Studies on the Synthesis of Metal Complexes. I. Synthesis of an Ammine-carbonato Series of Cobalt (III) Complexes*

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It has been well known that in the presence of alkali bicarbonates cobaltous salts such as chloride and sulfate give green coloration by the action of hydrogen peroxide on the aquous solution, and this reaction has been used for the iodometric or colorimetric determination of cobalt by several workers[1,2].

On the other hand, this reaction product has been regarded as tricarbonatocobalt (III) anion, $[Co(CO_3)_3]^{3-}$, from measurement of the absorption spectrum[2] or chemical analysis of a derivative with hexamminecobalt (III) cation, $[Co(NH_3)_6][Co(CO_3)_3]$[3].

The present study was first directed to the isolation of the complex salt and the determination of its chemical formula and then turned to the synthesis of cobalt (III) complexes belonging to an ammine-carbonato series. All the objects were attained with success.

Experimental

Synthesis—1) Potassium Tricarbonatocobaltate (III), $K_3[Co(CO_3)_3]\cdot 3H_2O$.—Twenty grams of $KHCO_3$ was mixed with 20 cc. of water and the mixture was cooled in an ice-bath. In a separate beaker 10 g. of $CoCl_2\cdot 6H_2O$ was dissolved in 10 cc. of water and 5 cc. of 30% H_2O_2 was added to this solution. This was added to the $KHCO_3$ solution drop by drop with stirring, allowing about an hour for the operation. The green solution obtained was quickly filtered by suction, and the clear filtrate was again cooled and kept in a dark place. When about 15 cc. of alcohol was added to the filtrate, crystals began to appear, but they were contaminated with bicarbonate. The precipitates, therefore, were filtered off and the filtrate was again kept in a dark place at nearly 0°C. Then a little more alcohol was added to the filtrate, and the solution was allowed to stand until the deposition of crystals ceased, which took more than half an hour. The crystals were collected on a glass filter, washed with alcohol and then by ether, and stored in a brown bottle. The yield was 13.5 g. The solid was soluble in water containing potassium bicarbonate, but suffered decomposition by pure water, yielding the hydrous oxide.

Some care had to be exercised in isolating this complex. If the addition of the $CoCl_2$-H_2O_2 mixture was too rapid it brought about precipitation of cobaltic hydroxide, while if too much alcohol was added, it caused co-precipitation of other salts such as potassium chloride.

2) Blue Variety of Potassium Dicarbonatodiamminecobaltate (III), Blue-$K[Co(NH_3)_2(CO_3)_2]$ H_2O.—To the clear green solution, prepared from $KHCO_3$ and CoCl-H_2O_2 mixture as described in 1), was added 5 g. of ammonium carbonate and the mixture was warmed on a water-bath until the green color of the solution changed into blue, which took about ten minutes. At the end of this period the vessel containing the warm solution was immediately dipped in the ice-bath in order to stop further progress of the reaction and to effect crystallization of the product. After the removal by filtration of the first crop of crystals another crop could be obtained from the residual solution by gradual addition of alcohol. These crops were collected together, recrystallized from water and washed with pure alcohol. Total yield, about 7 g.

3) Violet Variety of Potassium Dicarbonatodiamminecobaltate (III), Violet-$K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$.—The green solution containing 5 g. of ammonium carbonate was heated on the water-bath until the color of the solution turned into blue and finally violet. Then the solution was

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[1] H.A. Laitinen and L.W. Burdett, *Anal. Chem.*, 23, 1268 (1951).

[2] M. Mori and M. Shibata, *J. Chem. Soc. Japan*, 75, 1046 (1954).

[3] T.P. McCutcheon and W.J. Schuele, *J. Am. Chem. Soc.*, 75, 1845 (1953).

cooled rapidly and a large amount of alcohol was added to it, and the whole was allowed to stand for some time. The violet precipitate was collected and dissolved in a little cold water to remove impurities as residues, and then the complex sought for was reprecipitated from the solution by the addition of alcohol. After repeating this procedure, the product was washed with alcohol and ether in turn and finally dried in a vacuum desiccator over sulfuric acid. Thus about one gram of violet powder was obtained. The complex was hygroscopic and very readily soluble in water.

4) **Carbonatotetramminecobalt (III) Chloride, $[Co(NH_3)_4CO_3]Cl$.**—To the green solution were added 15 g. of ammonium carbonate and 30 cc. of conc. ammonia and the mixture was boiled on the water-bath until the color of the solution became blood-red. At the end of this heating the liquid was poured into an evaporating dish and concentrated to a small volume with the addition of a small amount of ammonium carbonate. On adding alcohol, the complex was precipitated, the yield being about 9 g.

5) **Hexamminecobalt (III) Chloride and Chloropentammine Cobalt (III) Chloride, $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$.**—Thirty grams of ammonium chloride, 40 cc. of conc. ammonia and 2 g. of active charcoal were introduced into the green solution and the mixture was boiled until its color became reddish-brown (about thirty minutes). In this case, a reflux condenser was used to avoid the escape of ammonia from the solution. After filtering and cooling, conc. hydrochloric acid was gradually added to the filtrate, until a yellow precipitate separated out. The purification of the product was effected by the usual method for this complex. Yield, about 4 g.

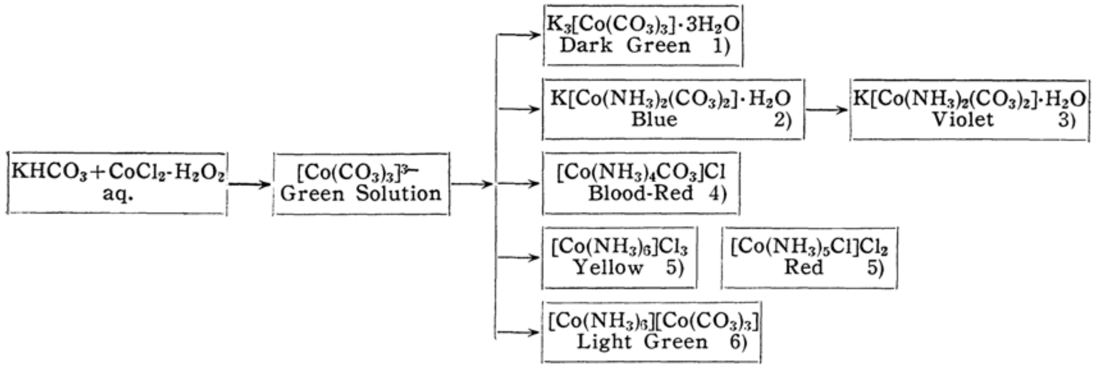
On evaporating the mother liquor, chloropentamminecobalt (III) chloride was obtained as a by-product.

6) **Hexamminecbalt (III) Tricarbonatocobaltate (III), $[Co(NH_3)_6][Co(CO_3)_3]$.**—This compound was quantitatively precipitated from the green solution by the addition of solid hexamminecobalt (III) chloride. The compound appeared as light-green powder. It was extremely insoluble in water, alcohol and acetone and was very stable against day-light.

All the complexes described above are shown in the accompanying flow sheet (Table I).

TABLE I

A FLOW SHEET OF SYNTHESIS OF AMMINE-CARBONATO Co(III) COMPLEXES



Analysis.—Determination of chemical formulas was carried out for the complexes obtained in 1), 2), 3) and 6). The other complexes were identified by their characteristic properties such as precipitation reaction and absorption spectrum.

Water of crystallization was determined from the loss of weight of the product at 100–130°C by means of a Shimazu Thermano Balance and the fact nothing but water of crystallization has been removed was confirmed by re-dissolving the dehydrated sample in water.

When the dehydrated sample was heated with gradual elevation of temperature up to 300°C, all of the ammonia molecules and part of the carbonate ions attached to the central cobalt atom were expelled from the sample, and the remainder consisted of potassium carbonate and an oxide of cobalt (perhaps, Co_2O_3). The reaction may be represented as follows:

$$2K_3[Co(CO_3)_3] \longrightarrow 3K_2CO_3 + Co_2O_3 + 3CO_2\uparrow$$

$$2K[Co(NH_3)_2(CO_3)_2] \longrightarrow K_2CO_3 + Co_2O_3 + 4NH_3\uparrow + 3CO_2\uparrow$$

$$[Co(NH_3)_6][Co(CO_3)_3] \longrightarrow Co_2O_3 + 6NH_3\uparrow + 3CO_2\uparrow$$

The quantity of ammonia and carbondioxide expelled was estimated from the observed loss of weight. The potassium carbonate was alkalimetrically estimated after the residue was extracted with hot water and the cobalt content was iodometrically determined after the oxide in the residue was dissolved with hot sulfuric acid.

To confirm the validity of the above methods, direct analysis of ammonia and carbondioxide was also carried out.

Absorption Spectra.—The absorption spectra of the above complexes in aqueous solution were measured with a Beckman Model DU Spectrophotometer using a cell 1.0 cm. in thickness.

Results and Discussion

The results of thermal decomposition are shown in Fig. 1 and all the numerical values

TABLE II

ANALYTICAL RESULTS

(amounts in %)

Complexes	H_2O		$CO_2+(NH_3)$		K_2CO_3		Co		CO_2*		NH_3*	
	calcd.	obs.	calcd.	obs.	calcd.	obs.	calcd.	obs.	calcd.	obs.	calcd.	obs.
$K_3[Co(CO_3)_3]\cdot 3H_2O$	13.5	13.2	16.1	15.5	50.4	45.0	14.4	14.9	44.6	46.9	—	—
Blue-$K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$	6.7	6.6	36.7	35.9	25.6	23.5	21.6	22.1	—	—	12.6	12.5
Violet-$K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$	6.7	6.5	36.7	36.0	25.6	23.5	21.6	20.6	—	—	12.6	13.8
$[Co(NH_3)_6][Co(CO_3)_3]$	—	—	58.5	58.0	—	—	29.5	28.0	—	—	—	—

* direct determination

TABLE III

ABSORPTION MAXIMA AND log ε

($10^{13}\cdot sec^{-1}$)

Complexes	ν_1	log ε_1	ν_2	log ε_2	ν_3	log ε_3
$K_3[Co(CO_3)_3]$	46.5	2.19	68.1	2.22	117.6	3.97
$K_3[Co(C_2O_4)_3]$	49.5	2.09	70.8	2.19	122.4	4.42
Blue-$K[Co(NH_3)_2(CO_3)_2]$	52.2	2.14	76.8	2.40	126.6	4.14
Violet-$K[Co(NH_3)_2(CO_3)_2]$	55.5	1.80	80.2	2.04	128.1	4.30
$NH_4[Co(NH_3)_2(C_2O_4)_2]$	54.0	1.95	82.4	2.10	129.3	3.24
Na[Coedta]	55.6	2.48	78.9	2.33	133.3	4.34

are given in Table II. These data seem to justify the assignment of such chemical formulae as $K_3[Co(CO_3)_3]\cdot 3H_2O$, blue- and violet-$K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$ and $[Co(NH_3)_6][CoCO_3)_3]$ to our compounds. Additional evidence of the validity of these formulae exists in the absorptiometric data (Fig. 2 and Table III). Thus, the absorption curve of $K_3[Co(CO_3)_3]$ is similar to that of $K_3[Co(C_2O_4)_3]$, and that of violet-$K[Co[NH_3)_2(CO_3)_2]$ to those of $NH_4[Co(NH_3)_2(C_2O_4)_2]$ and K[Coedta].

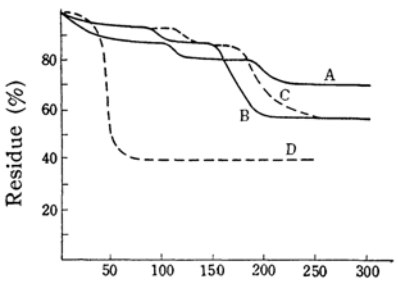


Fig. 1. Thermal decomposition of complexes at 100-300°C.

A. $K_3[Co(CO_3)_3]\cdot 3H_2O$
B. Blue-$K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$
C. Violet-$K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$
D. $[Co(NH_3)_6][Co(CO_3)_3]$

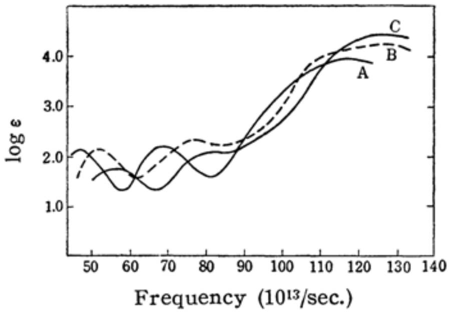


Fig. 2. Absorption spectra of:

A. $K_3[Co(CO_3)_3]$
B. Blue-$K[Co(NH_3)_2(CO_3)_2]$
C. Violet-$K[Co(NH_3)_2(CO_3)_2]$.

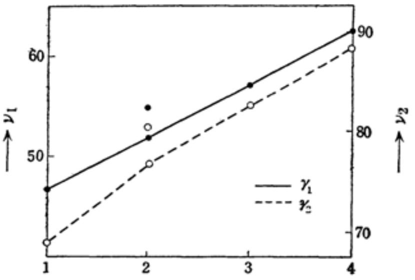


Fig. 3. Frequency positions of the ammine-carbonato Co(III) complexes.

1. $[Co(CO_3)_3]^{3-}$ 2. $[Co(NH_3)_2(CO_3)_2]^-$
3. $[Co(NH_3)_4CO_3]^+$ 4. $[Co(NH_3)_6]^{3+}$

$K_3[Co(CO_3)_3]\cdot 3H_2O$.—The exact formula for this complex had not been determined before. According to reference[1], Job assigned to it the formula K_3CoO_3, Durrant considered it to be $(KCO_2\text{-}O)_2\text{-}Co\text{-}O\text{-}Co\text{-}(O\text{-}O_2CK)_2$ and Duval called it cobalt (III) tricarbonatocobaltiate, $Co[Co(CO_3)_3]$. None of these formulas, however, correctly represents the constitution of the pure substances obtained by the present workers.

From the results of analysis and because of the absorption spectrum of this complex, it is reasonable to give it *tris*-structure. The difficulty of isolating this complex in the pure state will be appreciated by considering the fact that trioxalatocobaltate (III) easily decomposes in day-light. In order to draw a final conclusion, however, it is necessary to resolve the complex into the antipodes. In fact, attempts were carried out by using *l*-strychnine and *d*-*tris*-(ethylenediamine)-cobalt (III) ion. In both cases, green precipitates were fractionally obtained from the original solution of the complex. But, since decomposition of the complex took place during the process of removing the precipitants, the optical rotation of the fractionated complex was not measured. Further studies will be carried out.

Blue- and Violet-$K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$.—Now, it is important to determine the configuration of these stereoisomers. Provided that a bifunctional group such as carbonate ion can span only *cis*-positions and that no intramolecular change of configuration occurs during the reaction of ammonium salt on tricarbonatocobaltate, the blue compound formed at an earlier stage of the reaction must be *cis*-form, while violet one formed through blue complex is regarded as *trans*-form. Studies of the resolution of both complexes may shed light on this problem.

Absorption Spectra.—The frequency values for the first and second bands of a series of ammine-carbonato complexes are plotted in Fig. 3. From the diagram, it is seen that the values of the first band lie on a single line except for one of violet complex. On the other hand, such a linearity can not exist among the frequencies of the second band. It should be added that the violet complex has the absorption maximum at the same frequency as EDTA-Co (III) complex as indicated in Table III.

Synthesis.—Our methods in which green tris-cobaltate is used as starting material, have the advantage of simplicity. For example, carbonatotetramminecobalt (III) salt, which is useful for the synthesis of various complexes, is prepared by the successive substitution of carbonate ions with ammonia groups without atmospheric oxidation, and hexamminecobalt (III) salt is also prepared by further substitution in the presence of active charcoal. It has also been observed that the cobalt (III) complexes belonging to an ethylenediamine-carbonato series is synthesized in the same way, and this will be reported later.

Summary

A green compound is isolated from the concentrated solution obtained by the action of hydrogen peroxide on cobalt (II) ions in the presence of potassium bicarbonate, and the formula $K_3[Co(CO_3)_3]\cdot 3H_2O$ is assigned to it on the basis of the analysis of the solid and of the absorption spectrum of the solution.

A series of ammine-carbonatocobalt (III) complexes, $K_3[Co(CO_3)_3]\cdot 3H_2O$, blue (perhaps, *cis*)- and violet(perhaps, *trans*)-$K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$, $[Co(NH_3)_4CO_3]Cl$ and $[Co(NH_3)_6]Cl_3$, are synthesized from the abovementioned green solution by means of successive substitution of carbonate ions by ammonia groups. Hexamminecobalt (III) tricarbonatocobaltate, $[Co(NH_3)_6]$ $[Co(CO_3)_3]$, is also obtained by adding a hexamminecobalt (III) salt to the green solution of tricarbonato-complex. Three complexes, $K_3[Co(CO_3)_3]\cdot 3H_2O$ and blue- and violet-$K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$, are probably to be regarded as new complexes and may be identified by their absorption spectra.

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