Circular Dichroism Spectra of Cobalt(III) Complexes Containing Amino-Alcohols

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Several cobalt(III) complexes containing amino-alcohol (amOH) chelate rings, $[Co(amOH)(NH_3)_4]X_3$, $[Co(amOH)(en)_2]X_3$ and $[Co(amOH)(R\text{-chxn})_2]X_3$ (en=ethylenediamine, chxn=*trans*-1,2-diaminocyclohexane, $X^-=Cl^-$, Br^- or ClO_4^-, amOH=2-aminoethanol, 2-amino-1-propanol, 1-amino-2-propanol, *etc.*) were synthesized and separated into optical isomers. Their circular dichroism (CD) spectra change remarkably by the change in pH of the solution. The changes were ascribed to the dissociation of the alcoholic proton of coordinated amOH. The complexes containing a deprotonated chiral amO^- chelate ring exhibit strong vicinal CD bands in the first and second absorption band region. The signs and the magnitudes of these CD bands seem to depend mainly on the conformation of the amO^- chelate ring.

Extensive studies have been made on the circular dichroism (CD) spectra of cobalt(III) complexes containing diamine and aminocarboxylate chelate rings.[1] However there has been little work on the optical activity of amino-alcohol complexes.[2,3] In the previous communication,[3] we reported CD spectra of *Λ*-$[Co(etaH)(en)_2]^{3+}$ (etaH=2-aminoethanol, en=ethylenediamine) and *Δ*- and *Λ*-$[Co(S\text{-praH})(en)_2]^{3+}$ (praH=2-amino-1-propanol) complexes. The CD behavior of these complexes was found to be considerably different from that of $[Co(diamine)_3]^{3+}$ or $[Co(am)(en)_2]^{2+}$ (am^-=aminocarboxylate ion); the deprotonated *S*-pra^- chelate ring gives an exceptionally large vicinal contribution to the optical activity. We have extended the work to several other coablt(III) complexes containing an amino-alcohol chelate ring.

Experimental

Ligands.† Amino-alcohols except *S*-leucinol and *S*-2-amino-1-propanol were obtained commercially. *S*-Leucinol was kindly supplied by Mr. K. Ohashi of Ibaragi University. *S*-2-Amino-1-propanol was synthesized by the method of Vogl and Pöln.[4] *trans*-1,2-Diaminocyclohexane(chxn) was resolved into optical isomers by the method of Treptow.[5]

Syntheses of Aminoalcoholtetraammine Complexes, $[Co(amOH)(NH_3)_4]X_3$ (amOH=etaH, *S*-praH, *S*-leuH, *R*-abnH *and R and S*-isopraH). The etaH complex was prepared by the following procedure. $[CoCl(H_2O)(NH_3)_4]SO_4$ (2 g) was added to a mixture of 1 M sodium hydroxide (5 ml), water (1 ml), 2-aminoethanol (0.4 ml) and one drop of 28% aqueous ammonia. The solution was heated at 65—75 °C for 2.5 hr, cooled in an ice bath for 1 hr, and filtered. The filtrate was passed through a column ($\phi 2 \times 20$ cm) containing the anion exchanger Dowex 1X4 in the bromide form. The eluate was treated with hydrobromic acid to adjust the pH to 1—2 and evaporated to dryness under reduced pressure at 40—50 °C. The residue was dissolved again in about 40 ml of water and filtered. Addition of a few drops of 40% hydrobromic acid to the filtrate gave orange crystals, which were filtered off, washed with methanol and air-dried. Recrystallization was carried out from water containing hydrobromic acid. Found: C, 5.71; H, 4.65; N, 16.66%. Calcd for $CoC_2H_{19}N_5OBr_3$: C, 5.61; H, 4.48; N, 16.37%.

Other complexes, $(-)_D$-$[Co(S\text{-praH})(NH_3)_4]Cl_3$, $(-)_D$-$[Co(S\text{-leuH})(NH_3)_4]Cl_3 \cdot 3H_2O$, $(+)_D$-$[Co(R\text{-abnH})(NH_3)_4]Cl_3 \cdot H_2O$ and $[Co(R,S\text{-isopraH})(NH_3)_4](ClO_4)_3$ were synthesized by a method similar to that for the etaH complex. For *S*-praH complex, Found: C, 11.43; H, 7.07; N, 22.77%. Calcd for $CoC_3H_{21}N_5OCl_3$: C, 11.68; H, 6.86; N, 22.70%. For *S*-leuH complex; Found: C, 17.91; H, 7.97; N, 17.74%. Calcd for $CoC_6H_{32}N_5O_4Cl_3$: C, 17.85; H, 7.99; N, 17.35%. For *R*-abnH complex; Found: C, 14.15; H, 7.66; N, 20.32%, Calcd for $CoC_4H_{25}N_5O_2Cl_3$: C, 14.12; H, 7.40; N, 20.57%. For *R,S*-isopraH complex; Found: C, 7.57; H, 4.08; N. 13.99%. Calcd for $CoC_3H_{21}N_5O_{13}$: C, 7.20; H, 4.23; N, 14.00%.

The complex $(-)_D$-$[Co(R\text{-isopraH})(NH_3)_4]Cl_3 \cdot 2.5H_2O$ was obtained by the following method. $[Co(R,S\text{-isopraH})(NH_3)_4](ClO_4)_3$ (0.4 g) was adsorbed on an SP-C-25 Sephadex column ($\phi 5 \times 95$ cm) and eluted with 0.2 M potassium antimony *d*-tartrate at a rate of 0.6 ml/min. The column gave two separated orange bands. The $(-)_D$-isomer was eluted first and the $(+)_D$-isomer followed. The antimony *d*-tartrate salt of the $(-)_D$-isomer was converted into chloride by passing the first eluate through a column ($\phi 2 \times 10$ cm) of SP-C-25 Sephadex, and eluting the adsorbed band with 0.5 M hydrochloric acid. The eluate was evaporated to a small volume under reduced pressure below 35 °C, and filtered. The filtrate was dried up in a vacuum desiccator over diphosphorus pentoxide. The complex was hygroscopic powder. Found: C, 10.41; H, 7.30; N, 19.87%. Calcd for $CoC_3H_{26}N_5O_{3.5}Cl_3$: C, 10.19; H, 7.41; N, 19.81%. $(+)_D$-$[Co(S\text{-isopraH})(NH_3)_4]Br_3 \cdot 2.5H_2O$ was obtained similarly from the second eluate described above by use of a column containing anion exchanger Dowex 1X4 in bromide form. Found: C, 7.01; H, 5.48; N, 14.67%. Calcd for $CoC_3H_{26}N_5O_{3.5}Br_3$: C, 7.39; H, 5.38; N, 14.38%.

Syntheses of Aminoalcoholbis(ethylenediamine) Complexes. a) *cis*-$[CoBr(R,S\text{-isopraH})(en)_2]Br_2$. To *trans*-$[CoBr_2(en)_2]Br$ (5 g) in dimethyl sulfoxide (DMSO) (100 ml) was added *R,S*-isopraH (0.9 g) with stirring. The solution was stirred overnight and filtered. Ethanol and ether were added to the solution and then it was kept in a refrigerator for crystallization. Red-violet crystals were collected, washed with ethanol and air-dried. Found: C, 17.30; H, 5.34; N, 13.90 %. Calcd for $CoC_7H_{25}N_5OBr_3$: C, 17.02; H, 5.10; N, 14.18%.

b) $[Co(R,S\text{-isopraH})(en)_2]Br_3 \cdot 2.5H_2O$ and $[Co(N\text{-MeetaH})(en)_2]Cl_3 \cdot 2H_2O$. These complexes were prepared

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† The following abbreviations are used: etaH=2-aminoethanol, praH=2-amino-1-propanol, isopraH=1-amino-2-propanol, leuH=leucinol, abnH=2-amino-1-butanol, *N*-MeetaH=*N*-methylethanolamine.

TABLE 1. NUMERICAL DATA OF ABSORPTION AND CD SPECTRA OF AMINO-ALCOHOL COMPLEXES

Complex[a]	I band				II band			
	Absorption		CD		Absorption		CD	
	$\bar{\nu}/10^3$ cm^{-1}	log ε	$\bar{\nu}/10^3$ cm^{-1}	$\Delta\varepsilon$	$\bar{\nu}/10^3$ cm^{-1}	log ε	$\bar{\nu}/10^3$ cm^{-1}	$\Delta\varepsilon$
[Co(etaH)$(NH_3)_4$]$^{3+}$	20.12	1.82			29.10	1.89		
[Co(eta)$(NH_3)_4$]$^{2+}$	20.04	1.99			27.60	2.06		
[Co(*S*-praH)$(NH_3)_4$]$^{3+}$	20.12	1.77	18.45	+0.21	29.10	1.84		
			21.01	−0.36				
[Co(*S*-pra)$(NH_3)_4$]$^{2+}$	20.04	1.99	17.86	+0.17	27.60	2.04	24.80	+0.85
			20.20	−1.18				
[Co(*S*-leuH)$(NH_3)_4$]$^{3+}$	20.12	1.81	18.42	+0.21	29.10	1.87		
			21.14	−0.45				
[Co(*S*-leu)$(NH_3)_4$]$^{2+}$	20.04	2.00	17.89	+0.17	27.62	2.08	25.00	+1.04
			20.33	−1.36				
[Co(*R*-isopraH)$(NH_3)_4$]$^{3+}$	20.10	1.78	18.69	−0.44	29.07	1.86	28.57	+0.04
			21.51	+0.33				
[Co(*R*-isopra)$(NH_3)_4$]$^{2+}$	20.04	1.96	17.93	−0.60	27.62	2.05	25.00	−1.25
			20.33	+1.82				
[Co(*R*-abnH)$(NH_3)_4$]$^{3+}$	20.16	1.76	18.52	−0.26	28.74	1.83		
			21.10	+0.51				
[Co(*R*-abn)$(NH_3)_4$]$^{2+}$	20.04	1.99	17.86	−0.20	27.62	2.04	25.00	−1.18
			20.20	+1.58				
Λ-[Co(etaH)$(en)_2$]$^{3+}$	20.40	1.95	19.61	+1.96	28.80	1.99	26.67	+0.14
Λ-[Co(eta)$(en)_2$]$^{2+}$	20.20	2.05	18.87	+1.93	sh. 25.6	2.04	25.97	+0.45
			21.83	−0.68	28.40	2.09	sh. 28.6	+0.18
Λ-[Co(*S*-praH)$(en)_2$]$^{3+}$	20.53	1.94	19.22	+1.74	29.33	2.05	26.52	+0.20
			22.42	−0.12			29.6	+0.11
Λ-[Co(*S*-pra)$(en)_2$]$^{2+}$	20.37	2.06	18.50	+1.72	sh. 25	1.95	25.25	+1.16
			21.22	−1.52	28.82	2.09		
Δ-[Co(*S*-praH)$(en)_2$]$^{3+}$	20.49	1.94	20.41	−2.01	29.07	2.05	28.33	+0.13
Δ-[Co(*S*-pra)$(en)_2$]$^{2+}$	20.37	2.06	20.00	−2.82	sh. 25	1.95	24.88	+1.33
					28.65	2.09		
Λ-[Co(*R*-isopraH)$(en)_2$]$^{3+}$	20.28	1.95	20.58	+1.88	28.90	2.01	28.57	−0.11
Λ-[Co(*R*-isopra)$(en)_2$]$^{2+}$	20.12	2.02	sh. 17.54	+0.37	sh. 25.6	1.99	24.69	−1.55
			20.08	+3.13	28.40	2.12		
Λ-[Co(*S*-isopraH)$(en)_2$]$^{3+}$	20.03	1.95	19.46	+2.44	28.82	1.99	26.67	+0.13
Λ-[Co(*S*-isopra)$(en)_2$]$^{2+}$	20.22	2.04	18.48	+2.68	sh. 25.6	2.05	25.25	+1.55
			21.19	−1.97	29.85	2.09		
[Co(*N*-MeetaH)$(en)_2$]$^{3+}$	20.22	1.99			28.50	2.01		
[Co(*N*-Meeta)$(en)_2$]$^{2+}$	20.04	2.04			sh. 25.2	1.95		
					28.30	2.04		
[Co(*N*-Meeta)$(en)_2$]$^{2+}$ [b]	20.04	2.04			sh. 25.2	1.95		
					28.30	2.04		
Δ-[Co(etaH)(*R*-chxn)$_2$]$^{3+}$	20.24	1.94	19.05	−2.44	28.74	1.99	26.32	−0.09
Δ-[Co(eta)(*R*-chxn)$_2$]$^{2+}$	20.20	2.04	18.45	−2.69	sh. 25.6	2.02	25.32	−1.20
			21.28	+1.73	27.78	2.10		
Δ-[Co(*S*-praH)(*R*-chxn)$_2$]$^{3+}$	20.10	1.92	19.88	−2.40	28.61	1.97	28.01	+0.15
Δ-[Co(*S*-pra)(*R*-chxn)$_2$]$^{2+}$	20.00	2.06	19.65	−3.32	27.93	2.05	24.51	+1.48

a) The spectra of [M(amOH)]$^{3+}$ complexes were obtained by dissolving the salt of [M(amOH)]$^{3+}$ in acidic solutions (pH<2), and those of [M(amO)]$^{2+}$ complexes in solutions whose pH is above 5, unless otherwise stated.
b) Spectral data were obtained in an aqueous solution of [Co(*N*-Meeta)$(en)_2$]$(ClO_4)_2$.

by a method similar to that for [Co(etaH)$(en)_2$]$Br_3\cdot H_2O$ by Buckingham *et al.*[6] Anal. For 1-amino-2-propanol complex; Found: C, 15.21; H, 5.25; N, 13.11%. Calcd for $CoC_7H_{30}N_5O_{3.5}Br_3$: C, 15.60; H, 5.61; N, 13.00%. For *N*-methylethanolamine complex, Found: C, 20.89; H, 7.71; N, 17.80%. Calcd for $CoC_7H_{29}N_5O_3Cl_3$: C, 21.20; H, 7.37; N, 17.66%.

c) [Co(*N*-Meeta)$(en)_2$]$(ClO_4)_2$. This complex was obtained by adding lithium perchlorate to an aqueous solution of [Co(*N*-MeetaH)$(en)_2$]$Cl_3\cdot 2H_2O$ neutralized with sodium hydroxide. Found: C, 18.60; H, 5.66; N, 15.38%. Calcd for $CoC_7H_{24}N_5O_9Cl_2$: C, 18.59; H, 5.35; N, 15.49%.

*Separation of Λ,Δ-[Co(*R,S*-isopraH)(en)$_2$]$^{3+}$ Complexes.* a) *Λ*-(+)$_D$-[Co(*R*-isopraH)$(en)_2$]$Cl_3\cdot 3H_2O$. *Λ,Δ*-[Co(*R,S*-iso-

praH)(en)$_2$]Br$_3$·2.5H$_2$O was separated into four isomres by means of column chromatography. Two grams of the complex was adsorbed on an SP-C-25 Sephadex column (ϕ 3×90 cm) and the adsorbed orange band was eluted with 0.2M potassium antimony *d*-tartrate at a rate 0.5 ml/min. The eluate was fractionated into 25 ml portions. The CD spectrum of each fraction was checked, and the fractions were grouped into three parts (A,B,C) in the order of elution. The first part (A), about one tenth of the total eluate, was poured on an SP-C-25 Sephadex column (ϕ3×96 cm) again and eluted with 0.2 M potassium antimony tartrate. First several portions of the eluate showed the same CD curves. They were combined, adsorbed on an SP-C-25 Sephadex column (ϕ 1.7×10 cm) and eluted with 0.5 M hydrochloric acid. The eluate was evaporated to a small volume under reduced pressure below 35 °C, filtered and stored in a vacuum desiccator over diphosphorus pentoxide. The hygroscopic powder thus obtained was assigned to *Λ*-[Co(*R*-isopraH)(en)$_2$]Cl$_3$·3H$_2$O as shown later. Found: C, 20.50; H, 7.60; N, 16.37%. Calcd for $CoC_7H_{31}N_5O_4Cl_3$: C, 20.58; H, 7.54; N, 16.89%.

b) *Λ*-(+)$_D$-(*S*-isopraH)(en)$_2$](ClO$_4$)$_3$. The last a few fractions of the eluate(A) in the second elution (with 0.2 M potassium antimony tartrate) described above were found to contain only one isomer by measurement of CD. These portions were combined and passed through the anion exchange resin column containing Dowex 1X8 in the perchlorate form to give perchlorate salt. The hygroscopic powder was assigned to *Λ*-[Co(*S*-isopraH)(en)$_2$](ClO$_4$)$_3$ as shown later. Found: C, 15.38; H, 4.72; N, 12.71%. Calcd for $CoC_7H_{35}N_5O_{13}Cl_3$: C, 15.21; H, 4.56; N, 12.68%.

The fractions B and C mentioned in (a) were found to be mixtures of *Λ*-[Co(*S*-isopraH)(en)$_2$]$^{3+}$ and *Δ*-[Co(*S*-isopraH)(en)$_2$]$^{3+}$, and *Δ*-[Co(*S*-isopraH)(en)$_2$]$^{3+}$ and *Δ*-[Co(*R*-isopraH)(en)$_2$]$^{3+}$ isomers respectively. But the latter two isomers were not isolated.

*Syntheses of Aminoalcoholbis(*R-trans-*1,2-diaminocyclohexane)-complexes.* *a)* *Λ*-(−)$_D$-[Co(etaH)(*R*-chxn)$_2$](ClO$_4$)$_3$. A mixture of *trans*-[CoCl$_2$(*R*-chxn)$_2$]Cl[5] (1 g) and 2-aminoethanol (0.2 ml) in DMSO (50 ml) was stirred for two days. The solution was treated with ethanol (150 ml) and ether (700 ml) and kept in an ice bath for 6 hr. The supernatant was decanted and the remaining oily residue was dissolved again in water (50 ml) and hydrolyzed at pH 9 (pH-stat) with 1 N sodium hydroxide. After 2 hr, the pH of the solution was adjusted to 1.5 with 6 M hydrochloric acid. The solution was evaporated to a small volume under reduced pressure at 40 °C and passed through an SP-C-25 Sephadex column (ϕ3×77 cm). Elution with a mixture of 0.15 M sodium *d*-tartrate and 0.09 M hydrochloric acid gave several portions showing the same CD curves, which were combined and concentrated under reduced pressure. After removal of sodium salt by filtration, 60% perchloric acid and sodium perchlorate were added to the filtrate. Orange crystals were filtered off and dried in air. The CD specturm remains unchanged after three times recrystallization from water. The absolute configuration of this complex was assigned to *Λ* as shown later. Found: C, 26.20; H, 5.72; N, 10.54%. Calcd for $CoC_{14}H_{35}N_5O_{13}Cl_3$: C, 26.00; H, 5.46; N, 10.83%.

b) *Δ*-(−)$_D$-[Co(*S*-praH)(*R*-chxn)$_2$](ClO$_4$)$_3$. This complex was synthesized by a method similar to that for the etaH complex (a) using *S*-praH instead of etaH and purified by recrystallization from water. Found: C, 27.18; H, 5.77; N, 10.33%. Calcd for $CoC_{15}H_{37}N_5O_{13}Cl_3$: C, 27.26; H, 5.64; N, 10.60%.

Measurements. The absorption spectra were recorded with a Hitachi 323 Recording Spectrophotometer. The CD spectra were obtained with a JASCO Model ORD/UV-5 Spectrometer with CD attachment. The pH of the solution was adjusted to appropriate values either with perchloric acid or with sodium hydroxide solution. The acid dissociation constants of the complexes were determined with a Metrohm Combi Titrator 3D at 25 °C.

Results and Discussion

Acid-base Equilibria of Amino-alcohol Complexes. Absorption and CD spectra of the amino-alcohol complexes obtained in this work changed markedly with change in pH of the solution. The spectra of *S*-2-amino-1-propanoltetraammine complex at three pH's are shown in Fig. 1. Several isosbestic points are observed. The spectral changes are instantaneous and reversible, and attributed to an acid-base equilibrium of the alcoholic proton:

$$M(amOH)^{3+} \rightleftharpoons M(amO)^{2+} + H^+$$

where M denotes Co(diamine)$_2$ or Co(NH$_3$)$_4$ moiety. pH Titration of the complexes gave pK_a values of *ca.* 3.6, 3.2 and 3.2 for [Co(amOH)(NH$_3$)$_4$]$^{3+}$ (amOH =etaH, *S*-praH, *S*-leuH, *S*-abnH and isopraH), [Co(amOH)(en)$_2$]$^{3+}$ (amOH=etaH, *S*-praH and isopraH) and [Co(*S*-praH)(*R*-chxn)$_2$]$^{3+}$, respectively at 25 °C and ionic strength *ca.* 0.05. Thus the spectra of these complexes at pH below ~2 should be those of the protonated form, M(amOH)$^{3+}$ and the spectra at pH above~5 those of the deprotonated form, M(amO)$^{2+}$. The absorption spectrum of [Co(*N*-Meeta)(en)$_2$](ClO$_4$)$_2$ in an aqueous solution was almost identical with that of [Co(*N*-MeetaH)(en)$_2$]Cl$_3$·H$_2$O in an alkaline solution. This result supports the existence of acid-base equilibria. The reversible change of CD spectra upon pH change implies that the racemization or epimerization of the present amino-alcohol complexes is slow. Low pK_a values of hydroxyl group of coordinated alcohols have been reported for several complexes.[6,7]

Numerical data of the absorption and CD spectra of the complexes are shown in Table 1.

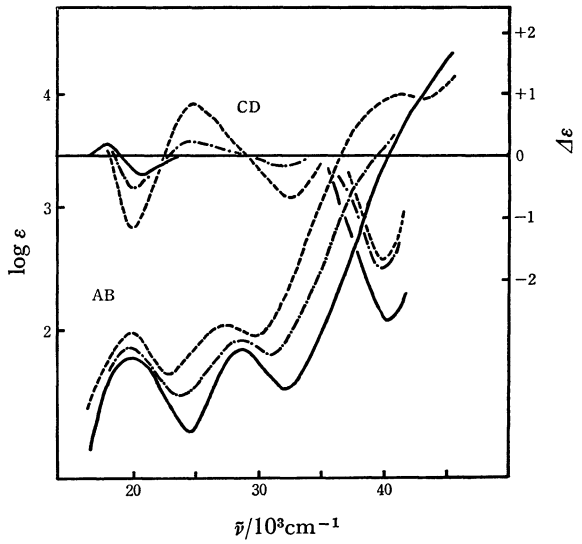

Fig. 1. Absorption and CD spectra of (-)$_D$-[Co(*S*-praH)(NH$_3$)$_4$]Cl$_3$ at pH 1.36 (——), at pH 2.75 (—·—) and at pH 9.50 (----).

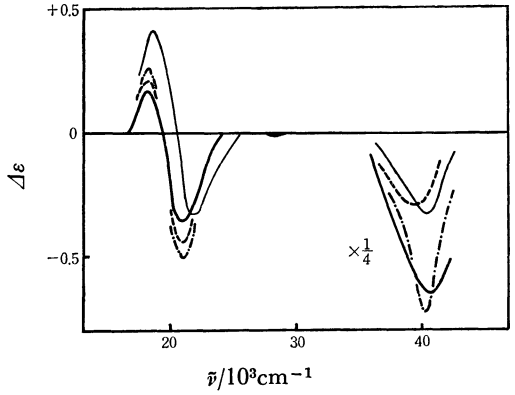

Fig. 2. CD spectra of $[Co(S\text{-amOH})(NH_3)_4]^{3+}$ complexes (protonated form).
——: *S*-praH complex ----: *S*-leuH complex
—·—: *S*-abnH complex : *S*-isopraH complex

CD Spectra of Tetraamminecobalt(III) Complexes. The CD spectra of $[Co(S\text{-amOH})(NH_3)_4]^{3+}$,[8] with protonated hydroxyl group are shown in Fig. 2. The patterns are similar to that of $[Co(NH_3)_4(S\text{-pn})]^{3+}$ (pn=1,2-diaminopropane)[9-11], a positive and a negative CD band are seen from lower to higher wave number in the first absorption band region, while the CD magnitude in the second absorption band region is almost zero except for $[Co(S\text{-isopraH})(NH_3)_4]^{3+}$. A large negative CD band is observed in the charge transfer region. The similarity suggests that both *S*-amOH and *S*-pn chelates in the complexes are in a similar conformational structure, *δ-gauche*.[9-11]

Since the complexes of the type, $[Co(S\text{-amOH})(NH_3)_4]^{3+}$ are approximated to C_{4v} symmetry, the positive and the negative CD band in the first absorption band region may be assigned to the $A_1 \rightarrow E$ and the $A_1 \rightarrow A_2$ component, respectively.[12]

$(+)_D$-$[Co(isopraH)(NH_3)_4]^{3+}$ shows the positive $A_1 \rightarrow E$ and the negative $A_1 \rightarrow A_2$ CD bands in the first absorption band region. Therefore, the isopraH in this isomer will be in *δ-gauche* conformation with an equatorial methyl group, and consequently of *S* absolute configuration. The CD magnitude of the $A_1 \rightarrow E$ band is greater than that of the $A_1 \rightarrow A_2$ band in contrast to the other *S*-amOH complexes. The relative CD magnitudes of the $A_1 \rightarrow E$ and the $A_1 \rightarrow A_2$ components may be related to the difference in the position of substituents on chelate rings. The isopraH has methyl group at α position to the hydroxyl group while the other *S*-amino-alcohols the substituents at β position.

The CD spectra of the deprotonated complexes, $[Co(S\text{-amO})(NH_3)_4]^{2+}$ are reproduced in Fig. 3. All the complexes including the *S*-isopra$^-$ complex show a similar pattern; a weak positive and a strong negative CD band in the first absorption band region, a fairly strong positive CD band in the second absorption band region (~25000 cm^{-1}) and two strong negative CD bands in the charge transfer region (~33000 and 37000—40000 cm^{-1}). This result confirms the previous assignment of the absolute configuration for the isopraH in the $(+)_D$-isomer.

The positive and the negative CD bands in the first absorption band region may be also assigned to the

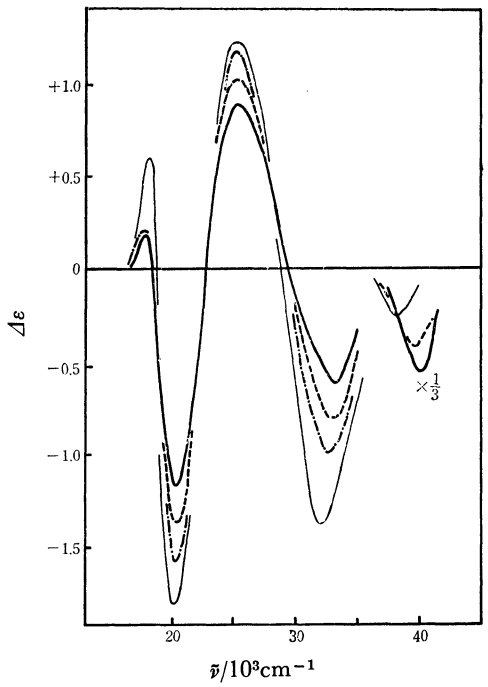

Fig. 3. CD spectra of $[Co(S\text{-amO})(NH_3)_4]^{2+}$ complexes (deprotonated form).
——: *S*-pra$^-$ complex ----: *S*-leu$^-$ complex
—·—: *S*-abn$^-$ complex : *S*-isopra$^-$ complex

$A_1 \rightarrow E$ and the $A_1 \rightarrow A_2$ component, respectively. The magnitude of the latter component is markedly enhanced in the deprotonated complexes as compared with that in the protonated complexes. The strong CD band at about 25000 cm^{-1} in the second absorption band region is quite characteristic of the deprotonated complexes. The CD corresponding to the second absorption band of a cobalt(III) complex is generally very weak, since this absorption is intrinsically magnetic dipole forbidden. The CD peak positions at about 25000 cm^{-1} do not coincide with the second absorption maxima at about 27600 cm^{-1}, and there seems to exist a band component at about 25000 cm^{-1} in the absorption spectra (see Fig. 1). The deprotonated isopra$^-$ complex which contains an asymmetric carbon atom adjacent to the alcoholic oxygen atom gives the biggest CD peaks among the *S*-amO$^-$ complexes in the first and the second absorption band region.

Very recently, Hawkins *et al.*[11] reported the CD of the tetraammine complexes containing *S*-lactic acid, *S*-2-amino-1-propanol, *S*-alanine and *S*-1,2-diaminopropane in 0.1 M perchloric acid, in aqueous solution and in 0.005 M potassium hydroxide solution. The CD spectra of *S*-2-amino-1-propanol complex show a strong pH-dependence as those in our study. A similar pH-dependence is also exhibited in the *S*-lactato complex.

CD Spectra of Bis(ethylenediamine)cobalt(III) Complexes. The absorption and CD spectra of *Λ*-$[Co(etaH)(en)_2]^{3+}$, *Λ*-$[Co(S\text{-praH})(en)_2]^{3+}$ and *Λ*-$[Co(S\text{-praH})(en)_2]^{3+}$ and their conjugate bases were reported in the previous communication.[3] The spectra of two isomeric isopraH complexes and their conjugate bases are shown in Figs. 4 and 5. The CD spectra of the protonated complexes

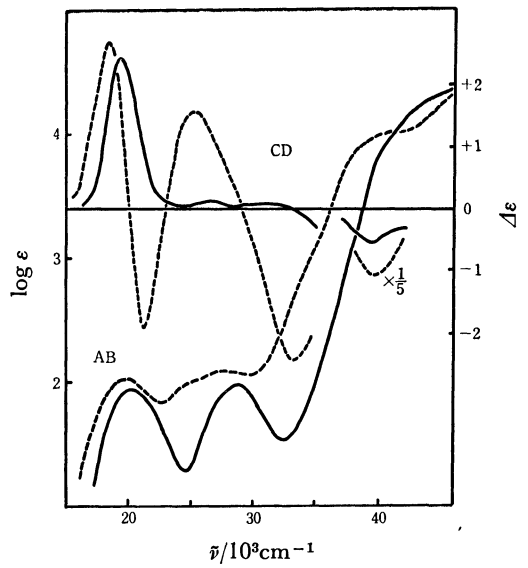

Fig. 4. Absorption and CD spectra of *Λ*-[Co(*S*-isopraH)(en)$_2$]$^{3+}$ (protonated form) (——) and *Λ*-[Co(*S*-isopra)(en)$_2$]$^{2+}$ (deprotonated form) (---).

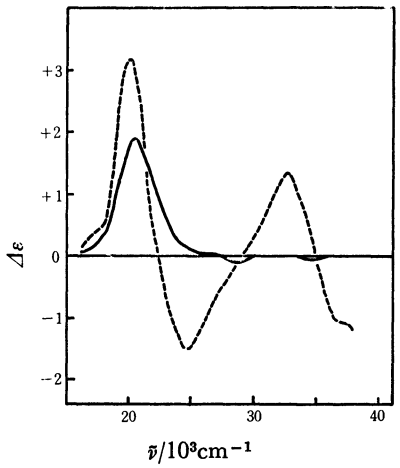

Fig. 5. CD spectra of *Λ*-[Co(*R*-isopraH)(en)$_2$]$^{3+}$ (protonated form) (——), and *Λ*-[Co(*R*-isopra)(en)$_2$]$^{2+}$ (deprotonated form) (----).

[Co(amOH)(en)$_2$]$^{3+}$ resemble those of [Co(diamine)$_3$]$^{3+}$ and [Co(am)(en)$_2$]$^{2+}$. A strong and a weak CD band are observed in the first and the second absorption band region, respectively.

The absolute configurations of the amino-alcohol complexes can be assigned on the basis of the sign of the main CD band at about 20000 cm^{-1}. Thus the complexes shown in Figs. 4 and 5 are assigned to *Λ* configuration. The absolute configuration of 1-amino-2-propanol in these complexes can be assigned from comparison of their CD spectra with those of the ethylenediamine analogs of *S*-praH and *S*-pra$^-$.[3] As the CD curves of the isopraH and isopra$^-$ complexes in Fig. 4 are similar to those of the corresponding *Λ*-[Co(*S*-praH)(en)$_2$]$^{3+}$ and its conjugate base respectively, the absolute configuration of isopraH in this isomer will be assigned to *S*. In an analogous manner, the absolute configuration of isopraH in the other isomer, whose CD curves are given in Fig. 5, was assigned

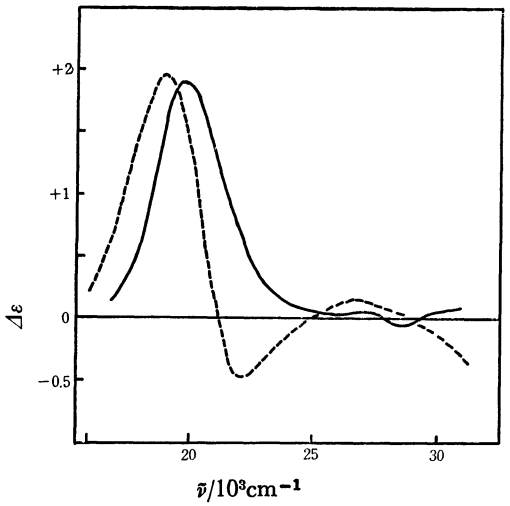

Fig. 6. Configurational effects of [Co(*R*-isopraH)(en)$_2$]$^{3+}$ (protonated form) (——) and [Co(*R*-isopra)(en)$_2$]$^{2+}$ (deprotonated form) (----).

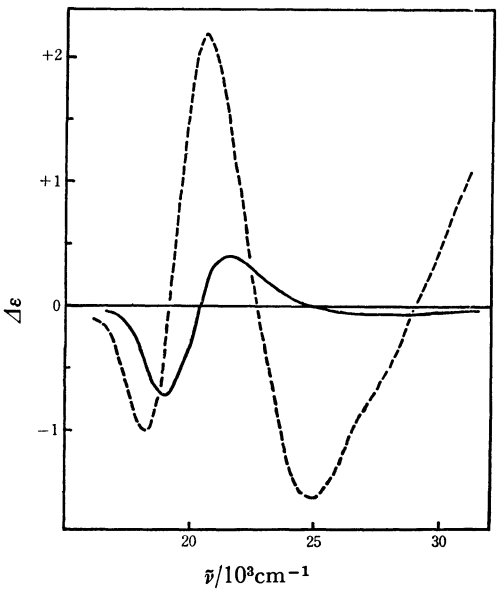

Fig. 7. Vicinal effect curves of [Co(*R*-isopraH)(en)$_2$]$^{3+}$ (——) (protonated form) and [Co(*R*-isopra)(en)$_2$]$^{2+}$ (----) (deprotonated form).

to *R*.

The CD magnitudes of the deprotonated complexes [Co(amO)(en)$_2$]$^{2+}$ are considerably enhanced as compared with those of their conjugate acids. The characteristics of the CD spectra of the deprotonated complexes are the appearance of two strong bands with opposite signs at 20000—21000 cm^{-1} and about 25000 cm^{-1}. In the absorption spectra of these complexes, a shoulder is observed at about 25000 cm^{-1}. These shoulder bands may also be related to the strong CD bands at about 25000 cm^{-1}, as seen in the tetraammine complexes with deprotonated amO$^-$.

It is known that the contributions of the configurational and vicinal effects are additive in the CD spectra of a series of cobalt(III) complexes containing five-membered chelate rings.[10,13] The configurational and the vicinal effects in the CD spectra of two isomeric

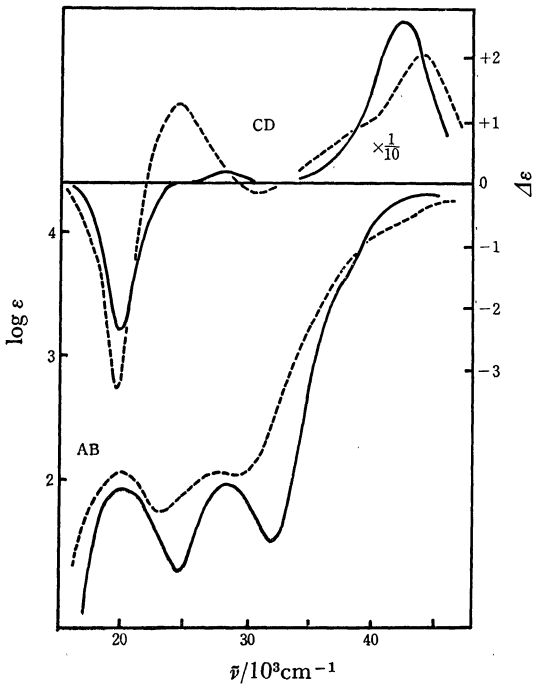

Fig. 8. Absorption and CD spectra of Δ-[Co(*S*-praH)-(*R*-chxn)$_2$]$^{3+}$ (protonated form) (——), Δ-[Co(*S*-pra)-(*R*-chxn)$_2$]$^{2+}$ (deprotonated form) (----).

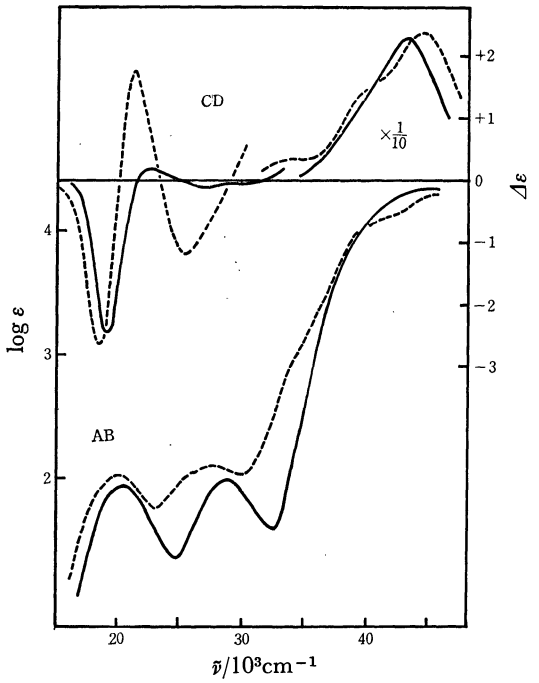

Fig. 9. Absorption and CD spectra of Δ-[Co(etaH)-(*R*-chxn)$_2$]$^{3+}$ (protonated form) (——), Δ-[Co(eta)-(*R*-chxn)$_2$]$^{2+}$ (deprotonated form) (----).

[Co(isopraH)(en)$_2$]$^{3+}$ and their conjugate bases, are estimated as shown in Figs. 6 and 7. The vicinal effect curves in Fig. 7 resemble the CD curves of the corresponding tetraammine complexes, indicating that the additivity of the two effects holds in these complexes. The configurational effect curves are similar between the protonated and the deprotonated complexes, while the vicinal effect curves are considerably different from each other, the CD magnitude of the deprotonated complexes being enhanced considerably. A similar result has been obtained for the CD spectra of Δ- and Λ-[Co(*S*-praH)(en)$_2$]$^{3+}$ and their conjugate bases.[3] Thus the enhanced CD magnitude of the deprotonated complexes may be attributed to the vicinal effect of an amino-alcoholate chelate ring. The similarity of the vicinal effect curves of *S*-pra$^-$ and *S*-isopra$^-$ complexes implies that the conformation of the five-membered chelate ring contributes to the CD more than does the position of substituent on the chelate ring. The CD band at $\sim$25000 cm^{-1} of Δ- or Λ-[Co(amO)(en)$_2$]$^{2+}$ depends only on conformation of amO$^-$ chelate ring because the configurational effect curve has no bands in this region.

The enhanced CD magnitude of the deprotonated amino alcoholato complexes might be related to the coordinated alcoholate oxygen atom with two sets of nonbonding electron pairs. Recently Kipp and Haines[14] reported that [Co(*R*-lac)(diamine)$_2$]$^+$(lac^{2-}= divalent lactate ion) complexes exhibit strong CD. These complexes also possess coordinated alcoholate oxygen atom.

*CD Spectra of Bis(*R-trans-1,2-*diaminocyclohexane)cobalt-(III) Complexes.* The absorption and CD spectra of [Co(amOH)(*R*-chxn)$_2$]$^{3+}$ complexes and their conjugate bases are shown in Figs. 8 and 9. The absolute configurations of the complexes around the cobalt(III) ion were assigned from the sign of the main CD band in the first absorption band region of the protonated complexes. In the present study Λ-isomers were formed too little, and we have isolated only the Δ-isomer for each complex.

The CD spectrum of Δ-[Co(*S*-praH)(*R*-chxn)$_2$]$^{3+}$ would consist of the configurational and the vicinal effects due to *S*-praH and the two *R*-chxn chelate rings. The *R*-chxn chelate ring will take λ-*gauche* conformation and consequently the C–C bond in the chelate ring is *lel*[15] to the pseude-three fold axis of the Δ-complex. The *S*-praH chelate ring will have the C–C bond *ob*[15] to the pseudo-three fold axis.

The CD spectra of Δ-[Co(*S*-praH)(*R*-chxn)$_2$]$^{3+}$ and its conjugate base are similar to those of Δ-[Co(*S*-praH)-(en)$_2$]$^{3+}$ and its conjugate base(see Table 1 and spectra in Ref. 3) respectively. This similarity indicates that these ethylenediamine chelate rings take λ(*lel*) conformation preferentially. The *S*-pra$^-$ chelate ring must give strong vicinal effect similarly to the en and the chxn complex and seems to have given similar patterns to them. The CD spectra of Δ-[Co(etaH)(*R*-chxn)$_2$]$^{3+}$ and its conjugate base are cosiderably different from the corresponding ethylenediamine analogs (see Table 1 and spectra in Ref. 3). The difference might be related to the difference in the conformation of etaH or eta$^-$ in the *R*-chxn and the en complexes. The complex ion Λ-[Co(eta)(en)$_2$]$^{2+}$ shows only small CD bands at 25970 cm^{-1}. The CD band in this region has been shown to depend only on the conformation of the amO$^-$ chelate ring. The conformation of eta$^-$ chelate ring in the en complex is thus considered to be in equilibrium between δ and λ, and the equilibrium to be in favor of the δ only to a small extent.

On the other hand, Δ-[Co(eta)(*R*-chxn)$_2$]$^{2+}$ exhibits fairly strong CD bands at 21280 cm^{-1} and 25320 cm^{-1} and the whole CD curve is almost enantiomeric with that of Λ-[Co(*S*-pra)(en)$_2$]$^{2+}$. Since the *S*-pra$^-$ chelate ring in the ethylenediamine complex will take δ conformation stereoselectively, the eta$^-$ chelate ring in Δ-[Co(eta)(*R*-chxn)$_2$]$^{2+}$ may be mostly in λ conformation. The stereoselectivity of the conformation of eta$^-$ chelate ring in the bis(*R*-chxn) complex seems to be much larger than that in the bis(en) complex. Such a large stereoselectivity might be brought about by the steric interaction between the eta$^-$ and *R*-chxn chelate rings.

It is concluded that an amino-alcoholate chelate ring without asymmetric atoms can give strong vicinal effect when it takes a chiral conformation stereoselectively.

Absorption Spectra. The first absorption bands of all the deprotonated amino-alcoholate complexes are at somewhat lower wave number than those of the corresponding protonated amino-alcohol complexes. However, the wave number differences are small compared with that observed for aqua- and hydroxo-pentaammine complexes which belong to the same [CoN$_5$O] type as the present amino-alcohol complexes.

It the second absorption band region, on the other hand, the spectra of the tetraammine complexes exhibit somewhat different behavior from those of the bisdiamine complexes. The tetraammine complexes with deprotonated amO$^-$ have the second absorption maxima at lower wave numbers than those of the protonated complexes by *ca.* 150 cm^{-1}. However, most of the bisdiamine complexes with deprotonated amO$^-$ give their second absorption bands at only slightly lower wave number than those of the protonated complexes, and exhibit a distinct shoulder band at about 25000 cm^{-1}. Such a shoulder band is the most pronounced in [Co(*N*-Meeta)(en)$_2$]$^{2+}$ among the amino-alcoholate complexes studied here. As stated previously, all the complexes containing deprotonated chiral amino-alcoholate chelate ring show a strong CD band in this region, $\sim$25000 cm^{-1}. Thus, it may be concluded that all the deprotonated complexes have an absorption component at about 25000 cm^{-1}, even though there is no obvious shoulder in the absorption spectra as in the tetraammine complexes. In such complexes the shoulder band might have been masked by the main component of the second absorption band. The apparrent second absorption maximum is thus seen at a relatively lower wave number.

A similar shoulder in the second absorption band region has been reported for several complexes; [Co(OH)(edta)]$^{2-}$,[16] (edta^{4-}=ethylenediaminetetraacetate ion), [Co(OH)(penten)]$^{2+}$ [17] (penten=*N*,*N*,*N*′,*N*′-tetrakis(2′-aminoethyl)-1,2-diaminoethane) and *mer*-(*trans*-NH$_3$)-[CoCO$_3$(am)(NH$_3$)$_2$][18] (am$^-$=aminocarboxylate ion). The nature of these shoulder bands is not clear at present. However, all the complexes including the present aminoalcoholate complexes are those containing both chelate rings and coordinated oxygen atom with two sets of nonbonding electron pairs. [Co(guH)(en)$_2$]$^{3+}$ and [Co(gu)(en)$_2$]$^{2+}$ (guH=guanylurea) show also a broad second absorption band but the structures of these complexes remain uncertain.[19]

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