LXIII.—$\gamma\gamma'\gamma''$-*Triaminotripropylamine and its Complex Compounds with Nickel.*

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THE preparation of $\gamma\gamma'\gamma''$-triaminotripropylamine is similar to that of $\beta\beta'\beta''$-triaminotriethylamine, for molten phthal-γ-bromopropylimide on treatment with gaseous ammonia gives $\gamma\gamma'\gamma''$-triphthalimidotripropylamine hydrobromide, which on hydrolysis furnishes the required base. Whereas, however, the tertiary nitrogen atom in triaminotriethylamine is so feebly basic that the amine may act as a tri- or a tetra-acidic base, that in triaminotripropylamine, by virtue of its greater distance from the primary amine groups, is strongly basic, and the amine therefore always acts as a tetra-acidic base. The strongly basic character of the tertiary amine group in triaminotripropylamine causes the synthesis to follow a rather different course from that of the corresponding ethyl base. Ammonia reacts with phthal-β-bromoethylimide to give triphthalimidotriethylamine, mixed with about 12% of the hydrobromide of this base: phthal-γ-bromopropylimide, however, gives solely triphthalimidotripropylamine hydrobromide, and none of the free base. The hydrobromide, moreover, is largely contaminated with various amorphous by-products, and the yield of the triphthalimido-compound is therefore low.

It has been shown (preceding paper) that nickel succinimide on treatment with triaminotriethylamine gives a mixture of two complex ions, the bivalent triaminotriethylaminenickelous ion, $[\mathrm{Ni\ tren}]^{\cdot\cdot}$, in which the metal shows a co-ordination number of 4, and the quadrivalent tristriaminotriethylaminebisnickelous ion, $[\mathrm{Ni_2\ tren_3}]^{\cdot\cdot\cdot\cdot}$, in which the metal has a co-ordination number of 6. Nickel succinimide on treatment with triaminotripropylamine gives, however, one complex of the first type only, and the triaminotripropylaminenickelous ion, $[\mathrm{Ni\ trpn}]^{\cdot\cdot}$, in which the metal shows a co-ordination number of 4, can be precipitated as the thiocyanate. The symbol "trpn" is here used to denote one molecule of the tetramine. This complex ion is less stable and less strongly electropositive than the corresponding ethyl complex ion; the thiocyanate undergoes slight decomposition even on recrystallisation from hot water, whilst precipitation with potassium iodide in the original preparation furnishes the hydroxy-iodide of the above complex. The normal iodide is prepared by the double decomposition of some far more stable salt such as the nitrate.

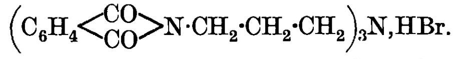
No complex compound of triaminotripropylamine with nickel or with platinum in which the metal showed a co-ordination number of 6 could be isolated. It would seem, therefore, that the very well defined dichlorotriaminotriethylamineplatinic chloride,

$$[\mathrm{Cl_2Pt\ tren}]\mathrm{Cl_2},$$

has no stable propyl homologue.

EXPERIMENTAL.

Triphthalimidotripropylamine Hydrobromide,



$$\left(\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}{>}\mathrm{N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2}\right)_3\mathrm{N,HBr}.$$

—A stream of dry ammonia gas is passed through molten phthal-γ-bromopropylimide at 150° until the product becomes too viscous to allow further passage of the gas, the reaction being about twice as rapid as that with phthal-β-bromoethylimide under like conditions. The cold pale-yellow product (with containing tube) is pulverised, and twice extracted with boiling alcohol: the residue is washed with water, and then recrystallised from hot acetic acid. The solution, when filtered and cooled, deposits *$\gamma\gamma'\gamma''$-triphthalimidotripropylamine hydrobromide* with one molecule of acetic acid of crystallisation. This product, when washed with acetic acid and ether and dried in the air, is pure; on heating, it liberates acetic acid at 100—105°, and finally melts at 243—244°, *i.e.*, at the melting point of the hydrobromide itself (Found: C, 58·5; H, 5·0; Br, 11·4. $\mathrm{C_{35}H_{35}O_8N_4Br}$ requires C, 58·4; H, 4·9; Br, 11·1%). The *hydrobromide* itself can be obtained by heating the above product in a vacuum at 100°, or by crystallisation from a large volume of very dilute hydrobromic acid, from which the hydrobromide separates in colourless needles, m. p. 243—245° (Found: Br, 12·1. $C_{33}H_{31}O_6N_4Br$ requires Br, 12·1%).

Triphthalimidotripropylamine, $(C_6H_4{:}C_2O_2{:}N{\cdot}C_3H_6)_3N$.—The hydrobromide with acetic acid of crystallisation (2 g.) is dissolved in boiling water (450 c.c.), and to the clear solution is added a slight excess of *N*-sodium hydroxide (6·0 c.c.). A white precipitate of *triphthalimidotripropylamine* immediately separates, and when filtered, washed with boiling water, and twice recrystallised from alcohol, is obtained in fine needles, m. p. 150—151° (Found: C, 68·8; H, 5·2. $C_{33}H_{30}O_6N_4$ requires C, 68·5; H, 5·2%).

$\gamma\gamma'\gamma''$-*Triaminotripropylamine Tetrahydrochloride*,

$$N(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_3,4HCl,\tfrac{1}{2}H_2O.$$

—Triphthalimidotripropylamine hydrobromide with acetic acid of crystallisation (10 g.) and hydrochloric acid (300 c.c., 1 : 1 by volume) are boiled under reflux. The solution becomes clear in about 4 hours, and after 7 hours is chilled, the phthalic acid separated, and the filtrate evaporated to small bulk. The tetrahydrochloride is so soluble in water that it cannot be crystallised, and prolonged evaporation of its solution merely gives a syrup: the concentrated solution is therefore poured into alcohol, and the heavy syrup which separates, solidifies on standing and stirring to a crystalline mass of the tetrahydrochloride, which is filtered off and washed with alcohol. The *tetrahydrochloride* is thus obtained as slightly deliquescent, white crystals which melt with foaming at 227—229°; the water of crystallisation is not liberated on heating in a vacuum at 100° (Found: C, 31·1; H, 8·2; Cl, 41·3, 41·7. $C_{18}H_{58}ON_8Cl_8$ requires C, 31·5; H, 8·45; Cl, 41·3%).

Triaminotripropylamine platinichloride,

$$N(C_3H_6{\cdot}NH_2)_3,4HCl,2PtCl_4,3H_2O,$$

is prepared in the usual way, and when recrystallised from a little water separates in orange-coloured needles (Found: C, 10·3; H, 3·2; Pt, 36·7; H_2O, 4·9. $C_9H_{34}O_3N_4Cl_{12}Pt_2$ requires C, 10·2; H, 3·2; Pt, 36·8; $3H_2O$, 5·1%). The anhydrous material darkens at 250° and melts with decomposition at 257—258°.

Triaminotripropylamine aurichloride,

$$N(C_3H_6{\cdot}NH_2)_3,4HCl,4AuCl_3,3H_2O,$$

separates when concentrated solutions of the tetrahydrochloride and of potassium aurichloride are mixed. It is filtered, washed with water, and dried without recrystallisation; the orange-yellow needles, m. p. 191—192° (decomp.), are even more soluble in alcohol and acetone than in water (Found: C, 6·9; H, 2·0; Au, 49·4, 49·5. $C_9H_{34}O_3N_4Cl_{16}Au_4$ requires C, 6·75; H, 2·1; Au, 49·2%).

Triaminotripropylamine picrate, $N(C_3H_6{\cdot}NH_2)_3,4C_6H_4O_7N_3,H_2O$, is almost insoluble in the usual liquids, but can be recrystallised from boiling water, one litre of which dissolves about 1 g. of the picrate. The latter separates in pale yellow needles which soften at 190° and melt with decomposition at 222° (Found : C, 35·2; H, 3·5. $C_{33}H_{38}O_{29}N_{16}$ requires C, 35·3; H, 3·4%).

Tribenzoyltriaminotripropylamine, $N(C_3H_6{\cdot}NH{\cdot}CO{\cdot}C_6H_5)_3$, prepared in the usual way, is obtained after three recrystallisations from anhydrous acetone as fine, white crystals, m. p. 129—131° (Found : C, 72·1; H, 7·2. $C_{30}H_{36}O_3N_4$ requires C, 71·9; H, 7·25%).

The Co-ordination Derivatives of Triaminotripropylamine.

Triaminotripropylaminenickelous thiocyanate, [Ni trpn](SCN)$_2$.—The tetrahydrochloride of the base (12·0 g.) is warmed with 33% aqueous caustic soda solution (16·0 c.c.) until sodium chloride alone remains undissolved : the mixture is then added to a hot solution of nickel succinimide (8·5 g.) in alcohol (250 c.c.). The colour of the solution changes rapidly from pale green to blue. The solution is now treated precisely as in the preparation of the corresponding ethyl derivative (p. 483), and the concentrated aqueous solution is filtered directly into a cold strong solution of potassium thiocyanate. The fine precipitate is filtered off and twice recrystallised from hot water, from which the *triaminotripropylaminenickelous thiocyanate* separates on rapid cooling in pale lilac-blue, crystalline leaflets, and on slow cooling in long needles of the same colour. The difference between these two forms, as in the case of the corresponding ethyl derivative, is apparently solely one of crystalline habit (Found : C, 36·6; H, 6·55; Ni, 16·2. $C_{11}H_{24}N_6S_2Ni$ requires C, 36·4; H, 6·7; Ni, 16·2%). The thiocyanate melts at 260—261° with decomposition; it is far less stable than the corresponding ethyl compound, and when recrystallised from hot water always leaves behind on the filter a small quantity of an amorphous green product, presumably nickel hydroxide.

Triaminotripropylaminenickelous Iodide, [Ni trpn]I$_2$,1½H$_2$O.—The thiocyanate in hot aqueous solution is treated with a solution of the calculated quantity of silver nitrate, and the product, after filtering, evaporated to small bulk. The cold concentrated solution is added to a cold saturated potassium iodide solution, and the crystalline precipitate filtered off and washed with a little water, alcohol, and ether. The *iodide* is thus obtained as a fine, apple-green, crystalline powder (Found : I, 48·05; Ni, 11·0. $C_{18}H_{54}O_3N_8I_4Ni_2$ requires I, 48·1; Ni, 11·1%).

Triaminotripropylaminenickelous Hydroxyiodide,

[Ni trpn]I(OH),2H$_2$O.

—If the warm concentrated aqueous solution obtained by treating nickel succinimide with the amine is mixed with about twice its volume of hot strong potassium iodide solution, fine, sea-green, crystalline leaflets rapidly appear. These crystals consist of the above *hydroxyiodide* combined with potassium iodide, and have the composition 2[Ni trpn]I(OH),KI,$2H_2O$. This compound is decomposed, however, even by cold water, and the preparation of the pure material is therefore almost impossible: slight dissociation occurs when the crystals are washed even with a little alcohol to free them from mother-liquor, and various preparations always give in consequence a low iodine and high carbon value (Found: C, 22·7; H, 5·3; N, 11·0; I, 37·7; Ni, 11·5. $C_{18}H_{54}O_4N_8I_3NiK$ requires C, 22·0; H, 5·5; N, 11·4; I, 38·7; Ni, 11·9%).

If the mother-liquor after the separation of these crystals is treated further with potassium thiocyanate solution, a small precipitate of triaminotripropylaminenickelous thiocyanate is obtained.

When the green crystals of the potassium iodide addition product are dissolved in warm water, a deep blue solution is at once obtained, and, on cooling, deep blue crystals of *triaminotripropylaminenickelous hydroxyiodide*, [Ni trpn]I(OH),$2H_2O$, separate. The hydroxyiodide is quite stable in the presence of water, and can be recrystallised repeatedly from boiling water without apparent change (Found: C, 25·5; H, 6·3; N, 13·0; I, 29·5; Ni, 13·5. $C_9H_{29}O_3N_4INi$ requires C, 25·3; H, 6·85; N, 13·1; I, 29·7; Ni, 13·75%). This compound when heated in a vacuum at 100° readily loses its water of crystallisation, but at the same time undergoes slight further hydrolysis, and the anhydrous product is therefore never quite pure. When the hydroxyiodide in strong aqueous solution is treated with strong potassium iodide solution, the sea-green crystals of the above potassium iodide addition product once again separate, and when recrystallised from water again furnish the pure deep blue hydroxyiodide. Moreover, when the hydroxyiodide in aqueous solution is treated with potassium thiocyanate solution, a rapid precipitation of triaminotripropylaminenickelous thiocyanate occurs, and the latter when once recrystallised from hot water is pure (Found: N, 23·2. $C_{11}H_{24}N_6S_2Ni$ requires N, 23·2%). Aqueous solutions of the hydroxyiodide are distinctly alkaline, and on exposure to air absorb carbon dioxide.

In view of the ready formation and great stability of dichlorotriaminotriethylamineplatinic chloride, [Cl_2Pt tren]Cl_2 (p. 482) many experiments were made to prepare the corresponding propyl derivative. No definite evidence of the formation of such a compound could be obtained, however, and the attempt was finally abandoned.

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