The Cobalt(III) Complexes of Ethylenediaminediacetic and Ammoniadiacetic Acids[1]

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In previous papers[2] of this series, some methods of preparation of the cobalt(III) complexes of ethylenediaminetetracetic acid and ammoniatriacetic acid were reported. The present paper is to report preparation of the cobalt(III) complexes of ethylenediaminediacetic and ammoniadiacetic acids. Since ethylenediaminediacetate ion commonly acts as a quadridentate ligand, the participation of its one molecule in the bonding to a cobalt(III) ion would be expected to be most regular. On the other hand, ammoniadiacetate ion usually acts as a tridentate ligand, and consequently the participation of the two molecules would seem most possible. Both of these possibilities are realized in this research.

Experimental

Chelating Agent. — Ethylenediaminediacetic acid (EDDA) was prepared by the action of monochloracetic acid on ethylenediamine. A solution of 10 g. monochloracetic acid in 10 ml. water was carefully neutralized with 17 g. of sodium bicarbonate, and then 7.5 g. of ethylenediamine (85%) was added to the solution. This was allowed to warm at about 50°C and a solution of 8 g. sodium hydroxide in 10 ml. water was added to it. After standing for few minutes, the solution was acidified with 6 N hydrochloric acid and then evaporated in vacuo, whereby some sodium chloride separated out. After the removal of the salt by filtration, two or three volumes of ethanol were added to the filtrate and the mixture kept in a refrigerator until white precipitates appeared. These were recrystallized from water. The nitrogen analysis and the potentomietric titration of this material gave satisfactory results for the desired ethylenediaminediacetic acid. Ammoniadiacetic acid (ADA) was provided by the Dojin Institute of Pharmaceutical Chemistry through the courtesy of Dr. K. Ueno.

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[1] Part VI : On the Syntheses of Metal Complexes. Previous paper on this series : V.: M. Mori, M. Shibata, E. Kyuno and M. Kanaya, This Bulletin, **34**, 1837 (1961). Presented at the 12th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1959.

[2] M. Mori, M. Shibata, E. Kyuno and H. Nakajima, This Bulletin, **29**, 887 (1956) ; M. Mori, M. Shibata, E. Kyuno and Y. Okubo, ibid., **31**, 940 (1958).

Preparation. — *1) Potassium Bisammoniadiacetatocobaltate(III),* $K[Co(ada)_2]\cdot 4H_2O$*.— About 2 g. of ADA was suspended in 5 ml. of water, and the solution was neutralized with 2 g. of potassium bicarbonate. To this solution were added a solution of 2 g. $CoCl_2\cdot 6H_2O$ in a little water and 2 ml. of hydrogen peroxide (10%), and the mixture was warmed on a water bath to nearly 40°C, whereupon the color of the solution became red-violet. By cooling this solution in a refrigerator, red-violet crystals of the desired complex were obtained. Yield, about 0.5 g.

Found: Co, 14.7; N, 6.5. Calcd. for $K[Co(ada)_2]\cdot 4H_2O$: Co, 14.6; N, 6.49%.

2) Potassium Carbonatoethylenediaminediacetatocobaltate(III), $K[Co(edda)(CO_3)]\cdot H_2O$**. — To a solution of the potassium tricarbonatocobaltate prepared by the method of a previous paper[3] were added equimoles of EDDA, and the mixture was warmed on a waterbath of 50°C for a few minutes. The resulting solution was evaporated in vacuo, whereby some salts were deposited. After the removal of these salts by filtration, about three volumes of ethanol were added to the filtrate, and it was kept in a refrigerator until red-violet crystals separated out.

Found: Co, 17.4. Calcd. for $K[Co(edda)(CO_3)]\cdot H_2O$: Co, 17.7%.

3) Ethylenediamminediacetatodiaquocobalt(III) perchlorate, $[Co(edda)(OH_2)_2]ClO_4$.—A solution of the carbonato-complex obtained in 2) was acidified with dilute hydrochloric acid, and then a certain amount of perchloric acid was added to it. After the removal of insoluble materials by filtration, the filtrate was treated in the same manner as mentioned in 2). In this case, some violet precipitates which may be regarded as the diaquo-complex were obtained, but the purity of the complex was not satisfactory.

Found: Co, 15.0. Calcd. for $[Co(edda)(OH_2)_2]\cdot ClO_4$: Co, 16.0%.

4) Potassium Dinitroethylenediaminediacetatocobaltate(III) $K[Co(edda)(NO_2)_2]\cdot H_2O$. — This was prepared by using the above-mentioned diaquo-complex. To a solution of the diaquo-complex was added the necessary amount of potassium nitrite, and the mixture was warmed to 50°C for some time until the color of the solution changed to yellow-brown. The solution was filtered once and the filtrate treated with ethanol in the same manner as mentioned in 2). The product was recrystallized from water in the form of red-brown prisms.

Found: Co, 15.2; N, 7.81. Calcd. for $K[Co(edda)(NO_2)_2]\cdot H_2O$: Co, 15.4; N, 7.36%.

For the determination of the chemical formulae of these complexes, chemical and thermal analyses, coagulation of ferric oxide sol and spectroscopic measurements were used in the same manner as described in previous papers[3,4].

Results and Discussion

Coagulation Value.—The values obtained in the present experiment were 4.1 mF for the $[Co(ada)_2]^-$, 3.4 mF for the $[Co(edda)(CO_3)]^-$, and 4.2 mF for the $[Co(edda)(NO_2)_2]^-$. These values were somewhat lower than the average value, 6.6 mF, for univalent complex anions, but far too high for that of bivalent anions (0.48 mF)[5]. Therefore, these complex anions may be regarded as univalent.

Absorption Spectra. — The visible and ultraviolet absorption spectra of these complexes are shown in Fig. 1 and the numerical data are given in Table I. Based upon these data, some discussion is possible about the geometrical structures of the complexes. In the case of the $[Co(ada)_2]^-$, two geometrically different structures, cis and trans in respect to the coordinated nitrogen atoms, are possible,

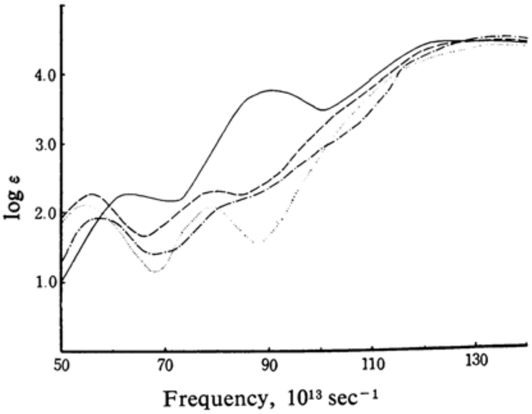

Fig. 1. Absorption spectra of:
.... : $K[Co(ada)_2]\cdot 4H_2O$
—·—· : $K[Co(edda)CO_3]\cdot H_2O$
– – – : $[Co(edda)(OH_2)_2]ClO_4$
——— : $K[Co(edda)(NO_2)_2]\cdot H_2O$

TABLE I. ABSORPTION MAXIMA AND log ε (10^{13}/sec.)

	ν_1	log ε_1	ν_2 or ν_{sp}	log(ε_2 or ε_{sp})	ν_3	log ε_3
$K[Co(ada)_2]\cdot 4H_2O$	53.8	2.13	79.4	2.08	134.5	4.40
$K[Co(edda)(CO_3)]\cdot H_2O$	57.0	1.94	79.0	2.08	136.4	4.38
$[Co(edda)(OH_2)_2]ClO_4$	55.4	2.27	79.8	2.30	132.1	4.49
$K[Co(edda)(NO_2)_2]\cdot H_2O$	62.8	2.29	90.4	3.74	122.5	4.47

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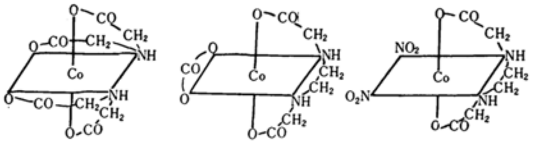
* "ada" stands for ammoniadiacetate ion.

** "edda" stands for ethylenediaminediacetate ion.

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

[4] M. Mori, M. Shibata, E. Kyuno and K. Hoshiyama, This Bulletin, **31**, 291 (1958).

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



a b c

Fig. 2. Probable structures.

but the cis structure illustrated by a in Fig. 2 must be adopted for the present complex ion because the absorption maxima of this complex ion are similar to those of the α-$[Co(NH_3)_2 \cdot (C_2O_4)_2]^-$ regarded as cis isomer in the previous paper[4]. As the most probable structure, formula b in the figure may be assigned to the $[Co(edda)(CO_3)]^-$, because ethylenediaminediacetate ion usually acts as a quadridentate ligand and carbonate ion as a bidentate ligand. The dinitro-complex ion $[Co(edda)(NO_2)_2]^-$ which can be derived from the corresponding carbonatocomplex, probably has a structure illustrated by c. Evidence for the validity of this assignment lies in the fact that the absorption maxima of this complex ion are more similar to those of the cis isomer of the $[Co \cdot en\,ox(NO_2)_2]^-$ [6]. For *cis*-$[Co\,en\,ox(NO_2)_2]^-$: ν_1, 63.3; ν_{sp}, 90.9; ν_3, 121.0. For *trans*-$[Co\,en\,ox(NO_2)_2]^-$: ν_1, 63.3; ν_{sp}, 85.7; ν_3, 116.3.

In order to check the coordination of the carboxylate ions, the infrared spectra of the $K[Co(ada)_2] \cdot 4H_2O$ and the $K[Co(edda)(NO_2)_2] \cdot H_2O$ as well as the free acids of the chelating agents were measured. For the ammoniadiacetic acid, strong split bands were observed at 1718 and 1585 cm^{-1}, and for the ethylenediaminediacetic acid, at 1721 and 1605 cm^{-1}. On the other hand, the ammoniadiacetato- and the ethylenediaminediacetato-complex showed strong absorption arising from the coordinated carboxylate ions at 1623 and 1619 cm^{-1} respectively.

Table II is a summary of the absorption maxima of the first bands for several complexes which belong to the $[CoN_2 \cdot O_4]$-type and which are also regarded as cis form with respect to the coordinated nitrogen atoms. Among these complexes, the tetraaquo-complexes $[Co(NH_3)_2(OH_2)_4](ClO_4)_3$ and $[Co\,en(OH_2)_4](ClO_4)_3$ were prepared from the corresponding dichlorodiaquo-complexes[7] by treating with glacial acetic acid. Both of these were quite hygroscopic and difficult to be isolated as crystals, but the complex ions were completely held on a cation exchanger from the solutions. If the maximum value ν_1^0 for the $[Co(NH_3)_2(OH_2)_4]^{3+}$ is chosen as a standard absorption for the $[CoN_2 \cdot O_4]$-type complexes, the deviations of the maximum values for the other complexes from this standard value, $\alpha = \nu_1^0 - \nu_1$, may be regarded as a measure for the chelation effect.

TABLE II. ABSORPTION MAXIMA OF $[CoN_2 \cdot O_4]$-TYPE COMPLEXES

		ν_1	α
1	$[Co(NH_3)_2(CO_3)_2]^-$	52.2	1.3
2	$[Co\,en(CO_3)_2]^-$	53.2	0.3
3	$[Co(NH_3)_2\,ox\,CO_3]^-$	53.4	0.1
4	$[Co(NH_3)_2(OH_2)_4]^{3+}$	53.5	0
5	$[Co(ada)_2]^-$	53.8	−0.3
6	$[Co(NH_3)_2\,ox_2]^-$	54.4	−0.9
7	$[Co\,en(OH_2)_4]^{3+}$	54.8	−1.2
8	$[Co\,en\,ox_2]^-$	55.6	−2.1
9	$[Co(edta)]^-$	55.9	−2.4
10	$[Co(edda)(CO_3)]^-$	57.0	−3.5

Summary

The cobalt(III) complexes containing ammoniadiacetate group (ada) and ethylene diaminediacetate group (edda) have been prepared:

1) $K[Co(ada)_2] \cdot 4H_2O$ Red-violet
2) $K[Co(edda)(CO_3)] \cdot H_2O$ Red-violet
3) $[Co(edda)(OH_2)_2]ClO_4$ Violet
4) $K[Co(edda)(NO_2)_2] \cdot H_2O$ Yellow-brown

The visible and the ultraviolet absorption spectra as well as the infrared spectra of these complexes have been measured and discussed in relation to the structures of these complex ions.

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6) E. Kyuno, ibid., **80**, 981 (1959).

7) E. Kyuno, ibid., **80**, 724 (1959).