CCCLIII.—*Polynuclear Cobalt Complexes containing Cobalt in the Anion.*

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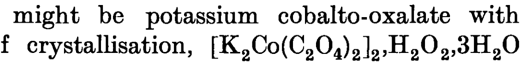
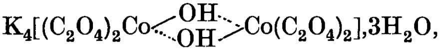
SOME years ago, Durrant (J., 1905, **87**, 1781) described the preparation of a new green potassium cobaltic oxalate by treating a solution of cobaltous oxalate in potassium oxalate solution with hydrogen peroxide at 65°. From his analytical data he concluded that the substance was either

(*a*) $[K_2Co(C_2O_4)_2,2H_2O]_2O$ or (*b*) $[K_2Co(C_2O_4)_2,2H_2O]_n$

where *n* was probably 2, and suggested the formulation



$$\begin{matrix}CO_2K\cdot C(OH)_2\cdot O\\ CO_2K\cdot C(OH)_2\cdot O\end{matrix}\!>Co\cdot O\cdot Co<\!\begin{matrix}O\cdot C(OH)_2\cdot CO_2K\\ O\cdot C(OH)_2\cdot CO_2K\end{matrix}$$

It appeared to the present authors, however, that possibly the green salt might be potassium cobalto-oxalate with hydrogen peroxide of crystallisation, $[K_2Co(C_2O_4)_2]_2,H_2O_2,3H_2O$; the reaction was therefore reinvestigated, but the results indicate that the empirical formula (*a*) proposed by Durrant is correct and that the compound does not contain hydrogen peroxide of crystallisation. Instead, it is a polynuclear cobalt complex containing the cobalt in the anion, and as far as can be ascertained, it represents the first example of this type of compound amongst derivatives of cobalt. In view of the fact that Werner (*Annalen*, 1914, **406**, 261) prepared a series of chromium oxalates, to which he assigned the formula  $R_4[(C_2O_4)_2Cr{<}\begin{smallmatrix}OH\\OH\end{smallmatrix}{>}Cr(C_2O_4)_2]$, a similar structure is possible for our series, and the potassium salt would be  $K_4[(C_2O_4)_2Co{<}\begin{smallmatrix}OH\\OH\end{smallmatrix}{>}Co(C_2O_4)_2],3H_2O$, in which cobalt has the usual co-ordination number of six.

By double decomposition, in aqueous solution, green insoluble *calcium*, *strontium*, *barium*, *lead*, and *silver* salts can be prepared, and it is considered very unlikely that hydrogen peroxide would remain as an addendum during these changes. Durrant showed, and it is now confirmed, that freezing-point measurements indicate the presence of a five-ion compound, which is in agreement with the present theory of its structure. The work was extended to other organic acids, but whilst green solutions could be obtained by treating alkali cobalt succinates, tartrates, malates, acetates, citrates, and carbonates with hydrogen peroxide, the only other compound isolated was a green *potassium cobalt oxy-malonate*. This substance seems to be of the same type as the oxy-oxalate but is less stable.

To determine whether iron behaved in a similar manner to cobalt, ferrous oxalate was dissolved in a potassium oxalate solution and then treated with hydrogen peroxide under various conditions, but basic ferric oxalates of variable composition were the only products formed.

EXPERIMENTAL.

Potassium Cobalt Oxy-oxalate.—Cobalt oxalate was slowly stirred into a solution of potassium oxalate (80 c.c. saturated at 20°), which was heated slowly to 100°, until no more dissolved on boiling. The magenta solution was filtered hot, and potassium oxalate solution (40 c.c.) added to the filtrate. The temperature was raised to 65° and hydrogen peroxide (20-vol.; 40 c.c.) was added slowly with stirring. The solution turned green, and the small crystals deposited on cooling were washed with water and dried in a vacuum over calcium chloride.

Analysis. (1) Cobalt was estimated as sulphate by treating the hydrated cobaltic oxide (obtained by boiling the substance with 1% alkali) with sulphuric and nitric acids in an air-bath gradually heated to about 400°. (2) Potassium and cobalt were estimated jointly as sulphates by ignition of the substance and treatment of the residue as previously indicated. (3) The total oxalate was estimated by titration as follows: the substance was covered with cold alkali (5*N*), 5 parts of water were added, and the mixture was warmed to 50° ; cobalt was removed as the brown oxide, the filtrate concentrated, acidified with sulphuric acid, and titrated against *N*/10-permanganate. (4) Three-quarters of the total oxalate could be estimated by boiling the substance for 10 minutes with water, then adding alkali and repeating the above procedure; during the boiling with water, carbon dioxide was evolved as the result of oxidation of one of the four oxalate groups by the oxygen contained in the molecule. (5) Combustion in oxygen enabled estimation to be made of the water and also of three-quarters of the total carbon, since potassium carbonate remained as a residue. (6) Oxygen was estimated by titration of the iodine, liberated from potassium iodide in hydrochloric acid, against *N*/10-sodium thiosulphate solution {Found : Co, 16·5; K, 22·0; H_2O, 10·0; C_2O_4, 49·3; O, 2·0; $\frac{3}{4}C_2O_4$ (titration), 37·3; $\frac{3}{4}C_2O_4$ (combustion), 37·1. Calc. for $K_4[Co_2O(C_2O_4)_4],4H_2O$: Co, 16·5; K, 21·9; H_2O, 10·1; C_2O_4, 49·3; O, 2·2%}. No water was removed when the substance was kept for 7 days in a vacuum over phosphoric oxide.

This complex is a dark green crystalline substance moderately soluble in water, the green solution yielding a brown precipitate when heated to 70°. The green colour is changed to pink by mineral acids and acetic acid, and evolution of carbon dioxide occurs. No free oxalate can be detected in the aqueous solution on the addition of calcium chloride.

Barium Cobalt Oxy-oxalate.—The foregoing potassium salt (3 g.) was dissolved in 200 c.c. of water by warming to 50°. To the cold solution barium chloride (15 c.c. of 5*N*) was added. The curdy light-green precipitate which was formed at once was washed with cold distilled water until free from chlorides, and dried in a vacuum over calcium chloride.

Analysis. Barium and cobalt were estimated jointly as sulphates. Barium was weighed as sulphate after precipitation from a hot solution of the salt made slightly acid with hydrochloric acid. The water and three-quarters of the carbon dioxide were estimated by combustion in oxygen. Oxygen was estimated in the manner described for the potassium salt (Found : Co, 14·2; Ba, 33·0; H_2O, 8·6; CO_2, 33·0; O, 1·9. $Ba_2[Co_2O(C_2O_4)_4],4H_2O$ requires Co, 14·2; Ba, 33·0; H_2O, 8·6; CO_2, 31·7; O, 1·9%).

Calcium Cobalt Oxy-oxalate.—The potassium salt (4 g.) was dissolved in water (250 c.c.) by warming to 50°, and calcium chloride ($CaCl_2,6H_2O$; 2 g. in 20 c.c.) added to the cold solution. The flocculent precipitate was washed and dried as before.

Analysis. Calcium and cobalt were estimated jointly as sulphates. Cobalt was precipitated as sulphide from a solution of the compound in dilute acetic acid containing excess of ammonium acetate;

the sulphide was converted to sulphate by nitric and sulphuric acids in the usual manner. Carbon, water, and oxygen were estimated as in the previous cases (Found: Co, 17·9; Ca, 12·3; CO_2, 39·8; H_2O, 13·9; O, 2·4. $Ca_2[Co_2O(C_2O_4)_4],5H_2O$ requires Co, 18·0; Ca, 12·2; CO_2, 40·3; H_2O, 13·7; O, 2·4%).

Strontium Cobalt Oxy-oxalate.—To an aqueous solution (300 c.c.) of potassium cobalt oxy-oxalate (4 g.), strontium nitrate (1·5 g.) in water (5 c.c.) was added. The precipitate was washed with 5 litres of water and dried in a vacuum over calcium chloride and phosphoric oxide.

Analysis. Cobalt and strontium were determined jointly as sulphates. After destruction of the oxalate by ignition, cobalt was precipitated as sulphide and converted into sulphate. Other estimations were effected as before (Found: Co, 15·3; Sr, 22·8; CO_2, 34·3; H_2O, 14·1; O, 2·0. $Sr_2[Co_2O(C_2O_4)_4],6H_2O$ requires Co, 15·3; Sr, 22·8; CO_2, 34·3; H_2O, 14·0; O, 2·1%).

Lead Cobalt Oxy-oxalate.—To the potassium salt (5 g.) in water (300 c.c.) lead acetate (5 g.) in water (20 c.c.) was added; the flocculent precipitate was washed and dried as before.

Analysis. Lead and cobalt were determined as sulphates together. Lead was estimated as sulphate by treatment of the compound with dilute sulphuric acid (Found: Co, 12·1; Pb, 42·6; CO_2, 35·1; H_2O, 7·5; O, 1·4. $Pb_2[Co_2O(C_2O_4)_4],4H_2O$ requires Co, 12·1; Pb, 42·6; CO_2, 36·2; H_2O, 7·4; O, 1·6%).

Silver Cobalt Oxy-oxalate.—To a solution of the potassium salt (4 g.) in water (300 c.c.), silver nitrate solution (4 g. in 20 c.c.) was added. The precipitate consisted of two forms, the one dark green and crystalline, and the other light green and flocculent. These were separated, washed, and dried in the usual way.

Analysis. Silver was estimated as chloride after solution of the compound in dilute nitric acid. After removal of the silver, cobalt was precipitated as sulphide in the presence of ammonium acetate and weighed as sulphate. The other constituents were determined as before. Both the amorphous and the crystalline sample had the same composition (Found: Co, 11·5; Ag, 41·9; H_2O, 10·2; CO_2, 33·4; O, 1·6. $Ag_4[Co_2O(C_2O_4)_4],6H_2O$ requires Co, 11·5; Ag, 42·0; H_2O, 10·5; CO_2, 34·3; O, 1·6%).

The general properties of all these compounds prepared by double decomposition are similar. When suspended in water and heated to about 70° they are decomposed, giving a brown precipitate. They are also decomposed by mineral acids and acetic acid, forming a pink solution, and by sodium hydroxide, giving a brown precipitate.

Potassium Cobalt Oxy-malonate.—Potassium cobaltous malonate, $K_2Co(C_3H_2O_4)_2,6H_2O$, was prepared thus: To a solution of malonic acid (100 g.) in water (200 c.c.) potassium carbonate (66 g.) was added slowly, followed by cobalt carbonate (53 g.) with heating and stirring. The mixture was boiled and filtered hot, and the fine red crystals which separated on cooling were washed with water and dried. Further crops were recovered from the mother-liquor.

To potassium cobaltous malonate (10g.) dissolved in water (30 c.c.), "hyperol" (hydrogen peroxide–urea containing 35% of H_2O_2; 12 g.) was added slowly in the cold, and the mixture gently warmed to 40°. A vigorous reaction took place, and the flask was immediately cooled. The cold green solution thus obtained was poured into a mixture of ether (300 c.c.) and alcohol (100 c.c.), and the green layer well stirred. The supernatant colourless alcohol–ether mixture was removed, and alcohol (100 c.c.) then added. This caused the separation of a green solid, which was washed with alcohol (95%) to remove urea and dried in a vacuum over calcium chloride and phosphoric oxide.

Analysis. The method employed was as described for the oxy-oxalate (Found : Co, 14·6; K, 19·4; CO_2, 54·2; H_2O, 22·6; O, 0·5. $K_4[Co_2O(C_3H_2O_4)_4],6H_2O$ requires Co, 14·6; K, 19·4; CO_2, 54·6; H_2O, 22·3; O, 2·0%). It is seen that the percentage of oxygen calculated from the amount of iodine liberated from potassium iodide in acid solution is low. It is suggested that the oxygen of the oxy-salt oxidises the carbon atom carrying the two labile hydrogen atoms of the malonic acid residue.

The oxy-malonate is much more soluble than the corresponding oxy-oxalate. It is sage-green and gives an olive-green aqueous solution which is more readily decomposed on warming than the oxy-oxalate solution. Even on standing, the aqueous solution decomposes in a few hours. The green colour is discharged by acids, carbon dioxide being evolved and a pink solution produced. A brown precipitate is formed on the addition of sodium hydroxide.

Attempts to prepare other metallic derivatives by double decomposition failed because of the instability of this solution of potassium cobalt oxy-malonate.

Physicochemical Measurements.

Cryoscopic determinations of apparent molecular weights were made in aqueous solution. In the data below, C is the concentration of the substance (g./100 g. of water), M_i the apparent molecular weight, and i the osmotic factor.

	Potassium cobalt oxy-oxalate.			*Potassium cobalt oxy-malonate.*				
C	0·510	0·634	0·781	2·129	4·300	4·730	5·810	6·793
M_i	158	159	162	128	133	148	139	150
i	4·5	4·5	4·4	6·3	6·1	5·4	5·8	5·4

Molecular conductivities.

Potassium cobalt oxy-oxalate at 25°.

v (litres/mol.) ……	43·9	87·8	178·4	702·4	1427·2
μ ……………………	302	337	359	386	385

Potassium cobalt oxy-malonate at 0°.

v (litres/mol.) ……	20·4	28·4	40·8	56·8	81·6
μ ……………………	153	166	186	193	199
v (litres/mol.) ……	113·6	227·2	454·4	908·8	1817
μ ……………………	215	227	243	241	246

Discussion of Results.—Since the osmotic factor for the oxy-oxalate is between 4 and 5, it appears that the complex splits up into 5 ions, in agreement with the present conception of its structure. The molecular-weight data for the oxy-malonate, however, appear to indicate that some decomposition occurs even at 0°.

The values for the molecular conductivity are low in both cases, as would be expected from the presence of a heavy complex anion.

Although, as already mentioned, a number of organic acids yield green solutions under the same conditions as do oxalic and malonic acids, nevertheless the isolation of pure complex salts from such solutions is a matter of great difficulty owing to the instability of the oxidised products. Moreover, the insolubility of the alkali cobaltous salts, in other cases, renders the experimental methods here described unsatisfactory for the preparation of the complex oxy-salts.

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