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Syntheses, Characterizations, and Reactions of the O-Bonded (Ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetato)pentaamminecobalt(III) Complex and Its Related Binuclear Complexes

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Three bonding modes of ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate (EDTA) toward metal ions which have not been reported are demonstrated through the syntheses and characterization of several complexes. $[Co(H_2edta)(NH_3)_5]ClO_4\cdot 6H_2O$ and $[Co(H_3edta)(NH_3)_5](ClO_4)_2\cdot 0.5H_2O$ were isolated as the complexes with the first mode, where the EDTA is coordinated to the $[Co(NH_3)_5]^{3+}$ moiety through an acetate arm. The complex with the second mode is $[(NH_3)_5Co(H_2edta)Co(NH_3)_5](ClO_4)_4$, where the EDTA is coordinated to the two $[Co(NH_3)_5]^{3+}$ moieties through two acetate arms. $[(NH_3)_5Co\{edtaNi^{II}(H_2O)\}]ClO_4\cdot 2H_2O$, $[(NH_3)_5Co\{edtaCo^{III}(H_2O)\}](ClO_4)_2$, $[(NH_3)_5Co\{edtaCo^{III}(NH_3)\}](ClO_4)_2\cdot H_2O$, $[(NH_3)_5Co\{edtaCo^{III}(NO_2)\}]ClO_4\cdot 3H_2O$, and $[(NH_3)_5Co\{edtaCr^{III}(H_2O)\}](ClO_4)_2$ were isolated as the complexes with the third mode, where the EDTA acts as a quinquedentate ligand in the { } moiety and the residual acetate arm is coordinated to the $[Co(NH_3)_5]^{3+}$ moiety in each complex. Some reactions of these complexes are also presented and discussed.

Introduction

Multidentate character of ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate (EDTA) has been investigated extensively.[1] In cobalt(III) complexes, EDTA has been known to act as a sexa-,[2] quinque-,[3] or quadridentate[4] ligand. Busch and Bailar[5] reported that, for platinum(II) and palladium(II), EDTA acts as a quadridentate (through two carboxylate groups and two nitrogen atoms) or bidentate (through two nitrogen atoms) ligand. Thorneley and Sykes[6] prepared Cr^{III}–EDTA complexes in which the EDTA is probably terdentate. However, complexes in which EDTA acts as a unidentate ligand have not been reported.

In this work, $[Co(H_2edta)(NH_3)_5]ClO_4\cdot 6H_2O$ and $[Co(H_3edta)(NH_3)_5](ClO_4)_2\cdot 0.5H_2O$ were isolated and characterized, where the EDTA is coordinated through an acetate arm. Each complex can be regarded as a sort of ligand, because the five potential coordination sites of the EDTA remain uncoordinated. Therefore, the complex should coordinate the other metal ion (M^{m+}) to give a binuclear complex formulated as $[(NH_3)_5Co\{edtaM(H_2O)\}]^{m-1}$, where the EDTA acts as a quinquedentate ligand for M^{m+} and a unidentate ligand for the $[Co(NH_3)_5]^{3+}$ moiety. Such binuclear complexes, $[(NH_3)_5Co\{edtaM(H_2O)\}](ClO_4)_{m-1}$ and $[(NH_3)_5Co\{edtaCo^{III}(X)\}](ClO_4)_{2-p}$, were isolated and characterized, where X denotes NH_3 or NO_2^- and *p*, the negative charge on X. $[(NH_3)_5Co(H_2edta)Co(NH_3)_5](ClO_4)_4$ was also isolated where the EDTA coordinates to the two $[Co(NH_3)_5]^{3+}$ moieties through two acetate arms.

Experimental Section

A. Syntheses of Complexes. The starting materials, $[Co(H_2O)(NH_3)_5](ClO_4)_3$,[7] $Na[Co(NO_2)(Hedta)]\cdot H_2O$,[3] and $[Cr(Hedta)(H_2O)]$,[8] were prepared as reported in the literature. Column chromatography was made mainly by use of SP-Sephadex C-25 (Pharmacia). Some complexes were found to be photosensitive. Therefore, column chromatography was always carried out in dark. The analytical data of the complexes prepared in this work are listed in Table I.

$[Co(H_2edta)(NH_3)_5]ClO_4\cdot 6H_2O$, $[Co(H_3edta)(NH_3)_5](ClO_4)_2\cdot 0.5H_2O$, and $[(NH_3)_5Co(H_2edta)Co(NH_3)_5](ClO_4)_4$. Thirty-two grams of H_4edta was suspended in 200 mL of water and partly neutralized with 7.3 g of NaOH. To this suspension, was added 10 g of $[Co(H_2O)(NH_3)_5](ClO_4)_3$. The suspension was warmed to 75–80 °C for 1 h with constant stirring and then cooled to 0 °C. After filtration, the filtrate was diluted to 3 L with water and poured on a column (4.5 × 30 cm) of SP-Sephadex in the Na^+ form. The column was washed with water. Then, the washings and the solution which had been passed through the column were combined and poured on a column (2.7 × 20 cm) of Dowex 50W-X8 in the Na^+ form. A small amount of reddish violet species which had no affinity to the Dowex resin passed through the column. It was identified as $[Co(edta)]^-$ from the measurement of its electronic absorption spectrum. The column of Dowex resin showed only one red band. The red species was eluted with a 0.3 M $NaClO_4$ solution. The eluate was evaporated to small volume in a rotary evaporator below 40 °C. Pink crystals of $[Co(H_2edta)(NH_3)_5]ClO_4\cdot 6H_2O$ deposited upon the addition of ethanol. The species adsorbed on the Sephadex column were eluted with $NaClO_4$ solutions, whose concentrations were changed from 0.1 to 0.6 M increasingly. The column showed four bands: red, reddish orange, red, and pink (a small amount) from the bottom to the top of the column. The first red species was found to be $[Co(H_2edta)(NH_3)_5]^+$ and eluted very easily with a 0.1 M $NaClO_4$ solution. The eluate was treated to crystallize $[Co(H_2edta)(NH_3)_5]ClO_4\cdot 6H_2O$ as described above;[9] the yield (the sum of the weights of the crystals obtained from the columns of Sephadex and Dowex) was 9.7 g. The molecular weight was determined to be 643 ± 12 from pH titrations with a standard NaOH solution. The calculated value is 641.96.

When the pH of the eluate containing $[Co(H_2edta)(NH_3)_5]^+$ was adjusted to 2.5 and the resulting solution was evaporated to almost dryness, red crystals of $[Co(H_3edta)(NH_3)_5](ClO_4)_2\cdot 0.5H_2O$ deposited.

The reddish orange species on the Sephadex column was eluted with a 0.4 M $NaClO_4$ solution and was found to be a mixture of $[Co(H_2O)(NH_3)_5]^{3+}$ and $[Co(NH_3)_6]^{3+}$. The sum of their amounts corresponded to 20% of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ used as the starting material. The third red species was eluted with a 0.5 M $NaClO_4$ solution. When the solution was evaporated to small volume with a rotary evaporator, red crystals of $[(NH_3)_5Co(H_2edta)Co(NH_3)_5](ClO_4)_4$ deposited; yield 0.1 g. On the repeated trials of the preparation, however, the $[(NH_3)_5Co(H_2edta)Co(NH_3)_5](ClO_4)_4$ sometimes crystallized in the column. In such a case, the column was washed with water. Then, the species was eluted with a 1.0 M sodium acetate–acetic acid solution of pH 4.7. After several drops of 60% $HClO_4$ were added to the eluate, the solution was concentrated until the red crystals appeared. The last pink species on the column was not characterized.

$[(NH_3)_5Co\{edtaNi^{II}(H_2O)\}]ClO_4\cdot 2H_2O$. To 50 mL of water, was added 0.5 g of $[Co(H_2edta)(NH_3)_5]ClO_4\cdot 6H_2O$. The solution was mixed with a solution containing 0.2 g of $Ni(OAc)_2\cdot 4H_2O$ dissolved in 50 mL of water and, then, neutralized with $NaHCO_3$. After the resulting solution was evaporated to small volume, ethanol was added. Purple powder of $[(NH_3)_5Co\{edtaNi(H_2O)\}]ClO_4\cdot 2H_2O$ precipitated; yield 0.5 g.

$[(NH_3)_5Co\{edtaCo^{III}(H_2O)\}](ClO_4)_2$. Two grams of PbO_2 was added to 150 mL of water containing 3.2 g of $[Co(H_2edta(NH_3)_5]ClO_4\cdot 6H_2O$ and 1.3 g of $Co(OAc)_2\cdot 4H_2O$. The solution was stirred overnight at room temperature. After filtration, the filtrate was diluted to 3 L with water and poured on a Sephadex column (4.5 × 35 cm). The reddish violet species which was identified as $[Co(edta)]^-$ passed through the column; yield 25%. After developing the adsorbed bands with $NaClO_4$ solutions of pH 3 adjusted with $HClO_4$, the column showed five bands: reddish violet (a small amount), reddish violet, reddish violet (a small amount), reddish orange, and reddish violet (a small amount) from the bottom to the top of the column. The first species was eluted with a 0.1 M $NaClO_4$ solution. The eluate showed

Table I. Analytical Data for the New Complexes

Complex	% C		% H		% N	
	Calcd	Found	Calcd	Found	Calcd	Found
$[Co(H_2edta)(NH_3)_5]ClO_4\cdot 6H_2O$	18.71	19.00	6.45	6.34	15.28	15.36
$[Co(H_3edta)(NH_3)_5](ClO_4)_2\cdot 0.5H_2O$	18.67	19.03	4.87	5.33	15.24	14.76
$[(NH_3)_5Co(H_2edta)Co(NH_3)_5](ClO_4)_4$	12.30	12.32	4.55	4.31	17.22	17.06
$[(NH_3)_5Co\{edtaNi(H_2O)\}]ClO_4\cdot 2H_2O$	18.63	18.84	5.17	5.48	15.21	14.85
$[(NH_3)_5Co\{edtaCo(H_2O)\}](ClO_4)_2$	16.96	17.01	4.14	4.40	13.85	13.55
$[(NH_3)_5Co\{edtaCo(NH_3)\}](ClO_4)_2\cdot H_2O$	16.56	16.41	4.46	4.56	15.45	15.82
$[(NH_3)_5Co\{edtaCo(NO_2)\}]ClO_4\cdot 3H_2O$	17.39	17.52	4.82	5.10	16.22	15.91
$[(NH_3)_5Co\{edtaCr(H_2O)\}](ClO_4)_2$	17.13	17.10	4.18	4.44	13.98	13.91

Table II. Electronic Absorption Spectra of the Complexes Prepared in This Work and Their Related Complexes

Complex	Medium	Absorption max,[a] nm (ϵ, M^{-1} cm^{-1})
$[Co(H_2edta)(NH_3)_5]ClO_4\cdot 6H_2O$	0.1 M $HClO_4$	505 (66.7), 347 (63.4)
	pH 3[b]	505 (67.4), 347 (63.6)
	pH 5[b]	505 (68.6), 310 sh (298)
	pH 7[b]	505 (74.7), 310 sh (409)
	pH 9.5[b]	505 (75.7), 310 sh (541)
	pH 11[b]	505 (78.6), 310 sh (575)
$[(NH_3)_5Co(H_2edta)Co(NH_3)_5](ClO_4)_4$	0.1 M $HClO_4$	503 (131), 340 (157)
$[(NH_3)_5Co\{edtaNi(H_2O)\}]ClO_4\cdot 2H_2O$	H_2O	1010 (29.1), 790 sh (5.5), 505 (77.9)
$[Co(OAc)(NH_3)_5]^{2+}$ + $[Ni(edta)]^{2-}$ [c]		1010 (29.7), 790 sh (5.2), 505 (78.6)
$[(NH_3)_5Co\{edtaCo(H_2O)\}](ClO_4)_2$	0.1 M $HClO_4$	538 (344), 379 (229)
$[Co(OAc)(NH_3)_5]^{2+}$ + $[Co(hedtra)(H_2O)]$[c]		540 (283), 379 (238)
$[(NH_3)_5Co\{edtaCo(NH_3)\}](ClO_4)_2\cdot H_2O$	H_2O	584 sh (116), 514 (259) 367 (281), 224 (28 000)
$[Co(OAc)(NH_3)_5]^{2+}$ + $[Co(edtra)(NH_3)]$[c]		~580 sh (110), 510 (217), 367 (251)
$[(NH_3)_5Co\{edtaCo(NO_2)\}]ClO_4\cdot 3H_2O$	H_2O	582 sh (144), 500 (337) 343 (3430), 230 sh (27 700)
$[Co(OAc)(NH_3)_5]^{2+}$ + $[Co(NO_2)(edta)]^{2-}$ [c]		~580 sh (116), 500 (298)
$[(NH_3)_5Co\{edtaCr(H_2O)\}](ClO_4)_2$	0.1 M $HClO_4$	533 (218), 378 (146), 218 sh (19 500)
$[Co(OAc)(NH_3)_5]^{2+}$ + $[Cr(edta)(H_2O)]^-$ [c]		533 (249), 385 (139)
$[Co(OAc)(NH_3)_5]^{2+}$	H_2O	503 (77.9), 353 (68.4)
$[Ni(edta)]^{2-}$	1 M acetate buffer (pH 4.86)	1010 (29.7), 790 sh (5.2) 590 (8.3), 383 (13.0)
$[Co(hedtra)(H_2O)]$[d]	H_2O	552 (245), 383 (203)
$[Co(edtra)(NH_3)]$[e]	0.01 M HCl	~580 sh (99.5), 513 (141), 370 (196)
$[Co(NO_2)(edta)]^{2-}$	H_2O	~584 sh (102), 499 (220)
$[Cr(edta)(H_2O)]^-$	H_2O	545 (199), 392 (112)

[a] sh = shoulder. [b] The pH of the solution was adjusted with NaOH or $HClO_4$. [c] Synthetic spectrum; see text for the details. [d] H. Ogino, M. Takahashi, and N. Tanaka, *Bull. Chem. Soc. Jpn.*, 47, 1426 (1974). [e] M.-K. Doh, J. Fujita, and H. Ogino, unpublished data.

an absorption maximum at 515 nm, but the species was not characterized further. The second reddish violet species was eluted with the 0.1 M $NaClO_4$ solution and the eluate was concentrated to small volume in a rotary evaporator. Reddish violet crystals of $[(NH_3)_5Co\{edtaCo(H_2O)\}](ClO_4)_2$ crystallized; yield 1.8 g.

The third species was eluted with a 0.2 M $NaClO_4$ solution. The eluate gave absorption maxima at 533 and 380 nm. The fourth species was eluted with a 0.4 M $NaClO_4$ solution and characterized as $[Co(H_2O)(NH_3)_5]^{3+}$. The yield, based on $[Co(H_2edta)(NH_3)_5]ClO_4\cdot 6H_2O$, was 23%. The fifth species which was eluted with a 0.9 M $NaClO_4$ solution showed an absorption maximum at 533 nm. The species of the third and fifth bands were not characterized further, because the amounts were too little to be examined.

The formation of $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$ was also confirmed upon heating a 0.2 M $HClO_4$ solution containing $[Co(H_2O)(NH_3)_5](ClO_4)_3$ and $Na[Co(edta)]\cdot 4H_2O$.

$[(NH_3)_5Co\{edtaCo^{III}(NH_3)\}](ClO_4)_2\cdot H_2O$. Ten milliliters of 30% hydrogen peroxide and 0.6 g of activated charcoal were added to 100 mL of water containing 3.2 g of $[Co(H_2edta)(NH_3)_5]ClO_4\cdot 6H_2O$ and 2 g of $Co(NO_3)_2\cdot 6H_2O$. Air was passed through the solution for 3 h. Activated charcoal was removed by filtration and washed with a small amount of water. The filtrate and the washings were combined and concentrated to 50 mL in a rotary evaporator. When the solution was cooled overnight in a refrigerator, reddish violet crystals of $[(NH_3)_5Co\{edtaCo(NH_3)\}](ClO_4)_2\cdot H_2O$ were obtained; yield 0.05 g.

$[(NH_3)_5Co\{edtaCo^{III}(NO_2)\}]ClO_4\cdot 3H_2O$. Twenty grams of $Na[Co(NO_2)(Hedta)]\cdot H_2O$ was dissolved into 500 mL of water and the pH of the solution was adjusted to 4.5 with $NaHCO_3$. Ten grams of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ was added to the solution. The solution was kept at 75–80 °C for 1 h and then cooled to room temperature. After filtration, the solution was diluted to 6 L with water and poured on a column (4.5 × 40 cm) of Sephadex in the Na^+ form. A reddish violet species which had no affinity to the resin was found to be the mixture of $[Co(NO_2)(edta)]^{2-}$ and $[Co(edta)]^-$. The sum of their amounts corresponded to 90% of $Na[Co(NO_2)(Hedta)]\cdot H_2O$ used as the starting material. Upon the elution with $NaClO_4$ solutions of pH 3 adjusted with $HClO_4$, the column showed five bands: yellow (a small amount), brownish violet, reddish violet, brownish orange, and reddish orange from the bottom to the top of the column. The first species was eluted with a 0.05 M $NaClO_4$ solution. The eluate showed absorption maxima at 444, 348, and 253 nm. These values and the spectral shape were found to agree with those of the *trans*-$[Co(NO_2)_2(NH_3)_4]^+$ ion. The second species was eluted with the 0.05 M $NaClO_4$ solution. The eluate was concentrated to small volume in a rotary evaporator. Brownish violet crystals of $[(NH_3)_5Co\{edtaCo(NO_2)\}]ClO_4\cdot 3H_2O$ precipitated; yield 1 g.

The third species was found to be $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$, eluted with a 0.1 M $NaClO_4$ solution and crystallized upon evaporation; yield 0.1 g. The fourth species was eluted with a 0.2 M $NaClO_4$ solution and found to be $[Co(NO_2)(NH_3)_5]^{2+}$. Upon evaporation, 0.5 g of $[Co(NO_2)(NH_3)_5](ClO_4)_2$ was obtained. The fifth species was found to be $[Co(H_2O)(NH_3)_5]^{3+}$. The recovered $[Co(H_2O)(NH_3)_5](ClO_4)_3$ was 7.5 g.

$[(NH_3)_5Co\{edta\ Cr^{III}(H_2O)\}](ClO_4)_2$. Into 100 mL of water were dissolved 2.3 g of $[Cr(Hedta)(H_2O)]$ and 2.3 g of $[Co(H_2O)(NH_3)_5](ClO_4)_3$. The solution was evaporated to 50 mL on a water bath at 75–80 °C and then cooled to room temperature. The reddish violet crystals of $[(NH_3)_5Co\{edtaCr(H_2O)\}](ClO_4)_2$ precipitated; yield 1.2 g. This complex was also obtained upon heating a solution containing equimolar amounts of $[Co(H_2edta)(NH_3)_5]ClO_4\cdot 6H_2O$ and $[Cr(H_2O)_6](ClO_4)_3$ at pH 4–5.

B. Apparatus. Electronic spectra were recorded on a Hitachi EPS-3 recording spectrophotometer. Infrared spectra (KBr disks) were recorded on a Hitachi EPI-S2 infrared spectrometer. Numerical data for electronic spectra of the complexes prepared in this work are given in Table II along with those of the other related complexes. For determining acid dissociation constants of the complexes, pH titrations were made with a Hitachi-Horiba F-5 pH meter, as described previously.[10]

Results and Discussion

When an aqueous solution which contains $[Co(H_2O)(NH_3)_5](ClO_4)_3$ and a carboxylate-containing ligand ($RCOO^-$ or RCOOH) is heated, the aqua ligand in $[Co(H_2O)(NH_3)_5]^{3+}$ is known to be replaced by the carboxylate group

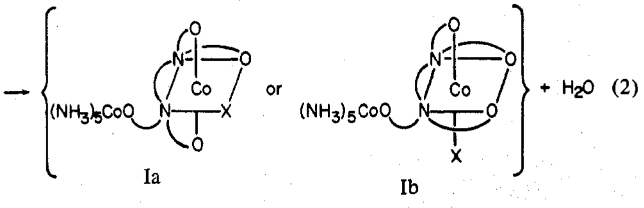
$$[Co(H_2O)(NH_3)_5]^{3+} + RCOOH \rightarrow [(NH_3)_5CoO_2CR]^{2+} \qquad (1)$$

After cooling of the solution, the complex $[Co(O_2CR)(NH_3)_5](ClO_4)_2$ can be isolated, though the reduction of the solution volume and the addition of $HClO_4$ or a perchlorate salt are often necessary to ensure the crystallization. Employing such a procedure, a pentaamminecobalt(III) complex binding the ligand through the COO^- group, e.g., acetate,[11] oxalate,[12] amino acids,[13] or NTA,[14] has been isolated. However, when an aqueous solution containing $[Co(H_2O)(NH_3)_5](ClO_4)_3$ and EDTA which is a carboxylate-containing ligand was heated and evaporated, only a viscous syrup was obtained. This may be explained by the fact that the coexistence of several species sometimes causes the difficulty in crystallization.[15] The separation and crystallization of the dissolved species were achieved successfully by use of the columns of cation-exchange resins as described in the Experimental Section.

From reaction 1, it is expected that the reaction of $[Co(H_2O)(NH_3)_5]^{3+}$ with EDTA gives $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$, in which $H_nedta^{(4-n)-}$ is coordinated to the $[Co(NH_3)_5]^{3+}$ moiety through one of the acetate arms. This complex ion still contains $-CH_2COO^-$ or $-CH_2COOH$ group(s) which can attack further on the water position of the other $[Co(H_2O)(NH_3)_5]^{3+}$ ions to give, at least, $[(NH_3)_5Co(H_nedta)Co(NH_3)_5]^{(n+2)+}$.

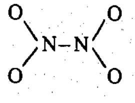
A number of complexes of the type $[Co^{III}(X)(edta)]^{(1+p)-}$ are known, where the EDTA acts as a quinquedentate ligand.[3,16,17] Therefore, the residual acetate arm in the $[Co(X)(edta)]^{(1+p)-}$ may attack on the aqua ligand in $[Co(H_2O)(NH_3)_5]^{3+}$ to produce $[(NH_3)_5Co\{edtaCo(X)\}]^{(2-p)-}$

$$[Co(H_2O)(NH_3)_5]^{3+} + [Co(X)(edta)]^{(1-p)-}$$



Ia Ib

where EDTA is expressed as



and the charge on the binuclear complex is omitted for simplicity. Similarly, $[Cr(Hedta)(H_2O)]$ is expected to react with $[Co(H_2O)(NH_3)_5]^{3+}$ to produce $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$.

Characterization of $[Co(H_2edta)(NH_3)_5]ClO_4 \cdot 6H_2O$ and $[Co(H_3edta)(NH_3)_5](ClO_4)_2 \cdot 0.5H_2O$. The analytical results of $[Co(H_2edta)(NH_3)_5]ClO_4 \cdot 6H_2O$ and $[Co(H_3edta)(NH_3)_5](ClO_4)_2 \cdot 0.5H_2O$ indicate that the EDTA is coordinated to the $[Co(NH_3)_5]^{3+}$ moiety as a unidentate ligand. There are two possible ways of bonding of the EDTA. One is coordination to the $[Co(NH_3)_5]^{3+}$ moiety with an acetate arm, and the other is coordination with a nitrogen atom. The position and molar absorption coefficient (ϵ) of the first absorption band of the complex $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ given in Table II (505 nm, ϵ 66.7–78.6) are quite similar to those of carboxylato- or O-bonded amino acid–pentaamminecobalt(III) complexes.[13,14,18] Therefore, it can be concluded that the EDTA is coordinated to the $[Co(NH_3)_5]^{3+}$ moiety through an acetate arm. The spectra of these complexes vary with the pH of the solution; especially, the spectral changes are significant in the ultraviolet region as shown in Figure 1. Cannon and Gardiner reported similar observations with $[Co(H_nnta)(NH_3)_5]^{n+}$. These changes indicate that, when the pHs of the solution increase, new bands centered around 290 nm appear. The new bands may originate from the formation of the hydrogen bonds between ammonia molecules of the $[Co(NH_3)_5]^{3+}$ moiety and free amino and carboxylate groups in the same complex ion.[19]

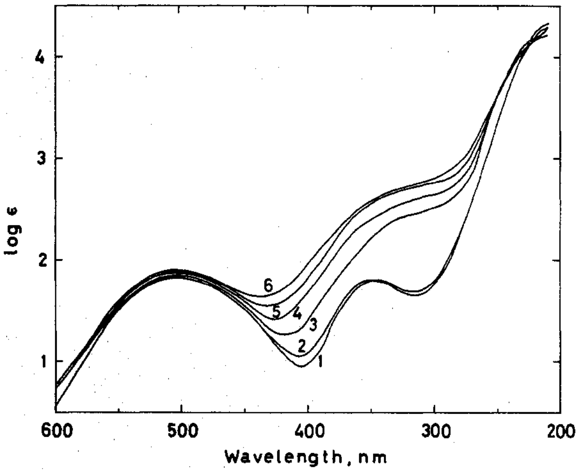


Figure 1. Electronic spectra of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ in aqueous solution: (1) 0.1 M $HClO_4$; (2) pH 3; (3) pH 5; (4) pH 7; (5) pH 9.5; (6) pH 11.

Table III. p*K* Values of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ and $H_nedta^{(4-n)-}$ [a]

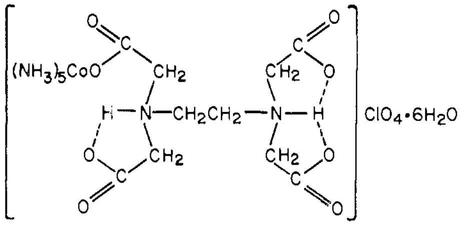
Compound	pK_1	pK_2	pK_3	pK_4
$[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ [b]	9.07	5.20	2.01	
$H_nedta^{(4-n)-}$ [c]	10.34	6.24	2.75	2.07

[a] $K_n = [H^+][[Co(H_{n-1}edta)(NH_3)_5]^{(n-2)+}]/[[Co(H_nedta)(NH_3)_5]^{(n-1)+}]$ for $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ and $K_n = [H^+] \cdot [H_{n-1}edta^{(5-n)-}]/[H_nedta^{(4-n)-}]$ for $H_nedta^{(4-n)-}$. [b] This work; at 25 °C and $I = 0.1$ (NaCl). [c] From A. E. Martell and L. G. Sillén, *Chem. Soc., Spec. Publ.*, No. 25 (1971); at 25 °C and $I = 0.1$ (KNO_3).

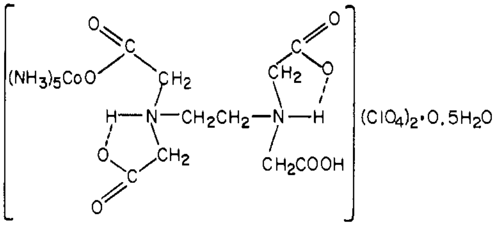
The p*K* values of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ are given in Table III along with the data for the parent acid (EDTA). The data show that EDTA coordinated to the $[Co(NH_3)_5]^{3+}$ moiety is more acidic than free EDTA. This may be attributable to the difference between the total charges of the complex and the parent acid.

Infrared spectra of all of the complexes prepared in this work show intense bands in the regions of 1300–1400 and 1600–1650 cm^{-1}, which can be assigned to the CO stretching vibrations, though these bands are obscured by the overlap of the NH_3 deformation vibrations.[20] The strong absorptions near 3300 cm^{-1} can be assigned to the vibrations due to the NH stretching of the NH_3 molecules and the CH stretching in the CH_2 groups of the EDTA. The NH_3 rocking vibrations which are expected to be observed near 850 cm^{-1} [20] are again obscured by the overlap of the vibrations due to EDTA. The band of $[Co(H_3edta)(NH_3)_5](ClO_4)_2 \cdot 0.5H_2O$ at 1725 cm^{-1} is assigned to the CO stretching vibration due to the –COOH group. The corresponding band is absent in $[Co(H_2edta)(NH_3)_5]ClO_4 \cdot 6H_2O$.

From the results given above, the most probable structures of $[Co(H_2edta)(NH_3)_5]ClO_4 \cdot 6H_2O$ and $[Co(H_3edta)(NH_3)_5](ClO_4)_2 \cdot 0.5H_2O$ may be given as II and III, respectively. The hydrogen bonds in the complexes are shown by dotted lines. Recent crystallographic studies on H_4edta revealed that the molecule of the EDTA exists in the crystal as the zwitterion.[21] The hydrogen atom of each charged amino group is associated with the two COO^- groups and the carbonyl oxygen atom in the COOH group. Therefore, for the present complexes, there may probably be such additional interactions between each amino group and the carbonyl oxygen atoms in $(NH_3)_5CoOCO$ and/or COOH.

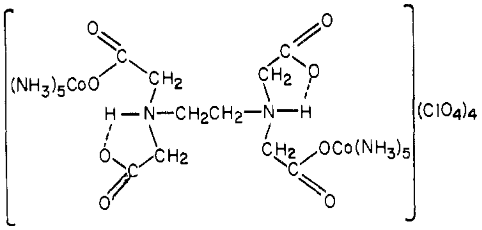


II

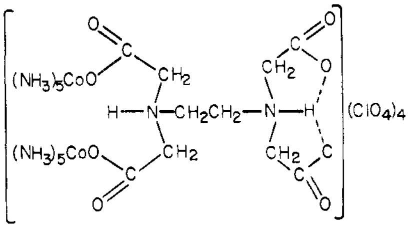


III

Characterization of $[(NH_3)_5Co(H_2edta)Co(NH_3)_5](ClO_4)_4$. The complex ion shows such a flow rate on a Sephadex column that the ion must be the 4+-charged species.[22] This complex gives the first absorption band at almost the same position as that of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ (Table II). The molar absorption coefficient is approximately 2 times larger than that of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$. These results support the thought that the complex ion is $[(NH_3)_5Co(H_2edta)Co(NH_3)_5]^{4+}$. The complex does not give the CO stretching vibration near 1700 cm^{-1} due to COOH. Therefore, the structure of this complex may be expressed as form IVa and/or IVb. Again, there is a possibility of the additional hydrogen bonding between amino groups and the carbonyl oxygen atoms in $(NH_3)_5CoOCO$ groups.



IVa

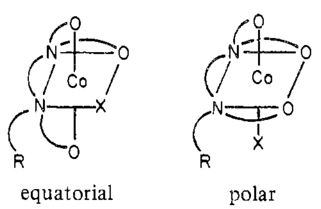


IVb

$[Co(NH_3)_6]^{3+}$ was found among the products of the reaction of $[Co(H_2O)(NH_3)_5]^{3+}$ with EDTA. However, the interpretation for the formation of $[Co(NH_3)_6]^{3+}$ cannot be given at present because the acidic condition was maintained during the reaction of $[Co(H_2O)(NH_3)_5]^{3+}$ with EDTA (see Experimental Section).

Characterization of $[(NH_3)_5Co\{edtaNi(H_2O)\}]ClO_4 \cdot 2H_2O$, $[(NH_3)_5Co\{edtaCo(H_2O)\}](ClO_4)_2$, $[(NH_3)_5Co\{edtaCo(NH_3)\}](ClO_4)_2 \cdot H_2O$, $[(NH_3)_5Co\{edtaCo(NO_2)\}]ClO_4 \cdot 3H_2O$, and $[(NH_3)_5Co\{edtaCr(H_2O)\}](ClO_4)_2$. Complex ions assigned to $[(NH_3)_5Co\{edtaNi(H_2O)\}]^+$, $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$, $[(NH_3)_5Co\{edtaCo(NH_3)\}]^{2+}$, $[(NH_3)_5Co\{edtaCo(NO_2)\}]^+$, and $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$ show reasonable flow rates on Sephadex columns. de Castellô et al. reported that the electronic spectrum of the binuclear complex $[(NH_3)_5CoNCCo(CN)_5]$ corresponds to the sum of the spectra of the two cobalt(III) moieties.[23] This rule may hold for the present binuclear complex ions of the type $[(NH_3)_5Co\{edtaM(X)\}]^{(m-1-p)+}$, because the two metal centers are separated by the O_2CCH_2N chain so that the interaction between the d–d transitions of the $[Co(NH_3)_5]^{3+}$ and {edtaM(X)} moieties may be negligible. Therefore, the spectrum of $[(NH_3)_5Co\{edtaM(X)\}]^{(m-1-p)+}$ may be predicted as the sum of the spectra of the model complexes for $[Co(NH_3)_5]^{3+}$ and {edtaM(X)} moieties. Here, as the model complex for the $[Co(NH_3)_5]^{3+}$ moiety, $[Co(OAc)(NH_3)_5]^{2+}$ was employed. The spectra of $[Ni(edta)]^{2-}$, $[Co(hedtra)(H_2O)]$, $[Co(edtra)(NH_3)]$, $[Co(NO_2)(edta)]^{2-}$, and $[Cr(edta)(H_2O)]^-$ were used as those of the corresponding {edtaM(X)} moieties, respectively. Then, the synthetic spectrum, the sum of the spectra of $[Co(OAc)(NH_3)_5]^{2+}$ and each model complex for the {edtaM(X)} moiety, was calculated. The peak positions and intensities of the synthetic spectrum thus obtained are given in Table II, which are in satisfactory agreement with the values measured for the genuine $[(NH_3)_5Co\{edtaM(X)\}]^{(m-1-p)+}$.

When an aminopolycarboxylate such as EDTA, EDTRA, or HEDTRA forms a cobalt(III) complex together with a unidentate ligand X, there are two possible geometric isomers, that is, the equatorial and polar isomers. It has been concluded that $[Co(edtra)(NH_3)]$ which was used as the model of the $\{edtaCo(NH_3)\}$ moiety has the equatorial structure,[24] because this complex gives a very broad first absorption band which is characteristic of the *mer*-$[CoO_3N_3]$ moiety.[25] The synthetic spectrum resulting from $[Co(OAc)(NH_3)_5]^{2+}$ and *mer*-$[Co(edtra)(NH_3)]$ is in satisfactory agreement with that of $[(NH_3)_5Co\{edtaCo(NH_3)\}]^{2+}$. This fact indicates that the binuclear complex has structure Ia. Blackmer and Sudmeir thought that $[Co(X)(edta)]^{(1+p)-}$, $[Co(X)(edtra)]^{p-}$, $[Co(X)(hedtra)]^{p-}$, and some other related complexes exist in the equatorial form, where X is NO_2^- or H_2O.[26] It is also known that the in-plane acetate arms in $[Co(edta)]^-$ are more strained than the out-of-plane acetate arms;[2] thus the unidentate ligand X is expected to occupy the equatorial site. These facts and the agreement between the spectrum of $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$ or $[(NH_3)_5Co\{edtaCo(NO_2)\}]^+$ and the corresponding synthetic spectrum suggest strongly that these complexes have structure Ia. It has also been proposed that $[Cr(edta)(H_2O)]^-$ takes the equatorial structure.[10] Therefore, it would be safe to conclude that $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$ has the equatorial structure.



equatorial polar

R = $CH_2CO_2^-$, H, and CH_2CH_2OH for edta, edtra, and hedtra, respectively
$\overset{\frown}{NO} = NCH_2CO_2^-$
$\overset{\frown}{NN} = NCH_2CH_2N$

Reactions of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ with Metal Ions. $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ reacts with Ni^{2+} and Cr^{3+} to produce $[(NH_3)_5Co\{edtaNi(H_2O)\}]^+$ and $[(NH_3)_5Co\{edtaCr(H_2O)\}]^{2+}$, respectively. This reveals that $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ has as strong coordination ability as EDTRA etc. Therefore, when $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ is added to a Co^{2+} solution, $[(NH_3)_5Co\{edtaCo^{II}(H_2O)\}]^+$ may be formed. Then, $[(NH_3)_5Co\{edtaCo^{III}(H_2O)\}]^{2+}$ may be formed by the addition of an appropriate oxidant to the solution. In fact, the isolation of $[(NH_3)_5Co\{edtaCo^{III}(H_2O)\}](ClO_4)_2$ was achieved successfully by such a procedure, where PbO_2 was used as the oxidant. It was also found that $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$ was formed upon heating an acidic solution containing $[Co(H_2O)(NH_3)_5]^{3+}$ and sexadentate $[Co(edta)]^-$. This can be understood as follows. It is known that in an acidic solution sexadentate $[Co(edta)]^-$ is converted to $[Co(Hedta)(H_2O)]$ in which Hedta acts as a quinquedentate ligand.[17,27] Therefore, one free COOH in this complex replaces the aqua ligand in $[Co(H_2O)(NH_3)_5]^{3+}$ to produce $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$.

Upon the oxidation of $[(NH_3)_5Co\{edtaCo^{II}(H_2O)\}]^+$ by H_2O_2 in the presence of activated charcoal, a small amount of $[(NH_3)_5Co\{edtaCo(NH_3)\}]^{2+}$ was formed. Activated charcoal is known to be a catalyst for the coordination of ammonia or amine molecules to cobalt(III) ions.[28,29] In the present case, the ammonia molecule in $[(NH_3)_5Co\{edtaCo(NH_3)\}]^{2+}$ is considered to be supplied by partial decomposition of $[(NH_3)_5Co\{edtaCo^{II}(H_2O)\}]^+$.

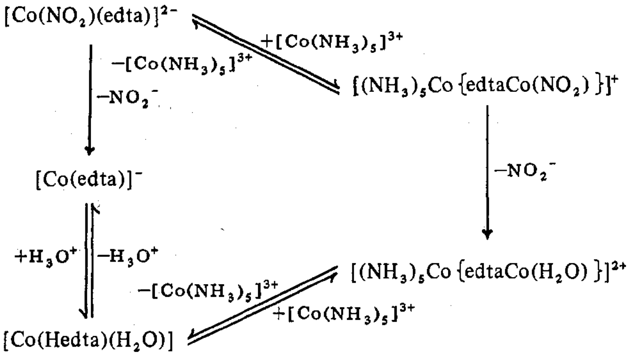
The complex-forming reaction of $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ with Cu^{2+} was examined on a Sephadex column. When the solution containing equimolar amounts of $[Co(H_2edta)(NH_3)_5]^+$ and Cu^{2+} was poured on the column in the Na^+ form, a violet band was developed on the top of the column. The band moved downward as only one band by the elution with a 0.1 M $NaClO_4$ solution and behaved as a species having a 1+ charge. This may indicate the formation of $[(NH_3)_5Co\{edtaCu(H_2O)\}]^+$. However, when 0.1 M $HClO_4$ solution was used as an eluent, the color of the band changed to reddish brown and then the band was separated into two bands: the lower blue and the upper pink. This suggests the occurrence of the reaction

$$[(NH_3)_5Co\{edtaCu(H_2O)\}]^+ + nH^+ \rightarrow [Co(H_nedta)(NH_3)_5]^{(n-1)+} + Cu^{2+} \qquad (3)$$

where $n > 2$. When the eluent was again changed to an $NaClO_4$ solution, the upper pink band moved faster than the lower band and finally they joined together. This indicates that $[Co(H_nedta)(NH_3)_5]^{(n-1)+}$ dissociates to a less protonated form and the species recombines with Cu^{2+} to give $[(NH_3)_5Co\{edtaCu(H_2O)\}]^+$.

Reaction of $[Co(H_2O)(NH_3)_5]^{3+}$ with $[Co(NO_2)(edta)]^{2-}$. The products of the title reaction were $[(NH_3)_5Co\{edtaCo(NO_2)\}]^+$, $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$, $[Co(edta)]^-$, $[Co(NO_2)(NH_3)_5]^{2+}$, and *trans*-$[Co(NO_2)_2(NH_3)_4]^+$. The formation of $[(NH_3)_5Co\{edtaCo(NO_2)\}]^+$ can be understood as the product of direct substitution of the aqua ligand in $[Co(H_2O)(NH_3)_5]^{3+}$ by $[Co(NO_2)(edta)]^{2-}$. The formation of $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$ may be interpreted as the aquation reaction of $[(NH_3)_5Co\{edtaCo(NO_2)\}]^+$. However, there is another possible route for the formation of $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$: $[Co(edta)]^-$ was found among the reaction products. This may be formed from $[Co(NO_2)(edta)]^{2-}$. The reaction of $[Co(H_2O)(NH_3)_5]^{3+}$ with $[Co(Hedta)(H_2O)]$ which is derived from $[Co(edta)]^-$ leads to the formation of $[(NH_3)_5Co\{edtaCo(H_2O)\}]^{2+}$. These reactions are summarized in Scheme I.

Scheme I



One of the products $[Co(NO_2)(NH_3)_5]^{2+}$ would be formed by the reaction of $[Co(H_2O)(NH_3)_5]^{3+}$ with NO_2^- which would be released from $[Co(NO_2)(edta)]^{2-}$ and/or $[(NH_3)_5Co\{edtaCo(NO_2)\}]^+$. The formation of a small amount of *trans*-$[Co(NO_2)_2(NH_3)_4]^+$ would be derived by the elimination of an ammonia molecule from $[Co(H_2O)(NH_3)_5]^{3+}$ or $[Co(NO_2)(NH_3)_5]^{2+}$.

Registry No. $[Co(H_2edta)(NH_3)_5]ClO_4$, 61813-08-9; $[Co(H_3edta)(NH_3)_5](ClO_4)_2$, 61813-09-0; $[(NH_3)_5Co(H_2edta)Co(NH_3)_5](ClO_4)_4$, 61900-92-3; $[(NH_3)_5Co\{edtaNi(H_2O)\}]ClO_4$, 61916-05-0; $[(NH_3)_5Co\{edtaCo(H_2O)\}](ClO_4)_2$, 61813-11-4; $[(NH_3)_5Co\{edtaCo(NH_3)\}](ClO_4)_2$, 61813-13-6; $[(NH_3)_5Co\{edtaCo(NO_2)\}]ClO_4$, 61813-15-8; $[(NH_3)_5Co\{edtaCr(H_2O)\}](ClO_4)_2$, 61813-17-0; $[Co(OAc)(NH_3)_5]^{2+}$, 16632-78-3; $[Ni(edta)]^{2-}$, 14931-84-1; $[Co(NO_2)(edta)]^{2-}$, 33972-14-4; $[Cr(edta)(H_2O)]^-$, 19610-17-4; $[Cr(Hedta)(H_2O)]$, 55637-94-0; $Na[Co(NO_2)(Hedta)]$, 61813-18-1; $[Co(H_4edta)(NH_3)_5]^{3+}$, 61813-19-2; $[Co(Hedta)(NH_3)_5]$, 61813-07-8; $[Co(H_2O)(NH_3)_5](ClO_4)_3$, 13820-81-0.

References and Notes

(1) Abbreviations used in this paper: EDTA, ethylenediamine-*N*,*N*,*N'*,-*N'*-tetraacetic acid; NTA, nitrilotriacetic acid; EDTRA, ethylenediamine-*N*,*N*,*N'*-triacetic acid; HEDTRA, *N'*-hydroxyethylethylenediamine-*N*,*N*,*N'*-triacetic acid; OAc^-, acetate.
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