Studies on the Synthesis of Metal Complexes. III. Synthesis of Ethylenediamine-carbonato, Ammine-oxalato and Ethylenediamine-oxalato Series of Cobalt(III) Complexes*

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In the preceding paper[1] of this series, a systematic method of synthesis for the ammine-carbonato series of cobalt(III) complexes was described. An important feature of the method was that it involved successive substitution of carbonate ions by ammonia groups. This method has now been extended to the synthesis of various complexes belonging to the ethylenediamine-carbonato, the ammine-oxalato and the ethylenediamine-oxalato series. All the attempts were successful; it is most interesting that a blue and a violet variety were found in every member of the present series, too. The two varieties are probably to be regarded as new complexes and also as stereoisomers.

Experimental

Synthesis.—1) *Starting material.*—Through all the procedures described below, a green cold solution of potassium tricarbonatocobaltate(III) was used as starting material. This was prepared from 20 g. of $KHCO_3$ and 10 g. of $CoCl_2 \cdot 6H_2O$—5 ml. of 30% H_2O_2 by the method described in the previous paper[1].

2) ***Blue variety of potassium dicarbonatoethylenediaminecobaltate*(*III*)**, Blue-$K[Co\,en(CO_3)_2] \cdot H_2O$.—To the green cold solution obtained in 1), was added 5 g. of ethylenediamine carbonate prepared by passing carbon dioxide into an aqueous solution of 70% ethylenediamine in the cold. The mixture was placed in an icebath until the green color of the solution changed into violetish blue within thirty minutes. When about 20 ml. absolute ethanol was added to the solution, crystals began to appear, but they were appreciably contaminated with other salts. The precipitates, therefore, were filtered off, another 50 ml. of ethanol was added to the filtrate and the solution was left for some time at nearly 0°C. The crystals were collected and purified by dissolving in as little cold water as possible and then by adding absolute ethanol. The product was washed with ethanol and ether in turn. Yield, about 4 g.

3) ***Violet variety of potassium dicarbonatoethylenediaminecobaltate*(*III*)**, Violet-$K[Co\,en(CO_3)_2] \cdot H_2O$.—After adding 5 g. of ethylenediamine carbonate to the starting material in the same manner as above, the mixture was allowed to stand at room temperature until a violet solution was obtained (about 20 min.). At the end of this period 20 ml. ethanol was added to the solution and then it was kept overnight in a refrigerator. After repeating reprecipitation three times in the same manner as in 2), the final precipitate was washed with ethanol and ether. Yield, about 6 g.

4) ***Carbonato-bis* (*ethylenediamine*) *cobalt* (*III*) *chloride***, $[Coen_2CO_3]Cl \cdot H_2O$.—This was prepared by adding 10 ml. ethylenediamine (70%) to the green solution, heating the mixture on a water bath until the color of the solution became reddish violet, and further continuing to heat the solution in an evaporating dish. After cooling, the crude product was collected and recrystallized from water by the usual procedure. Yield, about 11 g.

5) ***Tris* (*ethylenediamine*) *cobalt* (*III*) *chloride***, $[Co\,en_3]Cl_3 \cdot 3H_2O$.—Ethylenediamine (70%, 15 ml.), potassium chloride (3 g.) and active charcoal (1 g.) were introduced into the green solution,

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* Presented at the Symposium on Co-ordination Compounds, Tokyo, October 27, 1956. For previous paper in this series see M. Mori, M. Shibata, E. Kyuno and H. Nakajima, This Bulletin, 29, 887 (1956).

[1] M. Mori, M. Shibata, E. Kyuno and T. Adachi, This Bulletin, 29, 883 (1956).

TABLE I
THE FLOW CHART OF SYNTHESIS

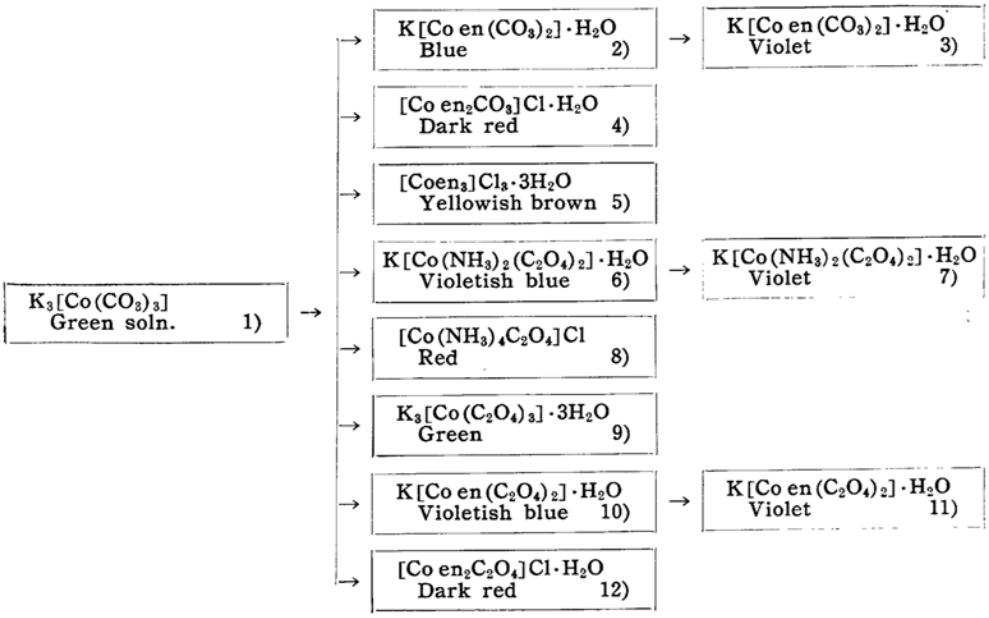

TABLE II
ANALYTICAL RESULTS (amounts in %)

	Co		N		K_2CO_3 or $K_2C_2O_4$		H_2O	
	calcd.	obsd.	calcd.	obsd.	calcd.	obsd.	calcd.	obsd.
Blue-K[Co en$(CO_3)_2$]·H_2O	19.9	19.8	9.5	9.5	23.3	24.5	6.1	5.9
Violet-K[Co en$(CO_3)_2$]·H_2O	19.9	19.6	9.5	9.4	23.3	24.6	6.1	6.2
Blue-K[Co$(NH_3)_2(C_2O_4)_2$]·H_2O	18.4	18.9	8.8	8.9	26.3	25.8	5.7	5.7
Violet-K[Co$(NH_3)_2(C_2O_4)_2$]·H_2O	18.4	18.1	8.8	8.8	26.3	26.5	5.7	5.8
Blue-K[Co en$(C_2O_4)_2$]·H_2O	16.7	16.8	7.7	7.8	23.6	23.4	5.1	5.1
Violet-K[Co en$(C_2O_4)_2$]·H_2O	16.7	16.2	7.7	7.6	23.6	25.6	5.1	5.2

and the mixture was heated on a water bath for about thirty minutes whereby the color of the solution changed into brownish yellow. After removal of the charcoal by filteration while hot, the filtrate was evaporated to about a half of the initial volume and then left to cool. The deposited crystals were washed with ethanol and dried in an oven. Yield, about 12 g.

6) *Blue variety of potassium dioxalatodiamminecobaltate (III)*, Blue-K[Co$(NH_3)_2(C_2O_4)_2$]·H_2O.—The green solution containing 10 g. of powdered ammonium oxalate was warmed on a water-bath at nearly 70°C. As soon as the solution became bluish, the vessel was dipped in an ice bath in order to stop further reaction. When the content was completely cooled, ethanol (50 ml.) was added to it and the whole was allowed to stand about an hour. The crude product was collected and reprecipitated from the cold solution by the addition of ethanol. After repeating this procedure twice, the final precipitate was washed with ethanol and ether in turn. Yield, about 7 g.

7) *Violet variety of potassium dioxalatodiamminecobaltate(III)*, Violet-K[Co$(NH_3)_2(C_2O_4)_2$]·H_2O.—The starting material, to which ammonium oxalate was added as described in the preceding paragraph, was allowed to remain on a water bath until the color turned blue and finally violet. After adding 80 ml. ethanol to the solution, it was kept overnight in a refrigerator. The violet precipitate was collected, dissolved in a small amount of cold water to remove impurities as residues, and then the complex reprecipitated by the addition of ethanol. After repetition of this procedure, the precipitate was washed with ethanol and then with ether. Yield, about 7 g.

8) *Oxalatotetramminecobalt(III) chloride*, [Co$(NH_3)_4C_2O_4$]Cl.—Powdered ammonium oxalate (5 g.) and concentrated aqueous ammonia solution (30 ml.) were added to the green solution and the mixture was warmed on a water bath at nearly 80°C with addition of ammonium chloride (in small portions, about 2 g. altogether), until the color of the mixture became pink. After cooling, about 10 ml. of ethanol was added to it

to precipitate all other salts; thereupon these were removed by filtration and another 20 ml. of ethanol was added in order to obtain the complex salt. Yield, about 6 g.

9) *Potassium trioxalatocobaltate(III)*, $K_3[Co(C_2O_4)_3]\cdot 3H_2O$.—To the cold green solution was added powdered oxalic acid (16 g.) little by little, whereby carbon dioxide was evolved and a bluish green solution was obtained. This was warmed on a water bath at nearly 60°C until no more carbon dioxide appeared. After cooling, the solution was acidified with dil. acetic acid and 50 ml. of ethanol was added to it. The product was purified as usual. Yield, about 12 g.

10) *Blue variety of potassium dioxalatoethylenediaminecobaltate(III)*, Blue-$K[Co\,en(C_2O_4)_2]\cdot H_2O$.—Potassium oxalate (5 g.) and ethylenediamine oxalate (5 g.) prepared by neutralizing 15 g. of ethylenediamine (70%) with 23 g. of powdered oxalic acid in the cold, were poured upon the cold green solution and the whole was left at room temperature until the color of the solution turned bluish violet, which took about half an hour. At the end of this period the solution was thoroughly cooled, and treated with a small amount of ethanol to remove foreign salts; the filtrate is further mixed with ethanol to precipitate the complex salt. The precipitate was purified from the cold solution by the addition of ethanol, and washed first with ethanol and then with ether. Yield, about 3 g.

11) *Violet variety of potassium dioxatatoethylenediaminecobaltate(III)*, Violet-$K[Co\,en(C_2O_4)_2]\cdot H_2O$.—This was synthesized in the same way as the blue variety, except for the mixture being heated for an hour instead of being left at room temperature. At the end of the reaction, the color of the solution changed completely to violet. Yield, about 7 g.

12) *Oxalato-bis (ethylenediamine) cobalt(III) chloride*, $[Co\,en_2(C_2O_4)]Cl\cdot H_2O$.—Oxalic acid (6 g.), potassium chloride (2 g.) and 70% ethylenediamine (16 ml.) were added to the green solution and the mixture was allowed to evaporate on a water bath until a crust was formed on the surface. After cooling, the crystals were filtered and washed with ethanol and ether in turn. Yield, about 10 g.

A flow chart of the synthesis of the above-mentioned complexes is given in Table I.

Determination of Chemical Formulae.—This was carried out for the six complexes obtained in 2), 3), 6), 7), 10) and 11), because they were thought to be new compounds. The results of thermal and chemical analysis and spectroscopic measurements were used for determining their chemical formulae in the same manner as that described in the previous paper[1]. Furthermore, coagulation values of ferric oxide sol by the complexes were measured in order to determine the valency of the complex ions. The measurements were carried out with the method used by S. Nakahara, K. Nakamoto and R. Tsuchida[2].

Results and Discussion

Analysis and Coagulation Value.—All the numerical values obtained from the chemical and the thermal analysis are given in Table II. These data seem to justify the assignment of such chemical formulae as are given in the experimental section.

Additional evidence for the validity of these formulae is afforded by the coagulation values given in Table III. Nakahara and co-workers have given 6.6 mF, 0.48 mF and 0.090 mF as the average values for uni-, bi- and tervalent complex anions respectively. In the present experiment, all of the complex species belonging to the blue variety showed coagulation values ranging from 6 mF to 7 mF, and they are consequently regarded as univalent anions. On the other hand, all the species belonging to the violet variety gave values about 3 mF, which are somewhat lower than the average value for a univalent ion, but far too high for a bivalent anion. These species may also be regarded as univalent anions provided that the deviation of their coagulation values from the average is attributed to partial liberation of the carbonate or the oxalate ion out of the complex radical by water molecules;

$$[Co\,en(CO_3)_2]^- + 2H_2O \rightleftarrows [Co\,en(H_2O)_2CO_3]^+ + CO_3^{--}$$

$$[Co(NH_3)_2(C_2O_4)_2]^- + 2H_2O \rightleftarrows [Co(NH_3)_2(H_2O)_2C_2O_4]^+ + C_2O_4^{--}$$

TABLE III

COAGULATION VALUES OF FERRIC OXIDE SOL

Blue-$K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$	ca. 6 mF
Violet-$K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$	ca. 3 〃
Blue-$K[Co\,en(CO_3)_2]\cdot H_2O$	ca. 6 〃
Violet-$K[Co\,en(CO_3)_2]\cdot H_2O$	ca. 3 〃
Blue-$K[Co(NH_3)_2(C_2O_4)_2]\cdot H_2O$	ca. 7 〃
Violet-$K[Co(NH_3)_2(C_2O_4)_2]\cdot H_2O$	ca. 3 〃
Blue-$K[Co\,en(C_2O_4)_2]\cdot H_2O$	ca. 7 〃
Violet-$K[Co\,en(C_2O_4)_2]\cdot H_2O$	ca. 3 〃

Absorption Spectra.—All the absorption data for newly synthesized complexes are given in Figs. 1 and 2 and Table IV together with those for previously synthesized potassium dicarbonatodiamminecobaltate(III).

Fig. 3 is a diagrammatic representation of the absorption maxima of the first band. It is seen from the figure that the frequencies for the blue variety increase in the order of NH_3-CO_3, en-CO_3, NH_3-ox and en-ox in an arithmetrical progression.

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[2] S. Nakahara, K. Nakamoto and R. Tsuchida, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi)*, **74**, 488 (1953).

TABLE IV

ABSORPTION MAXIMA AND log ε

(10^{13} sec.$^{-1}$)

	ν_1	log ε_1	ν_2	log ε_2	ν_3	log ε_3
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
Blue-K[Co en(CO$_3$)$_2$]	52.6	2.17	76.9	2.33	125.5	4.46
Violet-K[Co en(CO$_3$)$_2$]	54.9	1.94	77.3	2.31	129.8	4.29
Blue-K[Co(NH$_3$)$_2$(C$_2$O$_4$)$_2$]	53.1	2.09	79.4	2.35	129.3	4.56
Violet-K[Co(NH$_3$)$_2$(C$_2$O$_4$)$_2$]	55.3	2.08	79.3	2.58	130.4	4.06
Blue-K[Co en(C$_2$O$_4$)$_2$]	53.5	2.17	78.5	2.30	127.1	4.31
Violet-K[Co en(C$_2$O$_4$)$_2$]	54.7	1.98	77.9	2.10	129.8	3.98

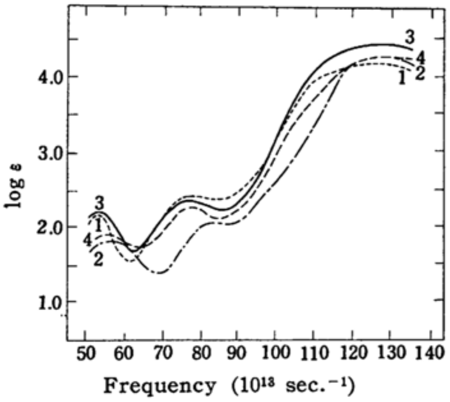

Fig. 1. Absorption spectra of:
1. Blue-K[Co(NH$_3$)$_2$(CO$_3$)$_2$]
2. Violet-K[Co(NH$_3$)$_2$(CO$_3$)$_2$]
3. Blue-K[Co en(CO$_3$)$_2$]
4. Violet-K[Co en(CO$_3$)$_2$]

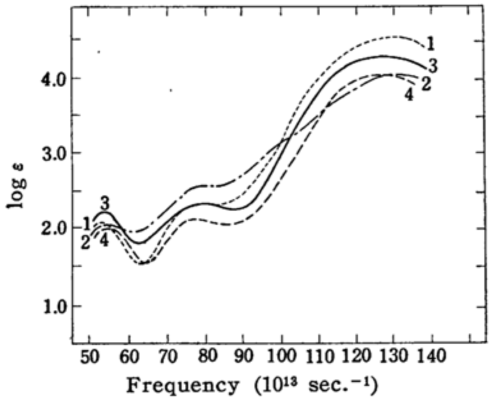

Fig. 2. Absorption spectra of:
1. Blue-K[Co(NH$_3$)$_2$(C$_2$O$_4$)$_2$]
2. Violet-K[Co(NH$_3$)$_2$(C$_2$O$_4$)$_2$]
3. Blue-K[Co en(C$_2$O$_4$)$_2$]
4. Violet-K[Co en(C$_2$O$_4$)$_2$]

(where, NH$_3$-CO$_3$ represents carbonatodiamminecobaltate(III) and so forth). These hypsochromic effects of the ligands may be explained by the familiar empirical rule that ethylenediamine is a more hypsochromic ligand than ammonia, and oxalate, than carbonate ion. On the other hand, the values for the violet variety increase in the order of en-ox, en-CO$_3$, NH$_3$-ox and NH$_3$-CO$_3$. In this case, the hypsochromic effects of the ligands are opposed to those predicted by the familiar rule.

The frequencies for the first and the second bands of the complexes belonging to each series are plotted in Figs. 4 and

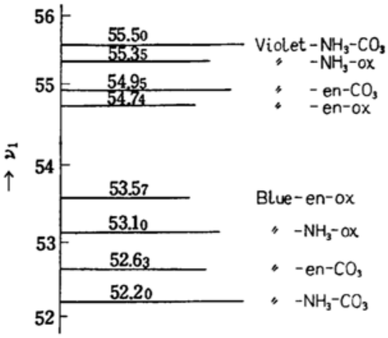

Fig. 3. Diagrammatic representation of absorption maxima.

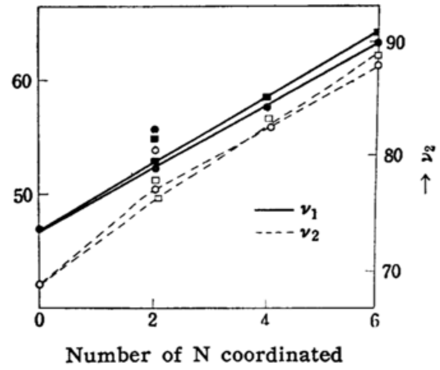

Fig. 4. Frequency position of the absorption bands of the complexes.

● ○ NH$_3$-CO$_3$ series

■ □ en-CO$_3$ series

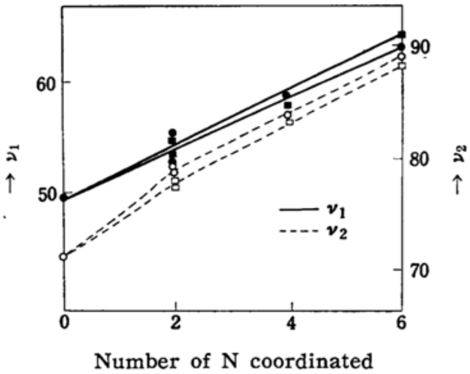

Fig. 5. Frequency position of the complexes.

●/○ NH$_3$-ox series

■/□ en-ox series

5, in the same manner as in the preceding paper[1)], and the result shows that the same relationship exists in the present case, too.

Configuration.—In the previous paper[1)] the authors assumed that the blue variety of K[Co(NH$_3$)$_2$(CO$_3$)$_2$]·H$_2$O to be the *cis* isomer and the violet one the *trans* isomer. The two varieties, blue and violet, of the complex salts obtained in the present experiment must also be regarded as stereoisomers because of 1) identity of the chemical composition, 2) equality of the valency and 3) similarity of the absorption spectra.

Assuming this to be true, the authors have attempted to find out which is *cis* and which *trans*. Y. Shimura[3)] has generalized that the first band of a *trans*-isomer of a [Co(NH$_3$)$_4$A$_2$]- or a [Co en$_2$A$_2$]-type ion (A=unidentate molecule or negative ion) has shorter or longer wave lengths than that of the corresponding *cis*-isomers according as A is ahead of or behind ammonia or ethylenediamine on the spectrochemical series. If such a generalization can be extended to our [CoX$_4$(NH$_3$)$_2$]- and [CoX$_4$ en]-type ions, the blue variety in question must be the *cis*-form and the violet variety, *trans*-form, since ethylenediamine or ammonia is ahead of the bidentate anions, carbonate and oxalate. But there is some doubt as to the legitimacy of such an extention.

There is an additional evidence; it was qualitatively observed that elution of the violet variety from the anion-exchanger column (Cl-form) was faster than that of the corresponding blue variety. The authors have already reported that the *trans*-form of [Co(NH$_3$)$_4$X$_2$]$^+$ or [Co en$_2$X$_2$]$^+$ is eluted more rapidly than the corresponding *cis*-form, and the stronger affinity of the *cis*-form to the cation exchanger may be attributed to the dipole moment resulting from the existence of acid groups in the *cis*-position[4)]. Provided that the same holds in the above case, the blue variety is to be regarded as *cis*-form and the violet one, *trans*-form.

Apart from the adequacy of the above discussion on the assignment of configuration, it is natural that the diammine-type ions should exist in the *cis*- and the *trans*-form. On the other hand, it seems unreasonable to suppose the corresponding (mono) ethylenediamine-type ions exist in both forms, because it is generally agreed that an ethylenediamine is sterically incapable of spanning *trans*-positions in an octahedron. The existence of stereoisomers, however, seems invulnerable at the present stage of investigation. Consequently, further studies must be carried out to solve this problem.

Summary

Three series of cobalt(III) complexes were systematically synthesized from the green solution of potassium tricarbonatocobaltate(III) by means of successive substitution of carbonate by other groups:

i) Blue-K[Co en(CO$_3$)$_2$]·H$_2$O,
Violet-K[Co en(CO$_3$)$_2$]·H$_2$O,
[Co en$_2$CO$_3$]Cl·H$_2$O, [Co en$_3$]Cl$_3$·3H$_2$O

ii) Blue-K[Co(NH$_3$)$_2$(C$_2$O$_4$)$_2$]·H$_2$O,
Violet-K[Co(NH$_3$)$_2$(C$_2$O$_4$)$_2$]·H$_2$O,
[Co(NH$_3$)$_4$C$_2$O$_4$]Cl,
K$_3$[Co(C$_2$O$_4$)$_3$]·3H$_2$O

iii) Blue-K[Co en(C$_2$O$_4$)$_2$]·H$_2$O,
Violet-K[Co en(C$_2$O$_4$)$_2$]·H$_2$O,
[Co en$_2$(C$_2$O$_4$)]Cl·H$_2$O.

Of these, the blue and the violet varieties are probably to be regarded as new complexes, stereoisomeric with each other.

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3) Y. Shimura, This Bulletin, **25**, 49 (1952).

4) M. Mori, M. Shibata and M. Nanasawa, ibid., **29**, 947 (1956).