep blue prisms, and two such recrystallisations of the crude product obtained by precipitation with potassium thiocyanate furnish the pure thiocyanate. The latter darkens in colour at 260° and melts with decomposition at 285°; it is soluble in hot, but almost insoluble in cold water [Found: C, 30·1; H, 5·6; N, 26·3; ionised (SCN), 35·95. $C_8H_{18}N_6S_2Ni$ requires C, 29·9; H, 5·65; N, 26·2; 2(SCN), 36·2%]. Very rarely the thiocyanate crystallises in long, narrow, and very thin plates: this form is of the same colour as the prismatic variety, and differs from it apparently only in crystalline habit.



Mr. J. W. Notman of Clare College, working under the direction of Mr. A. Hutchinson, F.R.S., has furnished the following report:

" Triaminotriethylaminenickelous thiocyanate. System, orthorhombic. Class, bipyramidal. $a : b : c = 0·736 : 1 : 1·167$. The substance occurs in fairly well-developed crystals, of elongated prismatic habit, of which four were measured. Forms present: *B* {010} *m* {110}, *l* {120} observed on one crystal only, *e* {011}, *f* {012}.

| | | | | Meas. | Calc. |
|---|---|---|---|---|---|
| Angles | $mm_3$ | $110 : 1\bar{1}0$ | = | 72° 42′ | — |
| | *Bm* | 010 : 110 | = | 53 33 | 53° 39′ |
| | *Bc* | 010 : 011 | = | 40 35 | — |
| | *ef* | 011 : 012 | = | 19 9 | 19 9 |
| | *ff′* | $012 : 0\bar{1}2$ | = | 60 52 | 60 32 |

The crystals were deep blue in colour and, being very opaque, did not lend themselves to optical examination. Some exceedingly thin plates obtained in the case of one preparation enabled straight extinction to be determined."

Both the nickel complexes recorded in this paper are very sensitive to acids, and the addition of hydrochloric acid immediately converts the deep blue of the complex into the pale green of the normal nickel salt. If a warm solution of the thiocyanate is treated with chloroplatinic acid solution, the normal platinichloride (II) of the base is therefore precipitated: if, however, a solution of sodium platinichloride is used, *triaminotriethylaminenickelous platinic tetrachloride dithiocyanate*, [Ni tren]$PtCl_4(SCN)_2$, is precipitated as a russet-brown powder, insoluble in water: it shrinks at 211—213°, but does not melt below 280° (Found : C, 14·9 ; H, 2·8 ; N, 12·8. $C_8H_{18}N_6Cl_4S_2NiPt$ requires C, 14·6 ; H, 2·8 ; N, 12·8%).

*Triaminotriethylaminenickelous Sulphate*, [Ni tren]$SO_4$,$7H_2O$.—Hot aqueous solutions of the thiocyanate (6·0 g.) and silver sulphate (5·82 g.) were mixed, and the product, after gently boiling for 15 minutes, was filtered and evaporated down to small bulk on the water-bath. The concentrated solution on cooling deposited deep blue crystals; these were recrystallised from a little hot water, filtered, and dried in air. This sulphate, like normal nickel sulphate, gives a series of hydrates. The product obtained as above is the *heptahydrate* (Found : $SO_4$, 22·7 ; $H_2O$, 29·4. $C_6H_{32}O_{11}N_4SNi$ requires $SO_4$, 22·5 ; $7H_2O$, 29·5%). The heptahydrate when placed over calcium chloride for 24 hours gives the *dihydrate* as a fine reddish-blue powder (Found : C, 21·3 ; H, 6·6 ; $SO_4$, 28·4. $C_6H_{22}O_6N_4SNi$ requires C, 21·4 ; H, 6·55 ; $SO_4$, 28·5%). The dihydrate on prolonged exposure to calcium chloride, or when heated in a vacuum at 100°, gives the *anhydrous sulphate* as a pale-blue powder, which does not melt below 300° (Found : $SO_4$, 32·25. $C_6H_{18}O_4N_4SNi$ requires $SO_4$, 31·9%).

If the anhydrous sulphate has the formula [Ni tren]$SO_4$, the molecular weight is 300·9, and the " apparent " molecular weight in dilute aqueous solution (if ionisation is complete) is 150·4. If, however, it has the formula [$Ni_2tren_2$]$(SO_4)_2$, the molecular weight is 601·8, and the " apparent " molecular weight 200·6. The results actually obtained by the cryoscopic method are as follows, *c* being the concentration of the anhydrous sulphate expressed as g. in 100 g. of water :

| *c* ................................ | 0·422 | 1·32 | 1·79 | 3·23 |
|---|---|---|---|---|
| " Apparent " mol. wt. ......... | 160 (157*) | 173 | 180 | 218 |

* Calculated value, correct to only two significant figures.

These results furnish strong evidence that the sulphate has the simple formula [Ni tren]$SO_4$, and that the " apparent " molecular weight approaches to 150 at great dilution, and increases with increasing concentration as the degree of ionisation falls. If the compound possessed the double formula, it could not show an apparent molecular weight of less than 200. This conclusion is confirmed by the close correspondence between the equivalent conductivities of normal nickelous sulphate and triaminotriethylaminenickelous sulphate at 25°.

| Vol. (litres) containing 1 g. equiv. of sulphate ........................ | | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|
| Equiv. cond. | $NiSO_4$ ............... | 88·2 | 98·9 | 109·3 | 117·4 |
| | [Ni tren]$SO_4$ ...... | 85·9 | 96·7 | 106·0 | 119·2 |

The values for nickel sulphate are those given by Franke (*Z. physikal. Chem.*, 1895, **16**, 472), those for the tetramine derivative have been determined by Mr. A. F. H. Ward of Jesus College and Mr. L. F. S. Ward of Trinity College, to whom the authors' thanks are due.

*Tristriaminotriethylaminebisnickelous Tetraiodide,* $[Ni_2tren_3]I_4,3\frac{1}{2}H_2O$. —The crude reddish-violet iodide obtained by precipitation with potassium iodide in the original preparation is recrystallised three times from hot water, and so obtained in heavy, deep violet crystals : if the hot aqueous solution is too concentrated or is chilled too rapidly, the tetraiodide separates as an oil which subsequently solidifies (Found : C, 18·9; H, 5·4; I, 45·1, 45·1, 45·2; Ni, 10·4, 10·3; $H_2O$, 5·5. $C_{36}H_{122}O_7N_{24}I_8Ni_4$ requires C, 19·2; H, 5·5; I, 45·1; Ni, 10·4; $H_2O$, 5·6%). On one occasion when a small quantity of the iodide was rapidly recrystallised from a little hot water, the *dihydrate* separated (Found : C,* 19·5, 19·6; H, 5·2, 5·2; N, 15·15; I, 46·2, 46·0. $C_{18}H_{58}O_2N_{12}I_4Ni_2$ requires C, 19·6; H, 5·3; N, 15·3; I, 46·2%). The anhydrous tetraiodide, obtained by heating either of the above hydrates in a vacuum at 110°, is a pale violet powder, m. p. 307—309° (decomp.) (Found : I, 47·4. $C_{18}H_{54}N_{12}I_4Ni_2$ requires I, 47·6%).

If, after the crude tetraiodide has been precipitated in the original preparation, the filtrate is treated with saturated potassium thiocyanate solution, triaminotriethylaminenickelous thiocyanate separates in fair yield and after two recrystallisations is pure; both complexes can thus be isolated from the same preparation.

The *tetrabromide*, $[Ni_2tren_3]Br_4$, can be obtained in small yield by treating the final solution in the original preparation with strong sodium bromide solution, or in better yield by treating a saturated solution of the tetracamphorsulphonate described later with sodium bromide. It is obtained on recrystallisation as a pale reddish-blue, anhydrous powder, which does not melt below 290° (Found : H, 6·1; Br, 36·4, 36·7; Ni, 13·6. $C_{18}H_{54}N_{12}Br_4Ni_2$ requires H, 6·2; Br, 36·5; Ni, 13·4%).

*Attempted Resolution of the Tristriaminotriethylaminebisnickelous Complex*, $[Ni_2tren_3]^{\cdot\cdot\cdot\cdot}$.—The *tetra*-d-*α-bromocamphor-π-sulphonate*, $[Ni_2tren_3](C_{10}H_{14}O_4BrS)_4$. Solutions of 16·0 g. of the tetraiodide ($3\frac{1}{2}H_2O$) and 23·56 g. of silver *d*-*α*-bromocamphor-*π*-sulphonate, each in 75 c.c. of hot water, were mixed and the product, after gentle

---

* Throughout this paper, repeated analytical results refer to analyses of different preparations of the compound, and not merely to repeated analyses of the same preparation : the figures given for this dihydrate are the only exception.

boiling, was filtered and evaporated until crystals appeared on the surface. The solution was now cooled and filtered, and the crystalline residue three times recrystallised from water. The anhydrous *tetra*-d-*bromocamphorsulphonate* was thus obtained as a pale violet, crystalline powder, which shrinks at 180° and melts with decomposition at 183—185° (Found : H,* 6·2; Br, 17·8; S, 7·05; Ni, 6·5. $C_{58}H_{110}O_{16}N_{12}Br_4S_4Ni_2$ requires H, 6·2; Br, 17·8; S, 7·1; Ni, 6·5%).

The tetrabromocamphorsulphonate is so slightly soluble in water that it could not be reconverted by double decomposition into the bromide or iodide. The hot aqueous solution was therefore added carefully to a hot dilute solution of sodium picrate, and the *tetrapicrate*, $[Ni_2tren_3](C_6H_2O_7N_3)_4,3H_2O$, precipitated as a fine, dark yellow powder, which when filtered, washed with water and alcohol, and air-dried melted with decomposition at 205—206° (Found: C, 33·25; H, 4·5; N, 22·2. $C_{42}H_{68}O_{31}N_{24}Ni_2$ requires C, 33·1; H, 4·5; N, 22·1%).

This tetrapicrate was found to be identical in composition and melting point with that obtained directly from the tetraiodide; it is only very slightly soluble in boiling water and insoluble in all ordinary organic solvents except formamide. No rotation could be detected in a 0·5% solution of the picrate in formamide in a 2-dcm. tube: stronger solutions could not be used owing to the high absorption of light.

The *tetra*-d-*camphor*-β-*sulphonate*, $[Ni_2tren_3](C_{10}H_{15}O_4S)_4$. Solutions of the tetraiodide (19·0 g.) and silver *d*-camphor-β-sulphonate (22·8 g.), each in warm water (80 c.c.), were mixed, and the product after gentle boiling was filtered and then evaporated until crystals appeared in the solution. The latter was cooled and filtered, and the crystallised product three times recrystallised from warm water. The *tetra*-d-*camphorsulphonate* was thus obtained as a reddish-violet, crystalline powder, which shrinks at 230° and melts at 233—235°: it is appreciably more soluble in water than the corresponding bromocamphorsulphonate (Found: H, 7·8; S, 8·9; Ni, 7·95. $C_{58}H_{114}O_{16}N_{12}S_4Ni_2$ requires H, 7·8; S, 8·7; Ni, 7·9%). A warm solution of the camphorsulphonate was mixed with that of potassium iodide, and the crystals which separated on cooling were rapidly recrystallised from a little hot water, the pure tetraiodide being thus obtained (Found: I, 45·1%). A 2% aqueous solution of this tetraiodide in a 4-dcm. tube gave no perceptible rotation.

Attempts to prepare a crystalline tartrate of the complex failed, only syrupy solutions being obtained.

---

* All the camphor derivatives (and certain others) recorded in this paper gave low and irregular values for carbon, but satisfactory values for hydrogen.

*Triaminotriethylaminenickelous* d-*bromocamphorsulphonate*,

$[\mathrm{Ni\ tren}](C_{10}H_{14}O_4BrS)_2,2H_2O$.

Attempts were also made to prepare the above tetra-*d*-bromocamphor-π-sulphonate by double decomposition of the tetraiodide with ammonium *d*-bromocamphorsulphonate. It was found, however, that when solutions of the tetraiodide (4 g.) and an excess of the ammonium sulphonate (6 g.), each in warm water (20 c.c.), were mixed, and the product warmed on the water-bath, ammonia was evolved, and crystals soon appeared on the surface. This product was twice recrystallised from warm water, and finally obtained as beautiful, bluish-violet, crystalline plates. These on analysis proved to be *triaminotriethylaminenickelous* d-*bromocamphorsulphonate* (Found: Br, 18·6; S, 7·5; Ni, 6·65; $H_2O$, 4·2. $C_{26}H_{50}O_{10}N_4Br_2S_2Ni$ requires Br, 18·55; S, 7·4; Ni, 6·8; $2H_2O$, 4·2%). Heating in a vacuum at 110° gives the pale blue, anhydrous product, m. p. 263—266° (decomp.). The identity of this compound was further confirmed by treating its warm aqueous solution with potassium thiocyanate solution, when triaminotriethylaminenickelous thiocyanate separated, and when once recrystallised was pure (Found: N, 25·85%). This degradation of the nickel complex of co-ordination number 6 to that of co-ordination number 4 by the action of an ammonium salt was found to be general, and to follow presumably the equation $[\mathrm{Ni_2tren_3}]X_4 + 4NH_4X' = 2[\mathrm{Ni\ tren}]X_2 + \mathrm{tren}\ 4HX' + 4NH_3$. It is noteworthy that the third molecule of the tetramine in the higher complex is evicted but not replaced by the ammonia under these conditions, and all attempts made to prepare compounds having the complex $[\mathrm{Ni\ tren}(NH_3)_2]^{\cdot\cdot}$ failed. In the particular case of the *d*-bromocamphorsulphonate described above, the colours of the dihydrate (bluish-violet) and the anhydrous product (pale blue) are characteristic of nickel complexes having co-ordination numbers of 6 and 4 respectively, and therefore the dihydrate has probably the composition

$$[\mathrm{Ni\ tren}(H_2O)_2](C_{10}H_{14}O_4BrS)_2.$$

*Triaminotriethylaminepalladious Iodide*, $[\mathrm{Pd\ tren}]I_2$.—A warm solution of triaminotriethylamine trihydrochloride (5·4 g.) in 33% aqueous caustic soda solution (7·4 c.c.) is added to a solution of palladium dichloride (3·0 g.) in hot water (70 c.c.). An amorphous, yellow precipitate at once appears, but redissolves when the solution is heated on the water-bath. After heating for 2 hours, the solution is evaporated to small bulk, filtered, and mixed with warm strong potassium iodide solution. The cream-coloured precipitate is filtered off, and recrystallised from much hot water, in which the iodide is only moderately soluble. The *triaminotriethylaminepalladious iodide* is thus obtained as a fine, cream-coloured powder, which after drying over sulphuric acid darkens in colour at 220° and melts at 224—226° (decomp.) (Found : C, 14·1 ; H, 3·9 ; I, 49·6 ; Pd, 20·9. $C_6H_{18}N_4I_2Pd$ requires C, 14·2 ; H, 3·6 ; I, 50·1 ; Pd, 21·1%).

If instead of adding potassium iodide to the above solution, the latter is chilled, made just acid with hydrochloric acid, and treated with an excess of dilute palladium dichloride solution, a fine dark brown precipitate separates. The latter redissolves if the solution is warmed, and on filtering and cooling, long, chocolate-coloured needles separate. These crystals decompose largely if an attempt is made to recrystallise them from boiling water, and their identity is therefore uncertain ; they would appear to be *triaminotriethylamine-palladious palladiochloride*, $[Pd\ tren]PdCl_6,H_2O$, and owe their formation presumably to partial atmospheric oxidation of the palladious chloride solution (Found : C, 12·3 ; H, 3·8 ; Cl, 35·3 ; Pd, 35·7. $C_6H_{20}ON_4Cl_6Pd_2$ requires C, 12·2 ; H, 3·4 ; Cl, 36·0 ; Pd, 36·15%).

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

[*Received, December 16th*, 1925.]