LIX.—*The Cobaltic Derivatives of ββ'β''-Triaminotriethylamine.*

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ββ'β''-TRIAMINOTRIETHYLAMINE, $N(CH_2{\cdot}CH_2{\cdot}NH_2)_3$, was first prepared by Ristenpart (*Ber.*, 1896, **29**, 2530), who showed that the presence of the three primary amine groups caused the fourth tertiary amine group to be neutral, since, for example, the base formed a trihydrochloride, $N(CH_2{\cdot}CH_2{\cdot}NH_2,HCl)_3$: in fact, all Ristenpart's derivatives are normal derivatives of a triacidic base. The chemistry of this polyamine was further investigated by Mann and Pope (*Proc. Roy. Soc.*, 1925, *A*, **109**, 444; J., 1926, 482), who showed that it furnished, when recrystallised from concentrated hydrochloric acid, a tetrahydrochloride; this, however, on exposure to air slowly lost hydrogen chloride, giving Ristenpart's trihydrochloride. Two distinct series of derivatives were obtained from the tri- and the tetra-hydrochloride respectively. Many complex salts of the amine with various metals were also prepared; in all these salts, the base co-ordinates as a tetra-amine, occupying four co-ordination positions, and these were the first complex salts of an aliphatic tertiary amine to be isolated. For instance, if one molecule of triaminotriethylamine be denoted by the symbol "tren," it was found that metals of co-ordination number 4 gave salts such as triaminotriethylaminenickelous thiocyanate, $[\mathrm{Ni\ tren}](\mathrm{SCN})_2$, and triaminotriethylamineplatinous iodide, $[\mathrm{Pt\ tren}]\mathrm{I}_2$, whereas metals of co-ordination number 6 gave salts such as dichlorotriaminotriethylamineplatinic dichloride, $[\mathrm{Cl_2Pt\ tren}]\mathrm{Cl}_2$, and tristriaminotriethylaminebisnickelous tetraiodide, $[\mathrm{Ni_2\ tren_3}]\mathrm{I}_4$.

The complex salts of this amine with cobalt were subsequently investigated by Jaeger and Koets (*Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 1). These authors apparently isolated no mononuclear derivative of cobalt, but by treating aquochlorobisethylenediaminecobaltic chloride with the tetra-amine they prepared the remarkable complex salt, hexaethylenediaminebistriaminotriethylaminetricobaltic nonaiodide, $[\mathrm{Co_3\ en_6\ tren_2}]\mathrm{I}_9$. In this compound the triaminotriethylamine is co-ordinated by the three primary amine groups alone, the tertiary amine group remaining free and unco-ordinated. The authors have discussed the stereochemistry of this compound in detail, and have described its probable symmetric configuration.

It is now shown, however, that more simple mononuclear compounds of this tetra-amine with cobalt can be prepared, since the metal furnishes salts of the normal diacidotetrammino-type, *e.g.*, *dithiocyanato-ββ′β″-triaminotriethylaminecobaltic monothiocyanate*, $[(\mathrm{SCN})_2\mathrm{Co\ tren}]\ \mathrm{SCN}$. This compound is thus of the same general type as the platinic salt above: the base is again co-ordinated by all four amine groups, and the complex ion, having a plane of symmetry, cannot be resolved into optically active forms. Several derivatives of this complex ion have been described, and they are all highly crystalline stable salts.

EXPERIMENTAL.

Dithiocyanatotriaminotriethylaminecobaltic Monothiocyanate Monohydrate, $[(\mathrm{SCN})_2\mathrm{Co\ tren}]\mathrm{SCN},\mathrm{H_2O}$.—A mixture of roseo-cobaltic chloride (4 g.) and triaminotriethylamine trihydrochloride (5·6 g.) is added to water (300 c.c.), and the whole boiled under reflux for 6 hours. The clear deep red solution is thrice evaporated to small bulk with intermediate addition of water, and the final solution chilled and diluted with concentrated potassium thiocyanate solution. A fine brown product separates and after a short time is followed by a deep red crystalline precipitate. After standing over-night, the mixture is collected, and twice recrystallised from hot water. The *monothiocyanate monohydrate* is thus obtained in deep red needles, m. p. 208—210° (decomp.), readily soluble in hot, but only slightly soluble in cold, water (Found: C, 27·2; H, 5·1; N, 24·8; S, 23·9. $C_9H_{18}N_7S_3Co,H_2O$ requires C, 27·2; H, 5·0; N, 24·7; S, 24·2%).

The *mononitrate monohydrate*, $[(SCN)_2Co\,tren]NO_3,H_2O$, is prepared by treating a cold supersaturated solution of the monothiocyanate with very dilute nitric acid. The crystalline nitrate rapidly separates, and is obtained by recrystallisation from hot water, in which it is readily soluble, in large deep red prisms, m. p. 226° (decomp.) (Found: C, 24·2; H, 5·0; N, 24·5; S, 16·2. $C_8H_{18}O_3N_7S_2Co,H_2O$ requires C, 23·9; H, 5·0; N, 24·4; S, 16·0%).

The anhydrous *monochloride*, $[(SCN)_2Co\,tren]Cl$, is prepared similarly by treating a cold aqueous solution of the monothiocyanate with dilute hydrochloric acid. A small crop of the crystalline monochloride separates over-night and, after recrystallisation from hot water, is obtained in fine deep red crystals, m. p. 225—226° (decomp.) (Found: N, 23·8; Cl, 9·9; S, 18·1. $C_8H_{18}N_6ClS_2Co$ requires N, 23·6; Cl, 9·9; S, 18·0%).

The *chloroplatinate*, $[(SCN)_2Co\,tren]_2PtCl_6$, is best prepared by adding an aqueous solution of the monothiocyanate, containing dilute hydrochloric acid, to a solution of chloroplatinic acid. The chloroplatinate is at once precipitated as a deep brick-red powder, which, when washed with much cold water and dried, is pure. It is insoluble in hot water and has m. p. 203—204° (decomp.) (Found: C, 18·4; H, 3·3; N, 15·8. $C_{16}H_{36}N_{12}Cl_6S_4Co_2Pt$ requires C, 18·3; H, 3·5; N, 16·0%).

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