CLXXII.—*New Polynuclear Co-ordination Compounds of Cobalt.*

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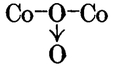
THE polynuclear metal-ammines have, in many cases, somewhat complex empirical formulæ, but by the application of simple rules their probable configurations can be deduced.

Werner assigned an octahedral distribution to the units associated with the central cobalt, chromium, or platinum atom and demonstrated that it was possible to link such octahedra at one, two or three points by suitable bridge atoms or groups. He specially emphasised that in such polynuclear complexes the metallic atoms are never directly linked with one another.

Werner explained that an OH or NH_2 group was able to link two cobalt atoms because the oxygen or nitrogen atom possessed both principal and auxiliary valency. The electronic theory of valency, however, presents a clearer explanation of why these and similar groups can act as linkages in the same way as O, O_2, SO_4, C_2O_4, NH. In the latter type of linkage the metal atoms form non-polar single bonds with the associating unit, whilst the other linkages are connected by one non-polar bond and one co-ordinate link.

The exact structure of salts containing the O_2 linkage is still unsettled. For such a linkage the structures  $\begin{array}{c}Co{-}O{-}Co\\ \downarrow\\ O\end{array}$ and Co–O–O–Co are both possible. A real difficulty arises, however, when an attempt is made to assign a suitable configuration to the product formed by the oxidation of such a compound as

$$[(NH_3)_5Co{-}O_2{-}Co(NH_3)_5]X_4.$$

The dark green substance obtained is stated by Werner to contain the oxygen molecule in a much more stable condition than before the oxidation, and he formulates the new product as

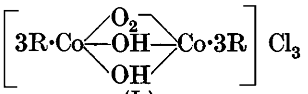
$$[(NH_3)_5Co^{III}-O_2-Co^{IV}(NH_3)_5]X_5.$$

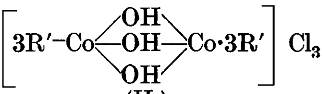
This formulation postulates the co-existence of ter- and quadrivalent cobalt and has been employed by Werner to give a suitable configuration to a large number of polynuclear cobalt ammines ("Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie," 1920 ed., pp. 293 *et seq.*).

A more satisfactory explanation is difficult to find in spite of the fact that such a formulation means, in the special case mentioned above, that two atoms of cobalt with effective atomic numbers of 36 form a less stable association with an oxygen molecule than one atom of effective atomic number 35 and another of effective atomic number 36.

Nevertheless Werner concluded from an investigation of a large range of metal-ammines that the maximum co-ordination number of the cobalt was 6 irrespective of whether the metal was ter- or quadrivalent.

It was this conclusion that led Bucknall and Wardlaw (J., 1928, 2648) to reinvestigate the reaction which takes place when dry air is drawn through an alcoholic solution of cobaltous chloride containing allylamine. As a result they concluded that the product obtained was not $[2O_2Co6R]Cl_3,H_2O_2$, containing cobalt with a co-ordination number of 8 as previously described by Pieroni (*Gazzetta*, 1921, **51**, i, 42), but a polynuclear complex of the probable configuration (I; R = $CH_2{:}CH{\cdot}CH_2{\cdot}NH_2$), where the cobalt has valencies of 3 and 4 and a co-ordination number of 6.


(I.)


(II.)

In view of the isolation of this compound from a non-aqueous solvent it seemed of interest to determine whether the reaction was typical of amines generally and whether the same type of product was always obtained.

Experiments soon indicated that certain amines such as aniline, pyridine, and quinoline formed products which were not amenable to further oxidation by the method outlined above. Aniline, for example, gave an insoluble blue compound of the composition $CoCl_2,2C_6H_5{\cdot}NH_2$, which on recrystallisation from alcohol yielded the red substance $CoCl_2,2C_6H_5{\cdot}NH_2,2C_2H_5{\cdot}OH$ (Lippmann and Vortmann, *Ber.*, 1878, **11**, 1069). It seems highly probable that in this case there is formed the very stable co-ordination compound

[$CoCl_2$·$2C_6H_5(NH_2)$·$2C_2H_5(OH)$], which is unaffected by atmospheric oxygen.

Of a large number of amines investigated, satisfactory results were only recorded in the case of propylamine and benzylamine and the reaction with allylamine was confirmed. With ethylamine the reaction appeared to follow a similar course, but the yield of product was insufficient for complete analysis. It is not without significance that each amine contains the group CH_2·NH_2, *viz.*, CH_2:CH·CH_2·NH_2, C_2H_5·CH_2·NH_2 and C_6H_5·CH_2·NH_2.

In all cases the amine occupies one position in the co-ordination sphere; the products from the reaction with allylamine and propylamine have the general formula (I), and the product from benzylamine the formula (II).

In formula (I) both ter- and quadri-valent cobalt atoms are present, whereas in (II) both cobalt atoms are tervalent. Cobalt exhibits throughout a co-ordination number of 6.

EXPERIMENTAL.

The ethyl alcohol used in the following experiments was dried by refluxing and distilling it twice over barium oxide and twice over calcium turnings. The amines were purchased samples dried by two distillations over sodium.

The red compound (I; R = CH_2:CH·CH_2·NH_2) produced by the oxidation of a mixture of cobaltous chloride (dried at 140°) in dry alcohol in the presence of dry allylamine (Bucknall and Wardlaw, *loc. cit.*) has again been prepared and analysed (Found: Co, 18·5; Cl, 16·7; C, 33·7; H, 7·1; N, 13·5. Calc.: Co, 18·6; Cl, 16·8; C, 34·1; H, 7·0; N, 13·3%).

Hexa-allylamineperoxodihydroxodicobalt Trinitrate (formula as I).—To a solution (40 c.c.) of the complex chloride (2 g.) in water, pure nitric acid (1 c.c.) was added. The pink precipitate produced was washed free from acid with water and dried in a vacuum over calcium chloride (Found: Co, 16·6; N, 17·6. $C_{18}H_{44}O_{13}N_9Co_2$ requires Co, 16·6; N, 17·7%).

These results confirm those set out in the previous communication and disprove the formula proposed by Pieroni (*loc. cit.*) for the complex chloride.

Hexapropylamineperoxodihydroxodicobalt Trichloride (I; R = Pr^a·NH_2).—To a saturated solution of cobalt chloride (dried at 140°) in dry alcohol (75 c.c.), dry *n*-propylamine (20 c.c.) was added in small quantities with constant shaking. Considerable heat was evolved and a bluish-red solution resulted, from which, however, no addition compound separated even on cooling in a freezing mixture (compare cobalt allylamines). The mixture was oxidised for about

30 hours by means of a slow stream of air, washed and dried by passage through soda lime tubes and sulphuric acid bubblers. The red crystalline precipitate which separated was washed with dry alcohol and dried in a vacuum over calcium chloride.

Cobalt was estimated as sulphate by ignition of the substance with sulphuric and nitric acids in an air-bath, gradually raised to about 410°. Chlorine was estimated as silver chloride after removal of cobalt as hydroxide on the addition of sodium hydroxide to a solution of the substance (Found: Co, 18·5; Cl, 16·6; C, 33·2; H, 8·6; N, 13·1. $C_{18}H_{56}O_4N_6Cl_3Co_2$ requires Co, 18·3; Cl, 16·5; C, 33·5; H, 8·7; N, 13·0%).

The complex chloride is very soluble in water, giving a neutral solution, and the addition of nitric acid produces, as in the case of the allylamine complex, an insoluble nitrate, all the chlorine having been displaced. Heated to 70°, an aqueous solution of the salt yields brown cobalt hydroxide and propylamine is liberated. Ammonium sulphide immediately precipitates cobalt as sulphide. Concentrated hydrochloric acid gives a green solution. The complex salt liberates iodine from potassium iodide solution on warming.

Molecular-weight determinations. The molecular weight of the complex chloride was determined by the depression of the freezing point of water. If the above formula is correct, four ions should be present in solution and the apparent molecular weight should be about 160 when ionisation is complete. The results furnish evidence in favour of this formulation :

G. of substance per 100 g. water.	Conc. (mols. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
1·251	0·01941	3·32	194
1·634	0·02536	3·13	205
1·822	0·02827	3·12	206

Molecular-conductivity determinations. The molecular conductivity of the complex chloride was found for various dilutions at 0° :

v (litres/mol.)	35·4	70·8	141·6	283·2	566·4
μ	94·7	108·4	132·0	140·0	145·0

The values of the molecular conductivities of two typical salts at 0° are given for comparison :

v (litres/mol.)	32	64	128	256	512	1024
$K_3Fe(CN)_6$	215	227	243	254	264	282
$K_3W(CN)_8$	211	224	238	250	259	264

From the results for the complex chloride, μ_∞ is estimated to be about 180. The values of μ, as in the case of the corresponding allylamine derivative, are less than would be expected for a normal four-ion compound. They are, however, in accordance with the formula if it is assumed, as is probably the case, that the large complex ion is slow-moving.

Hexabenzylaminetrihydroxodicobalt Trichloride (II; $R' = C_6H_5 \cdot CH_2 \cdot NH_2$).—To a saturated solution of cobaltous chloride (20 g., dried at 140°) in 200 c.c. of dry alcohol, dry benzylamine (25 g.) was added slowly with shaking; a white precipitate separated. The mixture was oxidised for about 150 hours by a slow current of air, dried and purified as previously described. The purple-red crystalline product was washed with alcohol and dried in a vacuum over calcium chloride (Found: Co, 12·7; Cl, 11·6; C, 54·2; H, 6·2; N, 9·2. $C_{42}H_{57}O_3N_6Cl_3Co_2$ requires Co, 12·9; Cl, 11·6; C, 54·9; H, 6·2; N, 9·2%).

The complex salt is very similar in colour to purpureo-cobaltic chloride, and is insoluble in water and alcohol, physico-chemical measurements thus being precluded. A suspension in water decomposed on being heated to 70°, with formation of cobalt hydroxide and the liberation of benzylamine and benzaldehyde. Cold concentrated nitric acid did not form a nitrate as in the two previous cases. Iodine was not liberated from potassium iodide solution by this salt (unlike the peroxo-compounds) on warming in the presence of acetic acid.

Oxidation of Cobaltous Chloride in Alcohol in the Presence of Other Amines.—Ethylamine. On the addition of the amine a violet solution was obtained which yielded on oxidation a red liquor, from which a small quantity of solid separated. The yields, however, were always very small.

Ethylenediamine. The amine was thoroughly dried over sodium. Many experiments were carried out, but the brown product isolated was of variable composition. It was, however, capable of recrystallisation from aqueous alcohol and the chief product after this treatment was triethylenediaminecobaltic chloride,

$$[\mathrm{Co\,3\,en}]Cl_3,3H_2O;$$

a small quantity of a red compound was also isolated. The above complex salt was also obtained when ethylenediamine was oxidised in aqueous solution in the presence of cobaltous chloride.

Methylamine, diethylamine, and piperidine. These bases always gave greenish precipitates, however thoroughly the drying process was carried out. In no case was the characteristic red oxidised solution produced.

It is evident that oxidation of cobaltous chloride in alcohol in the presence of amines does not always produce polynuclear complexes. So far, only primary amines containing the $CH_2 \cdot NH_2$ group have been satisfactory for this purpose.

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