CLXXII.—*Green Compounds of Cobalt produced by Oxidising Agents.*

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IN 1862, F. Field (*Quart. Journ. Chem. Soc.*, **14**, 51) discovered that "when nitrate of cobalt is added to a solution of bicarbonate of soda containing a small quantity of the hypochlorite of that alkali, an intense and beautiful green colour is produced, and no elimination of carbonic acid results."

Many years later, F. Kehrman (*Ber.*, 1886, **19**, 3101) obtained crystallised potassium cobaltic oxalate, $\text{Co}_2\text{K}_6(\text{C}_2\text{O}_4)_6 \cdot 6\text{H}_2\text{O}$, by slow atmospheric oxidation of cobaltous hydroxide mixed with certain proportions of potassium oxalate, oxalic acid, and water. This substance exhibits dark blue and green dichroism.

Gibson (*Proc. Roy. Soc. Edin.*, 1890, **17**, 56) showed that a green colour is produced by bromine in presence of sodium carbonate, as well as by hypochlorites.

H. Marshall (*Trans.*, 1891, **59**, 760) obtained Kehrman's potassium cobaltic oxalate by electrolysis, and similarly the ammonium compound, $\text{Co}_2(\text{NH}_4)_6(\text{C}_2\text{O}_4)_6 \cdot 6\text{H}_2\text{O}$, in the form of very dark dichroic prisms which dissolve readily in water, giving a green solution. Marshall also prepared cobaltic sulphate, $\text{Co}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, and cobalt alum in the form of dark blue octahedrons.

The author (*Proc.*, 1896, **12**, 96) obtained a green solution by the action of hydrogen peroxide on solutions of cobalt salts in presence of excess of alkali hydrogen carbonates, and expressed a belief that an acid, H_2CoO_4 , was present. Later in the same year (*Proc.*, **12**, 244), green solutions and a green precipitate were obtained by the use of various oxidising agents in the presence of bicarbonates. From these further experiments, the green solutions were regarded as containing cobaltic carbonate, $\text{Co}_2(\text{CO}_3)_3$, whilst the precipitate was regarded as being possibly the carbonate itself, and it appeared to be fairly stable in an atmosphere of carbon dioxide.

The following year, A. H. McConnell and E. S. Hanes (*Trans.*, 1897, **71**, 584) published a paper in which they claimed to prove that these green solutions contain cobaltites of the alkali metals, where CoO_2 takes the place of MnO_2 in the manganites. The evidence adduced in favour of this hypothesis appears to rest on results giving the atomic proportions $\text{K} : \text{Co} :: 2 : 1$, and on the circumstance that an acid reaction was obtained with a colourless filtrate from a mixture of cobaltous hydroxide and hydrogen peroxide. This colourless solution

they regarded as containing cobaltous acid, H_2CoO_3 , but they were unable to isolate the dioxide, and did not determine the ratio of oxygen to metal.

In 1900, André Job (*Ann. Chim. Phys.*, [vii], 20, 214) determined, by a volumetric method, the ratio of cobalt to oxygen in the green bicarbonate solution, and estimated the cobalt by electrolytic deposition of the metal. The atomic ratio $\text{Co}:\text{O}$ was 2:3, that is, $2\text{CoO} + \text{O} = \text{Co}_2\text{O}_3$.

The action of neutral hydrogen peroxide on cobalt salts in the presence of alkali hydrogen carbonate determines an evolution of carbon dioxide, each atom of oxygen, in oxidising two atoms of cobalt, disengaging two molecule of carbon dioxide.

EXPERIMENTAL.

(a) *The Green Bicarbonate Solutions.*

The following experiments were made in 1897 to obtain additional evidence as to the state of oxidation of the cobalt in these green solutions.

Solutions containing respectively one-tenth of a gram-molecule of cobalt nitrate and sulphate were mixed with potassium hydrogen carbonate and excess of hydrogen peroxide heated at 70° or 80° to remove excess of peroxide, cooled, and treated with potassium iodide and sufficient hydrochloric acid to decompose the carbonate. The iodine thus liberated was estimated.

{	i. 10 c.c. of $M/10 \text{ Co}(\text{NO}_3)_2$ finally required 19.2 c.c. of $N/10$ thiosulphate.	
	ii. 10 c.c. of $M/10 \text{ Co}(\text{NO}_3)_2$ finally required 19.5 c.c. of $N/10$ thiosulphate.	
	iii. 5 c.c. of $M/10 \text{ CoSO}_4$ finally required 20.5 c.c. of $N/20$ thiosulphate.	
	iv. 5 c.c. of $M/10 \text{ CoSO}_4$ finally required 19.3 c.c. of $N/20$ thiosulphate.	
	v. 5 c.c. of $M/10 \text{ CoSO}_4$ finally required 21.0 c.c. of $N/20$ thiosulphate.	
	Mean result	19.9 c.c.
	Theory for Co_2O_3 would require	20.0 c.c.

Later experiments with freshly prepared thiosulphate solution fully confirmed the above results, as also did other investigations with $M/100$ hydrogen peroxide, in which it was found that the necessary amount of the peroxide required to dissolve completely the finely-divided cobaltous carbonate precipitate (not quite dissolved by excess

of potassium hydrogen carbonate), thereby forming the green solution, was just over that required for the reaction

The author has attempted to repeat the experiments cited by McConnell and Hanes (*loc. cit.*), more particularly with the object of obtaining the colourless acid solution supposed to contain H_2CoO_3 ; but it was found that, except when commercial acid hydrogen peroxide was used, no acid filtrate could be obtained.

Pure, moist, pink cobaltous hydroxide, precipitated by caustic potash, was prepared in an atmosphere of hydrogen and repeatedly washed in that atmosphere until the filtrate gave no trace of any potassium compound. This filtrate continued to give an alkaline reaction owing to a slight solubility of cobaltous hydroxide in water. Commercial hydrogen peroxide, carefully neutralised by barium hydroxide, was added to the pink hydroxide, which was thereby oxidised and changed to an olive-brown colour. The filtrate from this brown substance still remained alkaline. It gave a green colour with potassium hydrogen carbonate, owing to the action of the bicarbonate on the mixture of dissolved cobaltous and cobaltic hydroxides in presence of the hydrogen peroxide which had passed into the filtrate.

(b) *Green Acetate Solutions.*

The green colour obtained by McConnell and Hanes, due to the action of hydrogen peroxide on cobaltous hydroxide in presence of potassium acetate, was subsequently obtained by the author. The absorption spectrum of this solution differs essentially from that of the bicarbonate solution—a fact which is inconsistent with their statement that this also is “a green solution of potassium cobaltite.”

Green acetate solutions were obtained :

- i. By the action of sodium hypochlorite on a mixture of cobalt chloride, glycerine, and excess of sodium acetate.
- ii. By the action of hydrogen peroxide on cobalt sulphate in large excess of very concentrated potassium acetate.
- iii. By the action of acetic acid on the bicarbonate green.

Owing to the comparative instability of these green solutions, quantitative examination was difficult and the results obtained were inconclusive.

(c) *Green Tartrate Solutions.*

A fairly permanent green solution, of rather a yellower tint than that of the bicarbonate green, is obtained in concentrated solutions of sodium tartrate, providing that some alkali hydroxide is present. Any

cobalt salt with sodium hypochlorite, bromine, or hydrogen peroxide may be used.

Although a great many experiments were made with these solutions, the exact nature of the product was not determined definitely. It appeared, however, probable from the following result that the cobalt is also in this instance in the cobaltic state. Using in each case a mixture of 5 c.c. of $M/10$ cobalt sulphate, 20 c.c. of concentrated aqueous sodium tartrate, and 2.5 c.c. of $\frac{4}{5}M$ potassium hydroxide, placed in three Nessler jars, it was found that $M/10$ hydrogen peroxide produced a green colour without evolution of oxygen.

i. 2 c.c. of $M/10$ hydrogen peroxide gave a yellowish-green tint which became browner after a few hours.

ii. 2.5 c.c. of $M/10$ hydrogen peroxide gave a green solution.

iii. 3.5 c.c. of $M/10$ hydrogen peroxide gave a similar green solution.

These two solutions (ii and iii) remained green for several hours and were greenish-brown after three days.

The hydrogen peroxide in ii was in proportion for the reaction $2\text{CoO} + \text{O} = \text{Co}_2\text{O}_3$, and the further addition in iii did not appear to make any further change in colour or stability.

(d) *Green Citrate Solutions.*

An alkaline solution of potassium citrate gave green solutions with hydrogen peroxide and cobalt sulphate—the more concentrated the citrate the deeper the green coloration. In very concentrated solutions, sodium hypochlorite furnished a good green colour, but bromine water only gave yellow tints.

(e) *Green Oxalate Solutions and the Green, Crystalline Potassium Cobaltic Oxalate.*

Potassium oxalate precipitates cobaltous oxalate from solutions and, if concentrated, redissolves the precipitate to form the deep red solution of the double oxalate, or cobaltous oxalate may be dissolved in excess of potassium oxalate to form the red solution.

In either case, the addition of hydrogen peroxide brings about a reaction which gradually causes a rise in temperature, an evolution of oxygen, and the formation of an intense bluish-green solution. If sufficiently concentrated, a green, crystalline precipitate forms either at once or on cooling.

Preparation of Green Potassium Cobaltic Oxalate Crystals.

One hundred c.c. of potassium oxalate solution (saturated at 15°) are gently warmed and cobalt oxalate powder is gradually added, with constant stirring, until the boiling solution will dissolve no more. After filtration, an additional 50 c.c. of the saturated potassium oxalate are added, the temperature is raised to 65°, and 50 c.c. of "20 volume" hydrogen peroxide are then introduced from a burette, the liquid being stirred throughout the experiment. On allowing to cool, the green, microcrystalline precipitate soon begins to form.

Considerable care was taken in ensuring the comparative purity of the crystals, and the following results were obtained on analysis. Firstly, weighed portions of the salt were strongly ignited, roasted in air, and the residue weighed. This residue consisted of potassium carbonate and the oxide Co_3O_4 .

	Gram of crystals.	K_2CO_3 and Co_3O_4 .	Per cent.
Crop (a)	i. 0.3665	0.2296	62.64
	ii. 0.2415	0.1512	62.61
Crop (b)	iii. 0.4532	0.2822	62.26
	iv. 0.8223	0.5123	62.30
From crop (b) 2 months later... }	v. 0.5482	0.3416	62.31
	vi. 0.5801	0.3615	62.31

From the residue of (a), i, after dissolving out the alkali carbonate, K_2CO_3 , the percentage of potassium was found to be 22.87, whilst that of cobalt was 16.26.

From the residue of (a), ii, by converting both the carbonate and oxide into the sulphates K_2SO_4 and CoSO_4 , and calculating by the simultaneous equation involved, the percentages were potassium = 22.43 and cobalt = 17.16. Whence the average percentage from crop (a) was potassium = 22.65, cobalt = 16.71. Including these and further experiments :

	Potassium.	Cobalt.	CO_2 (combustion).	H_2O (combustion).
For 100 grams of the crystals..... {	22.87	16.26	38.12	10.28
	22.43	17.16	38.43	10.55
	22.30	16.67		
Mean values from experiment..... }	22.53	16.63	38.27	10.41

Calculated values

for i, $[\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2, 2\text{H}_2\text{O}]_2\text{O}$:

$\text{K} = 21.87$; $\text{CO} = 16.43$; $\text{CO}_2 = 37.01$; $\text{H}_2\text{O} = 10.10$ per cent.

for ii, $[\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2, 2\text{H}_2\text{O}]_n$:

$\text{K} = 22.37$; $\text{CO} = 16.81$; $\text{CO}_2 = 37.86$; $\text{H}_2\text{O} = 10.32$ per cent

These results are also in keeping with the spectroscopic observations of various cobalt greens. These showed marked differences in their absorption bands, thereby indicating different associations of the cobalt

in the various complex ions. A deposit of oxidised cobalt on the anode, when a solution of these crystals is electrolysed, also points to the same conclusion.

Properties of the Potassium Cobaltic Oxalate Crystals.

The crystals were examined under the microscope and tracings were made with the aid of the camera lucida. They are rhombs, of the rhombohedral system, with an acute angle of 42° . The ammonium compound crystallises in rhombic prisms.

The solubility in water was determined

at	12.5°	13.5°	14.4°	17.5°
Solubilities :	5.65	6.04	6.47	7.8 in 1000 H_2O .

The solubility curve is practically a straight line.

The crystals appear to be practically insoluble in a strong solution of potassium oxalate, differing in this respect from the red crystals, $K_2Co(C_2O_4)_2 \cdot 6H_2O$, which are very soluble.

Action of Acids.—Mineral acids gradually change their colour to pink, but the crystals remain unchanged for years in glacial acetic acid. Aqueous acetic acid slowly effects a decomposition.

Action of Ammonium Oxalate.—Warm saturated ammonium oxalate solution dissolves the crystals forming a dark green solution, from which the ammonium compound crystallises out in green, rhombic prisms.

Action of Calcium Chloride.—A solution of this salt gives no precipitate of calcium oxalate when added to a dilute solution of potassium cobaltic oxalate; if added to a saturated solution, a green, crystalline precipitate forms which under the microscope shows very long prisms. This substance is completely decomposed at 100° , whereas the potassium compound is hardly affected at this temperature.

0.3157 gram, from the calcium compound thus decomposed, gave on analysis a ratio of calcium to cobalt = $Ca_5 : Co_6$. Probably the true ratio is $Ca_1 : Co_1$, the substance being a calcium cobaltic oxalate.

The potassium cobaltic oxalate itself is very permanent, and if mixed with glycerine may be used as a pigment; when applied to paper, the colour lasts for years. When dissolved in water, however, the solution slowly deposits a brown precipitate.

Ammonium Cobaltic Oxalate.

If crystals of ammonium oxalate mixed with cobaltous oxalate are warmed with water, insufficient in quantity to dissolve all the former salt, and the resulting clear red liquid is treated, while still warm (about 45°), with hydrogen peroxide, a reaction suddenly occurs

after about a minute, and the solution becomes dark green, but no crystals are deposited on cooling. If now absolute alcohol is added (2 vols. of the solution to 1 vol. of alcohol), a light green precipitate, consisting chiefly of ammonium oxalate, is produced. The green filtrate from this does not yield a further precipitate on treatment with alcohol. A portion of this filtrate was allowed to evaporate on a glass slide, when transparent, green, rhombic prisms appeared under the microscope, quite similar to those which had previously been prepared by the action of ammonium oxalate on the solution of the green potassium compound. It is therefore highly probable that these crystals consist of ammonium cobaltic oxalate,

(f) *Other Green Carboxylic Compounds of Cobalt.*

By treating potassium lactate, malate, succinate, and glycollate with oxidising agents (hydrogen peroxide and sodium hypochlorite being employed), deep green solutions, and in the case of potassium glycollate green, needle-shaped crystals, were obtained.

Spectroscopic Examination of Various Cobalt Solutions.

A two-prism mounted spectroscope with brass circular scale was calibrated for wave-lengths by mapping 18 different lines of well-known wave-length as seen through the instrument. Dr. A. C. Jones kindly undertook this calibration.

The observations were largely made by limelight, and the solutions placed in plate glass tanks. The values given for the breadth of bands were arrived at as the mean of several observations.

The numerical values can only be regarded as approximate owing to the following circumstances: (i) to the indistinctness of some of the band boundaries, (ii) to the varying depth of colour in the solutions, (iii) to the calibration being probably only approximately correct.

The more important results arrived at are as follows:

(i) The absorption band for red solutions of nitrate, chloride, sulphate, citrate, and formate of cobalt was practically identical, the mean centre of the absorption being $\lambda = 5020$. This single band (in the dilutions employed) extended from about 6040 to 5060, cutting out most of the green and blue.

(ii) In cobaltous acetate (of similar depth of tint), more green and more blue was cut off. The mean centre gave $\lambda = 5035$.

(iii) Addition of concentrated potassium acetate to No. ii produces a purple-blue solution and shifts the dark band toward the red end

just past the *D* line, so that all the green is absorbed, whilst the band now extends only to the *F* line. Mean centre gave $\lambda = 5400$.

(iv) The *acetate green*, obtained by adding sodium hypochlorite to cobalt chloride in concentrated potassium acetate, is much yellower than most of the greens.

The apparent mean centre of the bright band gave $\lambda = 5900$ close to the *D* line. The green boundary was fairly distinct, just including the thallium line. The other boundary faded gradually into the red, disappearing short of the *C* line.

(v) The purplish-red solution obtained by dissolving cobalt carbonate in excess of potassium hydrogen carbonate gives a dark absorption band fairly distinct toward the red end, but much less so toward the violet. It appeared more extended than that of No. iii on both sides, the red boundary being about $\lambda = 6070$.

(vi) The *bicarbonate green*, obtained by adding hydrogen peroxide to the solution of No. v, practically reverses the spectrum. A bright green band appears, not quite reaching the *D* line on the red side or the *F* line on the other. The centre of this band (mean of five experiments) gave $\lambda = 5365$ near the thallium line.

(vii) The purple liquid obtained by dissolving cobaltous oxalate in excess of potassium oxalate gave a shorter and sharper absorption band than did the purple acetate or purple bicarbonate solutions, the mean centre being $\lambda = 5183$ considerably nearer the violet end than was the case with the other two.

(viii) The corresponding ammonium cobaltous oxalate gave a very similar spectrum. The centre of the dark band ($\lambda = 5160$) appeared slightly nearer still to the violet end.

(ix) The *green oxalate solution*, obtained by adding hydrogen peroxide to No. vii, revealed a feature not previously observed in other green cobaltic solutions, namely, two bright bands—one in the red, the other in the green.

The green band is very sharply marked and almost exactly reverses the absorption band of No. vii; its centre (mean of seven experiments) gave the same value, $\lambda = 5183$. The bright red band, less sharply bounded, gave a mean centre (seven experiments) $\lambda = 6595$.

(x) The green solution, obtained by dissolving potassium cobaltic oxalate crystals in water, gave a very similar spectrum to No. ix, being rather shorter for the bright green band and longer for the red. The mean centre for green was $\lambda = 5150$, that for red being $\lambda = 6615$, each of these being the average value for three experiments.

Other green solutions examined were the glycollate green, which resembled the oxalate green in having a bright red, as well as a bright green band. The centre of both bands appeared to be nearer the red end of the spectrum.

The tartrate green showed a faint, short absorption band dividing the bright red from the bright green bands; the centre of the green band was still nearer to the red end of the spectrum.

The lactate green and the succinate green also gave two bands each. In the latter case, the centre of the green band appeared to be nearer the violet end than is the case with the oxalate green.

Conclusions.

(1) Cobaltous oxide and salts in the presence of carboxylic salts first form double salts of the carboxylic acid; then, on oxidation, green compounds are formed, the stability of which is increased by presence of excess of alkali salt.

In the case of oxalates (and the rest), the presence of the complex $\text{>Co}\cdot\text{O}\cdot\text{Co}<$ appears highly probable, for, in the case of the bicarbonates, Job (*loc. cit.*) has shown that two molecules of carbon dioxide are liberated for every two atoms of cobalt oxidised, whilst the author has shown that one molecule only of hydrogen peroxide is required to complete the oxidation.

These observations point to the reaction :

and suggest the structural formula :

A number of experiments (not cited) went to show that no similar green compound can be formed from normal alkali carbonates.

Gibson's green colour, obtained by the action of bromine water on sodium carbonate in presence of cobaltous salts, must have been due to formation of sodium hydrogen carbonate and subsequent oxidation :

(2) The green colour of these substances appears to be characteristic of cobaltic combination with salts of carboxylic acids, as opposed to other cobaltic compounds. This appears to depend on complex ions containing the nucleus $\text{>Co}\cdot\text{O}\cdot\text{Co}<$, which nucleus is neither present in Fischer's nitrite, $\text{K}_6\text{Co}_2(\text{NO}_2)_{12}$, nor in Kehrman's dichroic oxalate, $\text{K}_6\text{Co}_2(\text{O}_2\text{O}_4)_6, 6\text{H}_2\text{O}$.

(3) The differences in tint of green and in absorption spectra of the various compounds considered depend probably on the various association of carboxyl groups attached to the above nucleus.

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