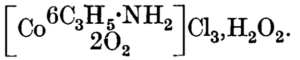
CCCXLVIII.—*Cobalt Allylamines: A Supposed Co-ordination Number of Eight for Cobalt.*

By William Ralph Bucknall and William Wardlaw.

From a careful survey of the chemical evidence, Sidgwick ("The Electronic Theory of Valency," p. 152) has concluded that up to the end of the first long period in the classification of the elements the highest covalency of an atom is six. He also states (*op. cit.*, p. 160) that "it should be noted that there are a certain number of compounds which appear to indicate values of the covalency in excess of those allowed by the rule. In none of these have the structure and molecular weight been definitely ascertained." There are recorded in the literature, however, the preparation and properties of an interesting complex salt of cobalt, which is mentioned by Weinland ("Komplexverbindungen," 1919, p. 13) as an example of a co-ordination number of eight for cobalt, instead of the usual six anticipated from Sidgwick's rule. The substance in question was prepared by Pieroni and Pinotti (*Gazzetta*, 1915, **45**, ii, 100), who found that when dry air was drawn through a saturated solution of cobaltous chloride (dried at 140°) in absolute alcohol to which dry allylamine had been added there separated a red, crystalline compound. It dissolved in cold water with the production of a neutral solution, and from cryoscopic molecular-weight determinations it was concluded that in aqueous solution the substance dissociated into a maximum of four ions. From these data and the percentages of cobalt and chlorine found in the compound, Pieroni and Pinotti assigned to the new substance the formula $[Co,8C_3H_5{\cdot}NH_2]Cl_3$. Later, however, Pieroni (*ibid.*, 1921, **51**, i, 42) reinvestigated the reaction and, as a result of a more complete analysis, deduced the new formula

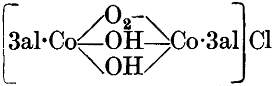


$$\left[Co\begin{matrix}6C_3H_5{\cdot}NH_2\\2O_2\end{matrix}\right]Cl_3,H_2O_2.$$

On titration with permanganate, the titre was in excess of that demanded by the unsaturated amine, and it was suggested that the excess was required by the hydrogen peroxide present in the molecule. As both formulæ assign a co-ordination number of eight to the cobalt and the reaction appeared to have several unusual features, it seemed of interest to reopen the investigation.

EXPERIMENTAL.

*Preparation of Hexa-allylamineperoxodihydroxodicobalt Trichloride,**



$$\left[3al{\cdot}Co\begin{matrix}O_2\\OH\\OH\end{matrix}Co{\cdot}3al\right]Cl_3$$

.—To a saturated solution of cobaltous chloride (10 g.; dried at 140°) in 100 c.c. of water-free alcohol, dry allylamine (32 g.) was added in portions, with constant shaking, air being displaced by a current of nitrogen; considerable heat was evolved and the solution became reddish-blue. On cooling, purplish-red, needle-like crystals separated in good yield. They were very deliquescent and unstable, allylamine being readily liberated. With alcohol, the crystals gave a blue solution, and in water they underwent decomposition, cobalt hydroxide being precipitated almost immediately. Pieroni assigned to these crystals the composition $CoCl_2,3C_3H_5{\cdot}NH_2$. When a current of dry air was passed through the reaction flask containing the crystals in contact with their mother-liquor, the

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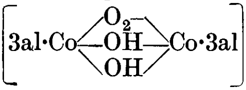
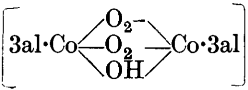
* al = $C_3H_5{\cdot}NH_2$.

solution changed in colour from purplish-red to brownish-red, and minute red crystals slowly separated. After oxidation for about 3 days, these crystals were collected, washed with absolute alcohol (in which they are insoluble) until the filtrate was colourless, and then air-dried on a porous plate. In the first attempts to obtain this oxidised product, cobalt hydroxide separated after the oxidation had proceeded for a short time. This was apparently due to the presence of moisture in the alcohol, for this difficulty did not arise when the solvent had been refluxed and distilled twice over barium oxide and twice over calcium turnings before use. The allylamine for the early experiments was prepared by the method of Pieroni and Pinotti (*Gazzetta*, 1915, **45**, i, 100), but later, purchased samples were dried by two distillations over sodium and then had b. p. 55°.

Analysis.—The cobalt was estimated as sulphate by gentle ignition of the substance with sulphuric and nitric acids in an air-oven. For the estimation of the chlorine, cobalt was removed as hydroxide by addition of sodium hydroxide to a solution of the substance, and the chloride then precipitated as silver chloride [Found: Co, 18·6; Cl, 16·7; C, 33·6; H, 6·7; N, 13·1.

$\left[3al\cdot Co\begin{matrix}O_2\\OH\\OH\end{matrix}Co\cdot 3al\right]Cl_3$ (I) requires Co, 18·65; Cl, 16·8; C, 34·1; H, 7·0; N, 13·3%.

$\left[3al\cdot Co\begin{matrix}O_2\\O_2\\OH\end{matrix}Co\cdot 3al\right]Cl_3$ (II) requires Co, 18·2; Cl, 16·45; C, 33·4; H, 6·7; N, 12·9%]. From the analytical results, formula (I) seems the more probable.

Molecular-weight Determinations.—The molecular weight was determined by the depression of the freezing point of water. If either of the above-mentioned formulæ represents the correct formulation, then four ions should be present in solution and the apparent molecular weight, when ionisation is complete, should be *ca.* 160. The results in Table I, calculated for formula (I), furnish evidence in favour of such a formulation.

TABLE I.

G. of substance per 100 g. water.	Conc. (mols. per 1000 g. water).	Osmotic factor.	Apparent mol. wt.
1·022	0·01616	3·60	176·0
1·159	0·01833	3·46	182·7
1·736	0·02744	3·11	203·0

Molecular-conductivity Determinations.—The molecular conductivity was determined at various dilutions at 0°. Table II gives the values of μ for the complex chloride, and for comparison the values of the molecular conductivities of typical salts at 0° are given in Table III.

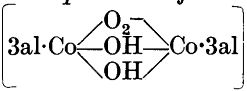
TABLE II.

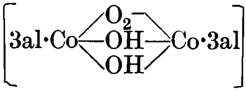
v (litres/mol.)	45·6	65·9	131·8	263·6	527·2	730·0
μ	119	128·8	144·3	159·3	176·3	184·8

TABLE III.

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	
$AlCl_3$						226	(approx.)
K_2SO_4					158	161	

From the results given in Table II, μ_∞ for the complex chloride is estimated to be *ca.* 210. Although the values of μ for the complex salt are less than would be expected for a normal four-ion compound, they are nevertheless in accord with the formula if we assume that the large complex ion is slow-moving, as is frequently the case. Since λ_∞ for Cl′ at 0° is *ca.* 46, then by Kohlrausch's law the ionic mobility of the complex ion is approximately 70, the usual figure for a tervalent ion being about 110.

Preparation of Hexa-allylamineperoxodihydroxodicobalt Trinitrate,  $\left[3al{\cdot}Co\overset{O_2}{\underset{OH}{—OH—}}Co{\cdot}3al\right](NO_3)_3$.—Pieroni and Pinotti noticed (*loc. cit.*) that the addition of nitric acid to a concentrated aqueous solution of the complex chloride produced red, acicular crystals, which were not further investigated. It has been found, however, that the addition of either nitric acid or a solution of any metallic nitrate will cause precipitation of a red compound. This new substance thus appears to be the result of an ionic reaction between the complex chloride and the nitrate ion.

The compound was prepared by the addition of about 1 c.c. of pure nitric acid to 20 c.c. of a solution of the complex chloride (2 g.), and was freed from acid by washing with cold water, in which it is slightly soluble; the filtered substance was air-dried on a porous plate. It contained no chlorine, and when it was moistened with sulphuric acid, nitric acid was liberated. It was slightly soluble in cold water, and on standing or by warming, hydrolysis occurred with the precipitation of hydroxide. Warming with sodium hydroxide caused the evolution of allylamine, and by distillation with sodium hydroxide and Devarda's alloy the nitrate groups were reduced to ammonia, which was titrated together with the liberated allylamine (Found: Co, 16·6; N, 17·8; N : Co = 9·03 : 2.  $\left[3al{\cdot}Co\overset{O_2}{\underset{OH}{—OH—}}Co{\cdot}3al\right](NO_3)_3$ requires Co, 16·6; N, 17·7%).

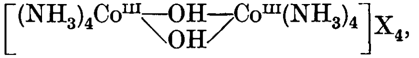
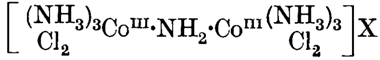
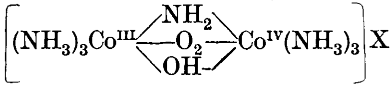
The nitrate hydrolyses in boiling water, but the presence of nitric acid prevents decomposition. Pieroni and Pinotti (*loc. cit.*) remarked on the formation of a yellow substance together with a heavy red compound when the complex nitrate was boiled with dilute nitric acid. It has been found, however, that the only product of this reaction is a red precipitate of the same composition as the above nitrate. It appears that the presence of the nitric acid merely retards the hydrolysis, and possibly decreases the solubility of the complex nitrate. If the concentration of the nitric acid is too high, the salt is dissolved and the complex ion is apparently destroyed.

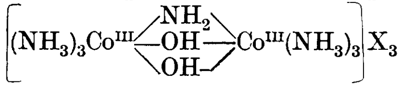
Reactions of the Complex Salts.—Concentrated hydrochloric acid gives, with either of the complex salts, a dark green, insoluble substance, which on warming dissolves to a bluish-green solution of cobaltous chloride and allylamine hydrochloride. The addition of concentrated hydrochloric acid to an aqueous solution of the complex chloride produces a green solution which reverts to the blue colour of cobaltous chloride only on warming. Sulphuric acid decomposes the complex ion and forms cobaltous sulphate. With silver nitrate solution, the complex chloride gives an immediate precipitate of silver chloride, together with a red precipitate, in concentrated solutions, of the complex nitrate. Ammonium sulphide immediately precipitates the cobalt as sulphide. The complex salts react, on warming, with potassium iodide solution with the liberation of iodine; with potassium bromide, however, no oxidation could be detected.

Discussion of Results.

The most important result of this investigation has been to indicate a new formulation for the salts originally prepared by Pieroni and Pinotti. The analytical data now obtained are compared below with those previously recorded for the complex chloride :

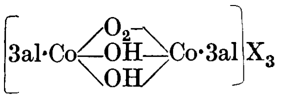
	Co.	Cl.	N.	C.	H.
Pieroni and Pinotti	9·7	17·4			
Pieroni	10·0; 9·25	17·1	13·7	35·76	7·76
Present authors	18·6	16·7	13·1	33·57	6·71

Our percentages for Cl, N, C, and H are of the same order as those determined by Pieroni and Pinotti for this compound, but there is a marked difference in the percentages of cobalt. Whereas the analytical figures of Pieroni and Pinotti indicate a ratio of Co : Cl = 1 : 3, the new figures show a ratio of 2 : 2·982. Such a ratio would be anticipated from the results obtained by Werner from the oxidation of ammoniacal solutions of cobaltous salts. He was able to isolate and examine many new substances which he formulated as bridge compounds ("Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie," 1920 ed., pp. 293 *et seq.*); for example, one of the first products of the atmospheric oxidation of ammoniacal cobalt solutions is a brownish-black oxy-compound of the composition $[(NH_3)_5Co^{III}\cdot O_2\cdot Co^{III}(NH_3)_5]X_4$, which on further oxidation yields the intensely dark green, so-called anhydro-oxy-cobaltate, $[(NH_3)_5Co^{III}\cdot O_2\cdot Co^{IV}(NH_3)_5]X_5$. Other products obtained by similar means include  $\left[(NH_3)_4Co^{III}\begin{matrix}-OH-\\-OH-\end{matrix}Co^{III}(NH_3)_4\right]X_4$, the melano-chloride  $\left[\underset{Cl_2}{(NH_3)_3}Co^{III}\cdot NH_2\cdot Co^{III}\underset{Cl_2}{(NH_3)_3}\right]X$, and also the three-bridge compound,  $\left[(NH_3)_3Co^{III}\begin{matrix}NH_2\\O_2\\OH\end{matrix}Co^{IV}(NH_3)_3\right]X_3$. From the melano-chloride by simple reactions the compound



$$\left[(NH_3)_3Co^{III}\begin{matrix}NH_2\\OH\\OH\end{matrix}Co^{III}(NH_3)_3\right]X_3$$

can be prepared.

The possibility that the compounds  $\left[3al\cdot Co\begin{matrix}O_2\\OH\\OH\end{matrix}Co\cdot 3al\right]X_3$ would result from the reactions dealt with in the present investigation is therefore not unexpected. The reaction is in accordance with the general tendency of alkaline solutions of cobaltous salts to produce polynuclear complex compounds on atmospheric oxidation. The new formulation assigns to cobalt valencies of three and four. Although quadrivalent cobalt is not normally considered to exist, yet Werner found it necessary to postulate its presence in such polynuclear compounds as those mentioned above. Moreover, it will be noticed that this formula assigns to cobalt the normal covalency of six, and there is no evidence that Pieroni and Pinotti's compounds necessitate any modification of Sidgwick's rule.

It is interesting to compare the results obtained from nickel salts under similar conditions. Pieroni and Pinotti (*Gazzetta*, 1914, **44**, ii, 366) found that by the action of allylamine on various nickel salts, several substances could be prepared which, like the compound of cobaltous chloride with allylamine, were very unstable, hydrolysing immediately in water. They concluded that in no case was there evidence of the existence of complex ions.

This investigation is being extended to a study of the products of the atmospheric oxidation of alcoholic solutions of cobalt salts in the presence of various other amines.

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