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Preparation and Properties of the Uni- and Binuclear $[\mathrm{Co(III)N_2O_4}]$ Type Complexes Containing (*S*)-2-Amino-1-propanol

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Reactions of (*S*)-2-amino-1-propanol (*S*-praH) with the tricarbonatocobaltate(III) solution gave binuclear complexes bridged by carbonates, or carbonate and hydroxide. The carbonate was replaced by oxalate ($\mathrm{ox^{2-}}$) to give binuclear complexes $[(S\text{-praH})_2\mathrm{Co(ox)_2Co}(S\text{-praH})_2]^{2+}$ and uninuclear *trans*(*N*)*cis*(*O*)-[Co(ox)(*S*-pra)(*S*-praH)]. Another uninuclear complex $[\mathrm{Co(ox)}(S\text{-praH})_2]^+$ was obtained by direct synthesis from *S*-praH and cobalt(II) acetate by oxidation with lead dioxide. Column chromatography with SP-Sephadex C-25 was useful for separating the geometrical isomers, which were identified by PMR, IR, visible, and UV absorption spectra. Their circular dichroism (CD) spectra changed depending on pH of the aqueous solution. All the $S\text{-pra}^-$ chelates have δ-conformation, which is characterized by an intensive plus CD component in the 25000 $\mathrm{cm^{-1}}$ region, regardless of the skeletal structure of the complexes.

In the previous papers[1,2] we reported the preparation of mixed ligand complexes of the type $[\mathrm{Co^{III}N_5O}]$ containing various amino alcohols (amOH), and ammines or diamines. The alcohol protons of coordinated aminoalkanols in complexes of the type $[\mathrm{Co^{III}(amOH)(L)]X_3}$ (amOH=2-aminoethanol [etaH], (*S*)-2-amino-1-propanol [*S*-praH] *etc.*; L=$\mathrm{(NH_3)_4}$, $\mathrm{(en)_2}$, and $((R,R)\text{-1,2-diaminocyclohexane})_2$; X=chloride, bromide and perchlorate) were deprotonated easily (pK 3 to 3.5 at 25 °C and ionic strength 0.05), and the aminoalkanolato complexes exhibited larger CD components than the protonated did in the first and second absorption band regions. Especially $[\mathrm{Co}(S\text{-amO})(\mathrm{L})]^{2+}$ gave characteristic large plus vicinal CD components at *ca.* 25000 $\mathrm{cm^{-1}}$ (second band region), which were due to the δ-conformation of the $S\text{-amO}^-$ chelate.

The study has been extended to related complexes containing two moles of aminoalkanol ligands per cobalt(III), and this paper deals with the preparation of complexes of $[\mathrm{CoN_2O_4}]$ type, *i.e.* the uninuclear complexes $[\mathrm{Co(ox)}(S\text{-praH})_2]\mathrm{ClO_4}$ and *trans*(*N*)*cis*(*O*)-[Co(ox)(*S*-pra)(*S*-praH)], and the binuclear complexes $[(S\text{-pra})_2\mathrm{Co(CO_3,OH)Co}(S\text{-pra})(S\text{-praH})]$, $[(S\text{-pra})(S\text{-praH})\mathrm{Co(CO_3)_2Co}(S\text{-pra})(S\text{-praH})]$, and $[(S\text{-praH})_2\mathrm{Co(ox)_2Co}(S\text{-praH})_2](\mathrm{ClO_4})_2$. Their structure and CD pattern have been discussed with reference to the characteristic nature of the coordinated aminoalkanolato ligand.

Experimental

Material. The *S*-praH ligand was synthesized by Vogl and Pöln's method.[3] The outline of the syntheses is shown in Fig. 1.

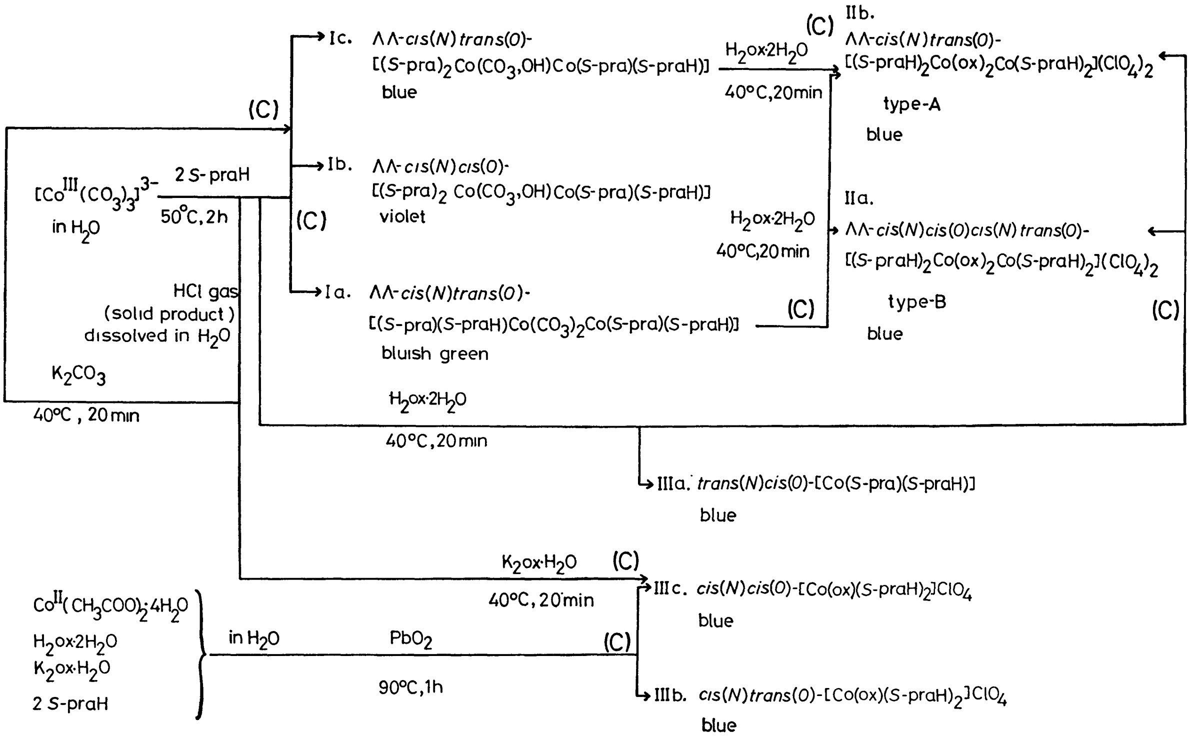

Fig. 1. Outline of the preparation. (C); Column chromatography (see the text).

Syntheses and Separation of μ-Carbonato Complexes: The tricarbonato $[Co(CO_3)_3]^{3-}$ solution (0.042 mol, 50 cm^3)[4] was heated with *S*-praH (0.1 mol) at 60 °C for 2 h and evaporated to dryness under a reduced pressure. The complexes were extracted with ethanol (300 cm^3), the solution was evaporated to dryness and the residue was extracted with a small amount of water. The aqueous solution was poured onto a column (3.5×60 cm) of Dowex 50W-X8 (Na form, 100—200 mesh). The adsorbed band was eluted with water to give three bands. The eluates were collected individually and each was evaporated to dryness under a reduced pressure at 40 °C to give higroscopic powder. The complexes were recrystallized from ethanol and found to have the following formulae. They were named Ia, Ib, and Ic in the order of elution.

Ia: [(*S*-pra)(*S*-praH)$Co(CO_3)_2Co$(*S*-pra)(*S*-praH)]·2NaHCO_3·$2H_2O$. Found: C, 26.16; H, 5.54; N, 7.06%. Calcd for $Co_2C_{14}H_{34}N_4O_{10}\cdot 2NaHCO_3\cdot 2H_2O$: C, 25.95; H, 5.45; N, 7.57%.

Ib: [(*S*-pra)$_2$Co(CO_3,OH)Co(*S*-pra)(*S*-praH)]. Found: C, 32.18; H, 7.13; N, 11.20%. Calcd for $Co_2C_{13}H_{33}N_4O_8$: C, 31.78; H, 6.77; N, 11.41%.

Ic: [(*S*-pra)$_2$Co(CO_3,OH)Co(*S*-pra)(*S*-praH)]·$2H_2O$. Found: C, 29.75; H, 7.36; N, 10.67%. Calcd for $Co_2C_{13}H_{33}N_4O_8\cdot 2H_2O$; C, 29.61: H, 7.07; N, 10.63%.

These complexes were also prepared by the following method. When the residue on the extraction of the initial reaction products with ethanol was treated with hydrogen chloride gas, blue violet hygroscopic powder was obtained with the composition [$CoCl_2$(*S*-praH)$_2$]Cl. Reaction of its aqueous solution with potassium carbonate gave a blue solution, which was treated with a similar ion exchange column to that mentioned above for separating Ia, Ib, and Ic from one another.

Syntheses and Separation of μ-Oxalato Complexes: The initial reaction mixture containing the *μ*-carbonato complexes (0.042 mol) was heated with oxalic acid (6.35 g, 0.05 mol) at 40 °C for 20 min. Blue prisms were filtered off and identified as the uninuclear complex *trans(N)cis(O)*-[Co(ox)(*S*-pra)(*S*-praH)]·0.5 H_2O. (IIIa, *vide infra*) The filtrate was submitted to column (4.5×82 cm) chromatography with SP-Sephadex C-25 and eluted with sodium perchlorate solution (0.2 mol·dm^{-3}). Three bands were observed, of which the first band was too small to be collected. Eluates from the remaining two bands were individually made acid to pH 1 with perchloric acid, and evaporated under a reduced pressure at 40 °C to decrease the volumes to *ca.* 20 cm^3. Both solutions were filtered, made pH 3 with sodium hydroxide solution (1 mol·dm^{-3}) and kept overnight in a refrigerator to give blue crystals. They were filtered off, washed with ethanol, and recrystallized from water, and named IIa and IIb in the order of elution.

IIa: [(*S*-praH)$_2$Co(ox)$_2$Co(*S*-praH)$_2$](ClO_4)$_2$·$6H_2O$. Found: C, 21.03; H, 5.00; N, 6.05%. Calcd for $Co_2C_{16}H_{36}N_4O_{10}Cl_2\cdot 6H_2O$: C, 21.32; H, 5.37; N, 6.22%.

IIb: [(*S*-praH)$_2$Co(ox)$_2$Co(*S*-praH)$_2$](ClO_4)$_2$·$2.5H_2O$. Found: C, 23.24; H, 5.38; N, 6.31%. Calcd for $Co_2C_{16}H_{36}N_4O_{10}Cl_2\cdot 2.5H_2O$: C, 22.92; H, 4.93; N, 6.69%.

Reaction of a concentrated aqueous solution of Ia with an equivalent amount of oxalic acid at 40 °C for 20 min gave a blue solution, which was treated with a similar column to that mentioned above to give two bands consisting of IIa and IIb respectively. On the other hand, when a concentrated solution of Ic was caused to react with an equivalent amount of oxalic acid at 40 °C for 20 min, a blue solution was obtained, which gave only one band consisting of IIb on a similar column chromatography.

Preparation of Uninuclear Complexes Containing Oxalate: Among the three geometrical isomers the *trans(N)cis(O)* isomer (IIIa) was obtained as shown before. The other two isomers were synthesized directly as in the following. An aqueous solution of cobalt(II) acetate (0.02 mol) was mixed with oxalic acid (0.024 mol), potassium oxalate (0.016 mol) and *S*-praH (0.048 mol) in water (total 140 cm^3). The solution was oxidized with lead dioxide (5 g) at 80—90 °C for 1 h. The product was filtered and the filtrate was poured into a column (4.5×45 cm) of SP-Sephadex C-25. The adsorbed band was eluted with sodium perchlorate solution (0.2 mol·dm^{-3}). A blue and a violet band were observed in the order of elution. Blue (IIIb) and violet (IIIc) crystals were obtained by treating the respective eluates similarly to those of the *μ*-oxalato complexes. They were assigned as follows.

IIIa: *trans(N)cis(O)*-[Co(ox)(*S*-pra)(*S*-praH)]·$0.5H_2O$. Found: C, 31.18; H, 6.36; N, 9.22%. Calcd for $CoC_8H_{17}N_2O_6\cdot 0.5H_2O$: C, 31.48; H, 5.95; N, 9.18%.

IIIb: *cis(N)trans(O)*-[Co(ox)(*S*-praH)$_2$]ClO_4·$2.5H_2O$. Found: C, 21.89; H, 5.01; N, 6.53%. Calcd for $CoC_8H_{18}N_2O_{10}Cl\cdot 2.5H_2O$: C, 21.75; H, 5.24; N, 6.34%.

IIIc: *cis(N)cis(O)*-[Co(ox)(*S*-praH)$_2$]ClO_4·H_2O. Found: C, 23.31; H, 5.13; N, 6.62%. Calcd for $CoC_8H_{18}N_2O_{10}Cl\cdot H_2O$: C, 23.17; H, 4.86; N, 6.76%.

An aqueous solution of the hygroscopic blue violet powder ([$CoCl_2$(*S*-praH)$_2$]Cl) was treated with an equivalent amount of potassium oxalate at 40 °C for 20 min to give a blue solution, which was similarly treated with a column containing SP-Sephadex C-25 to give only IIIc isomer.

Measurements. Visible and ultraviolet absorption spectra were recorded with a Hitachi 323 Recording Spectrophotometer. Circular dichroism (CD) spectra were recorded with a JASCO Model ORD/UV-5 Spectrometer with CD attachment. Proton NMR spectra were recorded with Varian T-60 and A-60 Spectrometers. A JASCO IR-A-2S Spectrophotometer was used for the measurement of infrared spectra in KBr disks. The acid dissociation constants of the complexes were determined by the titration with sodium hydroxide solution (0.1 mol·dm^{-3}) with a Metrohm Combi Titrator 3D at 25 °C and ionic strength 0.1. The pH of complex solutions for spectroscopic measurement was adjusted with perchloric acid (0.1 mol·dm^{-3}), sodium hydroxide (0.025 mol·dm^{-3}), or potassium carbonate solution (*ca.* 10^{-2} mol·dm^{-3}).

Results and Discussion

Determination of the Skeletal Structure. The skeletal structure has been identified on the basis of elemental analysis, column chromatography, and infrared (IR) spectroscopy.

Binuclear Complexes with Carbonate Bridges: Each of the complexes Ia, Ib, and Ic in aqueous solution gave an absorption peak in the region from 30000 to 31000 cm^{-1}. Hence they must have bi- or multinuclear structures. They gave antisymmetric stretching absorption of the carbonate ions in the region from 1500 to 1520 cm^{-1} in KBr disks (Fig. 2). Gatehause *et al.*[5] found that the antisymmetric CO stretching absorptions of bi- and unidentate carbonato ligands appeared in higher energy regions than 1520 cm^{-1} and 1493 cm^{-1}, respectively. The uninuclear complex *cisβ*-[$Co(CO_3)$(*N,N′*-Me_2-(*S,S*)-mhydaH)] gives the $\tilde{\nu}_{as}(CO)$ value 1600 cm^{-1}.[6] The *μ*-carbonato complex $[(NH_3)_5Co(CO_3)Co(NH_3)_5](SO_4)_2\cdot 4H_2O$ gives the $\tilde{\nu}_{as}(CO)$ value 1480 cm^{-1}.[7] Wieghardt prepared various binuclear complexes of the type $[(NH_3)_3Co(OH,OH,RCO_2)Co(NH_3)_3]^{3+}$, and found a linear relationship between the

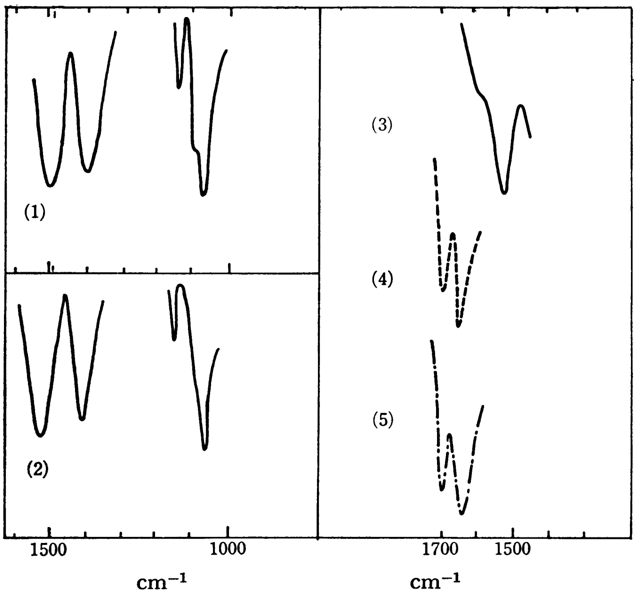

Fig. 2. IR Spectra of the binuclear complexes.
(1) $[(S\text{-pra})_2\text{Co}(\text{CO}_3,\text{OH})\text{Co}(S\text{-pra})(S\text{-praH})]\cdot 2\text{H}_2\text{O}$ (Ic).
(2) $[(S\text{-pra})(S\text{-praH})\text{Co}(\text{CO}_3)_2\text{Co}(S\text{-pra})(S\text{-praH})]\cdot 2\text{NaHCO}_3\cdot 2\text{H}_2\text{O}$ (Ia).
(3) $[(S\text{-praH})_2\text{Co}(\text{ox})_2\text{Co}(S\text{-praH})_2](\text{ClO}_4)_2\cdot 2.5\text{H}_2\text{O}$ (——) (IIb).
(4) $[(S\text{-praH})_2\text{Co}(\text{ox})_2\text{Co}(S\text{-praH})_2](\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$(----) (IIa).
(5) *trans(N)cis(O)*-$[\text{Co}(\text{ox})(S\text{-pra})(S\text{-praH})]\cdot 0.5\text{H}_2\text{O}$ (—·—) (IIIa).

$\tilde{\nu}_{\text{as}}$(CO) in cm^{-1} and the pK_a value of the carboxylic acid.[8] The $\tilde{\nu}_{\text{as}}$(CO)'s observed for the present binuclear complexes fall on the same line. On the basis of these facts the carbonate ligands in our complexes can be reckoned to bridge two cobalt(III) ions. Reactions with oxalic acid converted all the μ-carbonato complexes into μ-oxalato complexes (Fig. 1). This fact also supports binuclear structure of the carbonato complexes.

Nakamoto *et al.* measured the IR spectrum of the binuclear complex $\text{K}_4[(\text{ox})_2\text{Co}(\text{OH})_2\text{Co}(\text{ox})_2]$, and assigned the band near 1100 cm^{-1} to the Co–O–H bending.[9] Both the complexes Ib and Ic give the same absorption bands. Thus hydroxide ions must bridge two cobalt(III) ions in these complexes. The complex Ia gives no such IR absorption band. On the basis of these data we give the formulae to Ia, Ib, and Ic as mentioned before.

Binuclear Complexes Bridged by Oxalate: Chromatographic behavior of IIa and IIb and the presence of UV absorption bands in 30000—31000 cm^{-1} suggest that they have binuclear structure. The pH titration and IR spectra indicate the absence of unidentate ligands. Hence these complexes should be doubly bridged.

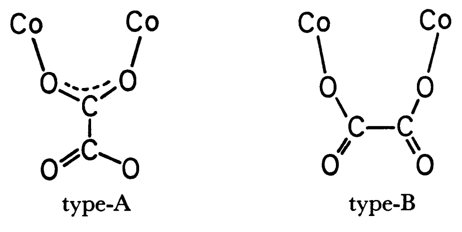

Fig. 3. Types of the bridging oxalate.

The oxalate can bridge cobalt(III) in two ways as shown in Fig. 3; *i.e.* by coordinating to two cobalt(III) through two oxygen atoms on one carbon atom (Type-A), or through two oxygens on different carbon atoms (Type-B). IR Spectroscopy was useful for distinguishing these bridges. Scott *et al.* found the $\tilde{\nu}$(CO) of oxalate in the Type-A bridging binuclear complex $[(\text{NH}_3)_4\text{Co}(\text{NH}_2,\text{ox})\text{Co}(\text{NH}_3)_4]^{3+}$ at 1640 and 1616 cm^{-1} and in $[(\text{NH}_3)_3\text{Co}(\text{OH},\text{OH},\text{ox})\text{Co}(\text{NH}_3)_3]^{2+}$ at 1634 and 1600 cm^{-1}.[10] The complex IIb gave $\tilde{\nu}$(CO)'s 1620 and 1570 cm^{-1} (Fig. 2). These are slightly lower in wave number than those of Scott *et al*'s complexes. However, such a shift can be caused by the difference in other bridging ligands between ours and theirs. So we conclude that IIb has two bridging oxalates of Type-A.

The complex IIa gave $\tilde{\nu}$(CO) 1700 and 1675 cm^{-1} (Fig. 2). These wave numbers are similar to those of the five-membered oxalate chelate. However, we tend to consider that the oxalates in this complex bridge two cobalt(III) through Type-B by the following reasons. First, the Type-B bridge will have a similar electronic state to chelating oxalate, so that the $\tilde{\nu}$(CO) can be similar to that of chelating oxalate. Scott *et al.* observed four $\tilde{\nu}$(CO)'s, 1721, 1701, 1629, and 1670 cm^{-1} for the Type-B binuclear complex $[(\text{NH}_3)_5\text{Co}(\text{ox})\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_4]^{4+}$.[10] They considered these bands to be the split peaks of the two bands of chelated oxalate at 1696 and 1667 cm^{-1} in $[\text{Co}(\text{ox})(\text{NH}_3)_4]^+$. IR peaks of our complex fail to show such a splitting, presumably because of the increase in symmetry around the bridging moiety. Second, an alcohol is a weaker ligand than amines and carboxylates toward cobalt(III). If amino alcohols doubly bridged two cobalt(III), the Co–O bonds would be compared to those between Co(III) and (*O*-coordinated) unidentate amino alcohol. Further, each cobalt(III) in such a complex is considered to be chelated by a large chelate ring consisting of two amino alcohols and one cobalt(III). Such a ring may not be stable enough to give a crystalline product. Thus we conclude the structure of IIa and IIb as shown before.

Uninuclear Complexes Containing Oxalates: The complexes IIIa, IIIb, and IIIc gave $\tilde{\nu}$(CO) values of oxalate ligands *ca.* 1700 and 1667 cm^{-1} (Fig. 3). Absence of UV peaks in the 30000 cm^{-1} region, as well as their chromatographic behavior, indicates that these complexes are uninuclear.

Synthetic Method. The tricarbonato method has been recognized as a very useful tool for preparing a variety of uninuclear cobalt(III) complexes containing bidentate carbonate. These products are also useful intermediates for synthesizing further varieties of uninuclear complexes containing other ligands.[4] However, no binuclear complexes have ever been known among the products. We have succeeded in preparing a few binuclear species with carbonate bridges and thus extended the usefulness of this method to the preparation of binuclear complexes.

Reactions of oxalic acid with such binuclear complexes under a mild condition gave binuclear species bridged by oxalate. These reactions appear to involve local substitution of the bridging part.

Table. Numerical data of absorption (AB) and CD spectra uninuclear oxalato complexes

Geometrical isomerism			I band		II band	
			AB $\tilde{\nu}/10^3\ \mathrm{cm}^{-1}$ (log ε)	CD $\tilde{\nu}/10^3\ \mathrm{cm}^{-1}$ ($\Delta\varepsilon$)	AB $\tilde{\nu}/10^3\ \mathrm{cm}^{-1}$ (log ε)	CD $\tilde{\nu}/10^3\ \mathrm{cm}^{-1}$ ($\Delta\varepsilon$)
IIIa	*trans*(*N*) *cis*(*O*)	a	17.61(1.81) 19.88(1.83)	16.05(+1.12) 18.69(−1.25)	25.13(2.12)	27.47(+0.4)
		b	17.57(2.14)	16.13(+0.64) 18.12(−2.05)	23.06(2.07) sh. 28.17(2.10)	23.70(+1.74)
IIIb	*cis*(*N*) *trans*(*O*)	a	17.92(2.03)	18.02(−0.51)	24.81(2.21)	25.32(+0.11)
		b	18.12(2.17)	17.86(−1.18)	sh. 23.60(2.26) sh. 25.20(2.29)	22.94(+1.17)
IIIc	*cis*(*N*) *cis*(*O*)	a	18.38(1.99)	16.67(+0.52) 19.23(−0.62)	26.11(2.18)	25.77(+0.22)
		b	18.08(2.11)	15.92(+0.84) 18.45(−1.69)	25.13(2.30)	23.47(+1.50)

a: Protonated form $[Co(ox)(S\text{-praH})_2]^+$. b: Deprotonated form $[Co(ox)(S\text{-pra})_2]^-$.

Acid-base Equilibria. The uninuclear complexes IIIb and IIIc were titrated with sodium hydroxide, and their pK_1 and pK_2 values were determined to be *ca.* 3.2 and *ca.* 6, respectively, at 25 °C and ionic strength 0.1. The pK_1 values are similar to the pK_a values of uninuclear complexes containing one amino alcohol.[1,2] The pK_2 values are similar to the pK_a values of aqua ligands in various cobalt(III) complexes. The pK_a values of other complexes were not determined by technical reasons. These data, as well as the pH dependence of the absorption and CD spectra, and the chromatographic behavior, indicate that all the complexes containing oxalate have *S*-praH ligands in protonated form in an aqueous solution of pH$\leq$1, and in completely deprotonated form at pH$\geq$9. μ-Carbonato complexes are only stable in aqueous solutions of pH$\geq$7, so that the amino alcohol logands are in deprotonated forms.

Geometrical Isomerism and Absorption Spectra of the Uninuclear Complexes. Octahedral cobalt(III) complexes containing two *S*-praH and one oxalate exist in three geometrical isomers, *trans*(*N*)*cis*(*O*), *cis*(*N*)*trans*(*O*), and *cis*(*N*)*cis*(*O*), which have C_2, C_2, and C_1 symmetry, respectively. The absorption spectra of protonated and deprotonated forms of IIIa, IIIb, and IIIc are shown in Fig. 4. Change in pH always brings about reversible change of the absorption spectra between the protonated and the deprotonated form. IIIa in the protonated form gives split bands in the first band region and is assigned to *trans*(*N*)*cis*(*O*) isomer. IIIb and IIIc give similar absorption patterns to each other. The IIIc isomer gives more complicated methyl signals in the pmr spectra than the IIIb isomer does, so that they are assinged to *cis*(*N*)*cis*(*O*) and *cis*(*N*)*trans*(*O*) isomer, respectively.

Data of the absorption and CD spectra in the d-d transition region are shown in the Table for both the protonated and the deprotonated form of the complexes. The locations of absorption peaks of the protonated forms are almost equal to those of the corresponding isomers of $[Co(ox)(gly)_2]^-$ (gly=glycinate ion).[11] Hence the alcoholic hydroxyl group has the same position in the spectrochemical series with carboxylates.

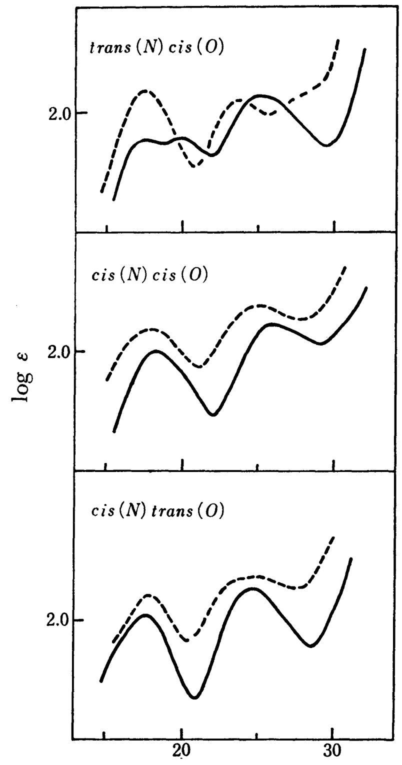

Fig. 4. Absorption spectra of geometrical isomers of $[Co(ox)(S\text{-praH})_2]^+$ (protonated form) (——) and $[Co(ox)(S\text{-pra})_2]^-$ (deprotonated form) (----).

On deprotonation of the hydroxyl groups, peaks in the first band region change in quite characteristic ways depending on the geometrical isomerism. Split peaks of the *trans*(*N*)*cis*(*O*) isomer unite apparently into one peak. The *cis*(*N*)*trans*(*O*) isomer gives blue shift, whereas the *cis*(*N*)*cis*(*O*) isomer red shift. (In the [CoN_5O] type complex containing one (*S*)-2-amino-1-propanol, the peak in the first band region gives blue shift in a basic solution[2]). In the second band region, the peaks of *trans*(*N*)*cis*(*O*) and *cis*(*N*)*trans*(*O*) isomers split on deprotonation. The *cis*(*N*)*cis*(*O*) isomer gives apparently only a broad band. Since all these absorption bands consist of more than one component, the deprotonation brings about not only splitting but also shift and intensity change of the component peaks. It also causes increase in number of lone pair electrons on coordinating oxygen atoms. These factors give influence in a complicated manner, to result in very diverse change in the absorption pattern.

CD Spectra of the Uninuclear Complexes. Attempts to resolve the isomers were unsuccessful. Intensity of the PMR methyl signals of IIIb and IIIc suggests that these complexes consist of almost equal amounts of Δ- and Λ-isomers. Hence their CD patterns should reflect the vicinal contribution of *S*-praH and *S*-pra$^-$.

In the first band region, large minus components are commonly seen for both protonated and deprotonated forms of all the geometrical isomers. Such minus components reflect δ-conformation of the *S*-praH or *S*-pra$^-$ chelate.[1,2] The $\Delta\varepsilon$ values are large for the deprotonated than for protonated forms. These facts were also seen in [CoN$_5$O] type complexes with one optically active amino alcohol.[2] The spectral patterns are, however, different among the geometrical isomers. They should be dependent on the symmetry, and related to the change in absorption patterns.

In the second band region, the change of CD pattern with pH is more marked than in the first band region. All the three isomers in the deprotonated form give characteristic large plus components at 23000 to 24000 cm^{-1}. Such a marked plus CD was also observed in the deptonated forms of [CoN$_5$O] type complexes. We considered that it reflected δ-conformation of *S*-pra$^-$ and the unusually large $\Delta\varepsilon$ values in this region were related to the presence of three lone pairs in alcoholate –O$^-$ moiety.[2] The same consideration is

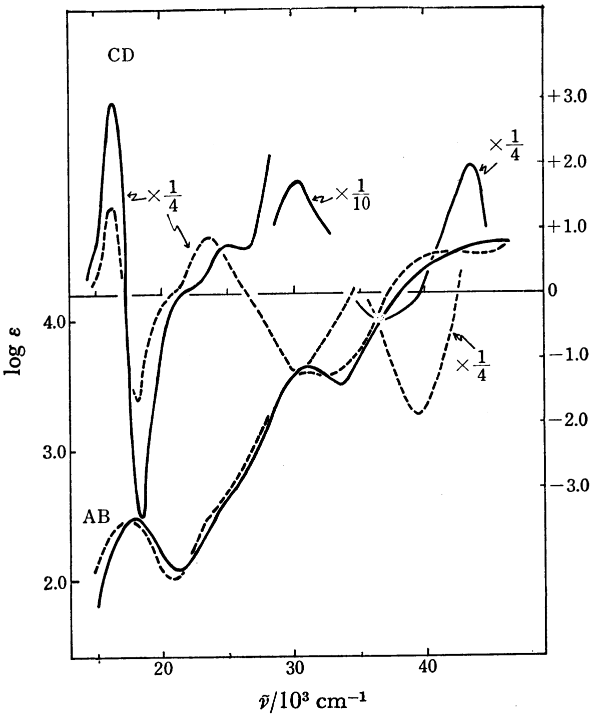

Fig. 5. Absorption and CD spectra of [(S-praH)$_2$Co(ox)$_2$Co(S-praH)$_2$]$^{2+}$ (——) and [(S-pra)$_2$Co(ox)$_2$Co(S-pra)$_2$]$^{2-}$ (------) (IIb).

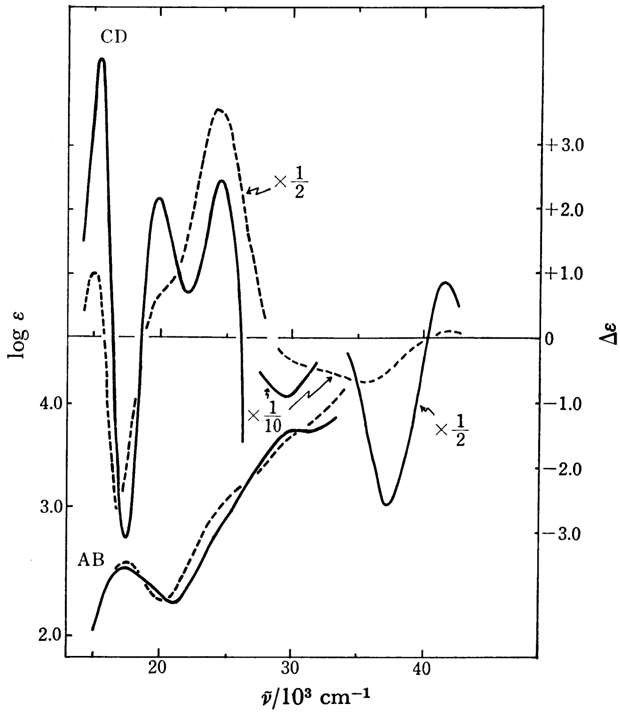

Fig. 6. Absorption and CD spectra of [(S-praH)$_2$Co(ox)$_2$Co(S-praH)$_2$]$^{2+}$ (——) and [(S-pra)$_2$Co(ox)$_2$Co(S-pra)$_2$]$^{2-}$ (------) (IIa).

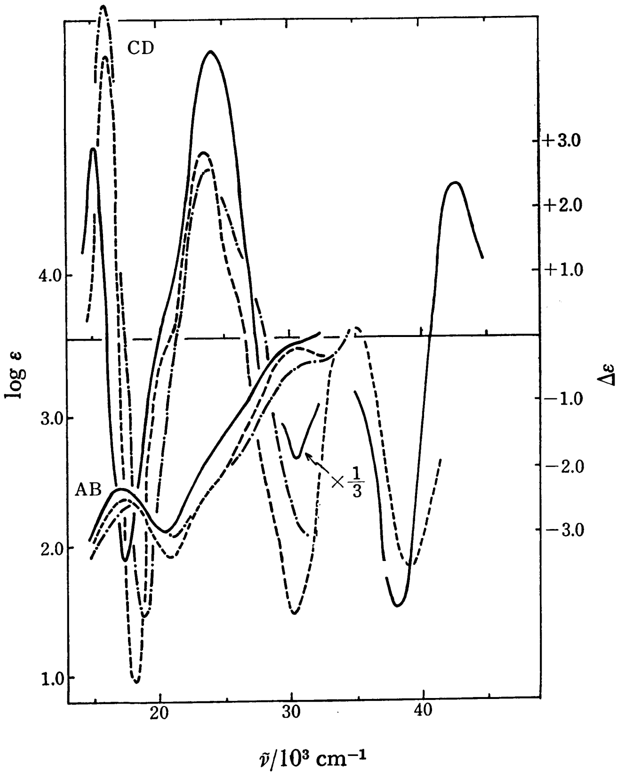

Fig. 7. Absorption and CD spectra of μ-carbonato complexes.
[(S-pra)$_2$Co(CO$_3$)$_2$Co(S-pra)$_2$]$^{2-}$ (——) (Ia),
[(S-pra)$_2$Co(CO$_3$,OH)Co(S-pra)$_2$]$^-$ (—•—) (Ib), and
[(S-pra)$_2$Co(CO$_3$,OH)Co(S-pra)$_2$]$^-$ (------) (Ic).

applicable to the present complexes containing two *S*-pra$^-$ ligands.

Geometrical Isomerism and CD Spectra of the Binuclear Complexes. A large number of geometrical isomers can exist for such types of binuclear complexes. Only two μ-oxalato complexes and three μ-carbonato complexes have been obtained. Attempts to assign the crystalline products to individual isomers have turned out unsuccessful, because of too complicated absorption and CD patterns.

The CD spectra of μ-oxalato complexes are shown in Figs. 5 and 6, and those of μ-carbonato complexes in Fig. 7. Each of these complexes gives a large plus component in the first band region. It must be due to the $\Lambda\Lambda$-configurational effect around cobalt(III). It appears as if the $\Lambda\Lambda$-isomers were preferentially formed. The reason may be related to the larger stability of lel- than ob-structure, because the chelated *S*-praH ligands give δ-conformation exclusively.

There is one common characteristic pattern in the second band region; *i.e.* the deprotonated forms give remarkable plus CD components. The $\Delta\varepsilon$ values are nearly equal to four times of that of [Co(*S*-pra)(NH_3)$_4$]$^{2+}$ ($\Delta\varepsilon$=0.85). The vicinal effect of *S*-pra$^-$ ligand in the second band region does not appear to be much affected by the skeletal structure throughout all the cobalt(III) complexes.

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