Circular Dichroism and Stereochemistry of Tetranuclear Cobalt(III) Complexes of Hexol Type. II.[1] Hexakis(ethylenediamine)-hexa-μ-hydroxo-tetracobalt(III) Ion, $[\mathrm{Co}\{(\mathrm{OH})_2\mathrm{Co}(\mathrm{en})_2\}_3]^{6+}$

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The theoretically possible eight optical isomers of hexakis(ethylenediamine)-hexa-μ-hydroxo-tetracobalt(III) ion, $[\mathrm{Co}\{(\mathrm{OH})_2\mathrm{Co}(\mathrm{en})_2\}_3]^{6+}$, were separated by column chromatography, absorption and circular dichroism spectra being measured in the visible and ultraviolet region in 0.01 mol dm^{-3} HCl and 0.15 mol dm^{-3} Na_2SeO_3 solutions. Absolute configurations were determined by means of circular dichroism spectra and the characterization of mononuclear cobalt(III) ions produced by decomposition of the tetranuclear isomers in an acid solution. The additivity of the two main circular dichroism contributions due to the chiral CoO_6 and CoN_4O_2 chromophores is discussed, and the configurational chirality of CoO_6 chromophore is expressed by summing up the contributions from three pairs of CoN_4O_2 chromophores as in the so-called ring-pairing method.

Hexakis(ethylenediamine)-hexa-μ-hydroxo-tetracobalt(III) complex salt was prepared by Werner for the first time.[2] For this tetranuclear hexol-type complex there are eight possible optically active isomers which then compose four racemic isomers. The structures of two of the four racemic isomers have been found by X-ray analysis of the salts of $\Delta(\Delta\Lambda\Lambda)/\Lambda(\Delta\Delta\Lambda)$ and $\Delta(\Lambda\Lambda\Lambda)/\Lambda(\Delta\Delta\Delta)$ isomers.[3–5] However, little success has been made concerning the optical resolution of this complex ion.[6,7] Kern and Wentworth reported that four of the eight possible optical isomers of $[\mathrm{Co}\{(\mathrm{OH})_2\mathrm{Co}(\mathrm{en})_2\}_3]^{6+}$ are formed in solution, only two of them (a couple of enantiomers) being obtained in pure fractions.[6] They could not assign the configurations of the isomers. The present paper deals with successful separation of all the eight isomers and assignments of their configurations. Discussion is given on their circular dichroism (CD) spectra including CD change by ion-pairing with some oxoanions as compared with the spectra of the corresponding dodecaammine complex.[1]

Experimental

Preparation and Separation of the Isomers of $[\mathrm{Co}\{(\mathrm{OH})_2\mathrm{Co}(\mathrm{en})_2\}_3]^{6+}$. The complex was prepared by a modification of the method of Werner.[2] To 14.5 g of $Co(NO_3)_2\cdot 6H_2O$ in 15 cm^3 of water was slowly added 30 cm^3 of a 10% solution of ethylenediamine with stirring. The mixture was stirred vigorously by blowing compressed air on the surface for about one hour at room temperature, the remaining solid being filtered off and washed with a small amount of water. The filtrate and washings were poured into a column (5×120 cm) of strong-acid exchanger (SP Sephadex C-25, Na^+ form). After a broad pink-red band had been swept out with 0.1 M (1 M=1 mol dm^{-3}) sodium *d*-tartrate solution, the adsorbed band was eluted with 0.3 M sodium *d*-tartrate solution. During the course of elution the column was cooled by flushing cold water of 5 °C. Eight brown bands eluted were numbered f-1, f-2, ···, and f-8 in the order of elution. At this stage, it was confirmed by measurements of CD spectra that each pair of isomers f-1 and f-2, f-3 and f-4, f-5 and f-6, and f-7 and f-8 represents a couple of enantiomers. Each eluate was concentrated in a vacuum rotatory evaporator at 20 °C, when necessary, and then a saturated aqueous sodium tetraphenylborate solution was added to the eluate to precipitate the desired product. The precipitate was collected by filtration and washed with cold water and then air-dried. The precipitate was dissolved in cold ethanol. The solution was filtered, and a cold ethanol solution of calcium nitrate was added to the filtrate. A voluminous pale-brown nitrate immediately precipitated was filtered off and washed with ethanol several times and then dried in the air. The product was dissolved in a small amount of water, and powdered sodium nitrate was added to the solution which was kept in a refrigerator overnight. Fine brown needle crystals which appeared were collected by filtration and recrystallized from a small amount of water by adding powdered sodium nitrate, and then dried in a vacuum desiccator over calcium chloride. Found for isomer f-3: C, 13.01; H, 5.35; N, 22.12%. Calcd for $[\mathrm{Co}\{(\mathrm{OH})_2\mathrm{Co}(\mathrm{en})_2\}_3](\mathrm{NO}_3)_6\cdot 3\mathrm{H}_2\mathrm{O}=\mathrm{C}_{12}\mathrm{H}_{54}\mathrm{N}_{18}\mathrm{O}_{24}\mathrm{Co}_4\cdot 3\mathrm{H}_2\mathrm{O}$: C, 12.82; H, 5.38; N, 22.42%. Found for isomer f-4: C, 12.96; H, 5.38; N, 22.26%. Calcd for $C_{12}H_{54}N_{18}O_{24}Co_4\cdot 3H_2O$: C, 12.82; H, 5.38; N, 22.42%. Found for isomer f-5: C, 12.91; H, 5.10; N, 22.72%. Calcd for $C_{12}H_{54}N_{18}O_{24}Co_4\cdot 1.5H_2O$: C, 13.13; H, 5.24; N, 22.97%. Found for isomer f-6: C, 12.96; H, 5.32; N, 22.36%. Calcd for $C_{12}H_{54}N_{18}O_{24}Co_4\cdot 3H_2O$: C, 12.82; H, 5.38; N, 22.42%. Found for isomer f-7: C, 12.49; H, 5.34; N, 22.03%. Calcd for $C_{12}H_{54}N_{18}O_{24}Co_4\cdot 3.5H_2O$: C, 12.72; H, 5.42; N, 22.24%. Found for isomer f-8: C, 12.76; H, 5.09; N, 22.94%. Calcd for $C_{12}H_{54}O_{24}Co_4\cdot 1.5H_2O\cdot 0.5NaNO_3$: C, 12.64; H, 5.04; N, 22.73%. Isomers f-1 and f-2 were not obtained as solid salt because of low yields, and partial overlapping of the chromatographic bands of f-1 and f-2 with those of the Λ and Δ isomers, respectively, of a by-product complex, $[\mathrm{Co}(\mathrm{en})_3]^{3+}$.

Measurements. The visible and ultraviolet absorption spectra were measured with a Shimadzu UV-200 spectrophotometer. The CD spectra were recorded with a JASCO MOE-1 spectropolarimeter. Measurements were carried out at room temperature in 0.01 M HCl, 0.15 M Na_2SeO_3, and aqueous solutions.

Results and Discussion

Characterization of Isomers. The absorption and CD data of eight isomers are summarized in Table 1. It is evident that the isomer f-1 is enantiomeric to the isomer f-2, as is f-3 to f-4, f-5 to f-6, and f-7 to f-8. The CD curves of isomers f-1, f-3, f-5, and f-7, all of which have a positive CD band at about 16400 cm^{-1}, are shown in Fig. 1. Isomers f-1 and f-2 were not obtained as solid salt, their CD values being estimated on the basis of the concentration calculated from the absorbance at 620 nm assuming the molar absorption coefficient $\varepsilon_{620}=113\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$; the absorption intensities of all the other isomers were almost equal to this value (Fig. 1 and Table 1). The absorption and CD spectra remained unchanged in 0.3 M sodium *d*-tartrate (eluting solution) at room temperature for about 24 h, being the same in 0.01 M HCl and in H_2O, in which the complex, except for isomer f-7, is considerably stable to mutarotation. Isomers f-3 and f-5 are considerably stable against mutarotation also in 0.15 M Na_2SeO_3 in a sharp contrast to the case of the dodecaammine complex, $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$, which undergoes mutarotation in 0.17 M Na_2SeO_3 and in H_2O.[1] Isomers f-7 undergoes mutarotation in 0.15 M Na_2SeO_3 and in H_2O, but it is considerably stable against mutarotation in 0.01 M HCl. Judging from the chromatographic band strech and the degree of coloration on the column, the yields of isomers are in the order f-3 (f-4)>f-5 (f-6)>f-7 (f-8)>f-1 (f-2). The isomers reported by Kern and Wentworth[6] and Mason and Wood[10] correspond to the present isomers f-5 and f-6.

Configuration of CoO_6 Chromophore. The hexakis-(ethylenediamine)-hexa-μ-hydroxo-tetracobalt(III) ion, $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$, is regarded as being composed of a $Co(OH)_6$ and three $Co(OH)_2(en)_2$ chromophores. In the following discussion the former chromophore is abbreviated to CoO_6, and the latter to CoN_4O_2. The CoO_6 chromophore has a configurational chirality, Δ or Λ, due to the tris-chelate type arrangement of three $Co(OH)_2Co$ four-membered rings. Each CoN_4O_2 chromophore also has a configurational chirality, Δ or Λ, due to the tris-chelate type arrangement of two ethylenediamine chelate rings and a $Co(OH)_2Co$ four-membered ring. Thus eight isomers are possible in

TABLE 1. THE ABSORPTION AND CD DATA OF $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ IN 0.01 M HCl UNLESS OTHERWISE STATED
Wave numbers are given in $10^3\ \mathrm{cm^{-1}}$ unit and log ε or $\Delta\varepsilon$ values (in parentheses) $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$.

Isomer	Absorption		CD	
	σ_{max}	(log ε)	σ_{ext}	($\Delta\varepsilon$)
f-1			14.77	(− 2.99)
	16.12		16.64	(+ 18.1)
	20.31		20.41	(− 31.8)
			26.25	(+ 1.57)
	32.36		30.96	(− 8.41)
			38.96	(+ 10.3)
	49.02		45.77	(+114)
f-2			14.73	(+ 2.95)
	16.14		16.61	(− 18.2)
	20.29		20.37	(+ 32.0)
			26.16	(− 1.58)
	32.36		30.96	(+ 8.43)
			38.76	(− 10.2)
	48.90		45.87	(−110)
f-3			14.53	(− 2.31)
	16.13	(2.04)	16.31	(+ 18.4)
	20.33	(2.56)	20.16	(− 28.9)
			25.84	(+ 1.23)
	32.36	(3.77)	31.45	(− 7.16)
			37.04	(+ 3.55)
			40.32	(− 8.26)
	48.78	(4.76)	45.15	(+139)
f-3[a]			14.63	(− 2.46)
	16.26	(1.99)	16.37	(+ 15.2)
	20.20	(2.59)	20.16	(− 30.1)
			25.97	(+ 2.72)
	31.95	(3.76)	30.86	(− 3.57)
			37.60	(+ 6.05)
			39.92	(− 1.11)
f-4			14.52	(+ 2.28)
	16.13	(2.05)	16.31	(− 19.0)
	20.33	(2.56)	20.14	(+ 29.3)
			25.77	(− 1.30)
	32.36	(3.77)	31.35	(+ 7.25)
			37.04	(− 3.62)
			40.40	(+ 8.31)
	49.02	(4.75)	45.25	(−135)
f-5			14.56	(− 2.52)
	16.13	(2.05)	16.37	(+ 17.3)
	20.37	(2.50)	20.16	(− 21.9)
			25.71	(+ 1.30)
	32.36	(3.74)	31.60	(− 10.9)
			40.73	(− 33.7)
	49.14	(4.73)	45.35	(+103)
f-5[a]			14.64	(− 2.61)
	16.18	(2.01)	16.39	(+ 13.5)
	20.28	(2.52)	20.16	(− 21.5)
			25.77	(+ 2.38)
	31.95	(3.74)	31.20	(− 7.01)
			35.78	(+ 0.18)
			40.49	(− 19.6)
f-6			14.56	(+ 2.58)
	16.16	(2.05)	16.39	(− 16.8)
	20.33	(2.51)	20.18	(+ 22.4)
			25.71	(− 1.41)
	32.36	(3.75)	31.65	(+ 10.5)
			40.82	(+ 33.6)
	49.02	(4.74)	45.25	(− 98.7)
f-7			14.64	(− 2.37)
	16.16	(2.05)	16.53	(+ 17.2)
	20.28	(2.54)	20.28	(− 19.6)
			25.87	(+ 1.41)
	32.36	(3.77)	31.70	(− 12.4)
			41.15	(− 49.1)
	49.02	(4.75)	46.19	(+85.9)
f-8			14.66	(+ 2.34)
	16.16	(2.05)	16.53	(− 17.1)
	20.33	(2.54)	20.33	(+ 19.4)
			25.87	(− 1.44)
	32.36	(3.77)	31.65	(+ 12.0)
			40.98	(+ 48.6)
	48.90	(4.75)	46.08	(− 88.0)

a) In 0.15 M Na_2SeO_3.

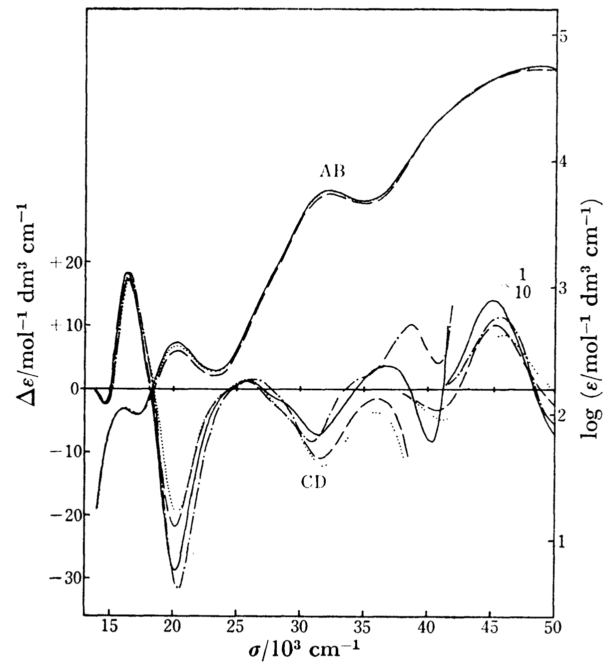

Fig. 1. Absorption (AB) and CD curves of isomer f-1 (–·–·–), f-3 (——), f-5 (– – –), and f-7 (····) of $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ in 0.01 M HCl.

total: $\mathit{\Delta}(\mathit{\Delta\Delta\Delta})$, $\mathit{\Delta}(\mathit{\Delta\Delta\Lambda})$, $\mathit{\Delta}(\mathit{\Delta\Lambda\Lambda})$, $\mathit{\Delta}(\mathit{\Lambda\Lambda\Lambda})$, $\mathit{\Lambda}(\mathit{\Delta\Delta\Delta})$, $\mathit{\Lambda}(\mathit{\Delta\Delta\Lambda})$, $\mathit{\Lambda}(\mathit{\Delta\Lambda\Lambda})$, and $\mathit{\Lambda}(\mathit{\Lambda\Lambda\Lambda})$; the chirality symbols in parentheses denote the configurations of CoN_4O_2 chromophores. The eight isomers are classified into four geometrical isomers, since each of them finds its enantiomer in themselves.

Since the first and second d-d transition bands of $[Co(H_2O)_6]^{3+}$ are located at 16500 and 24700 cm^{-1}, respectively,[8] and those of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ at 20200 and 27700 cm^{-1},[9] the absorption bands of $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ at *ca.* 16100 and 20300 cm^{-1} are assigned to the first d-d transition bands of CoO_6 and CoN_4O_2 chromophores, respectively. The second d-d transition bands of both chromophores seem to be masked by an intense band at 32360 cm^{-1}, which is due to the charge transfer transition from the oxygen atom of the OH bridge groups to the central metal, $p_\pi(O) \rightarrow e_g(Co)$. The assignments are in line with those for those of similar hexa-μ-hydroxo-tetracobalt(III) type ions.[1,6,10,11] For all four geometrical isomers, the band positions and intensities are almost equal for the CoO_6 chromophore region, but not for the CoN_4O_2 chromophore region (Fig. 1 and Table 1).

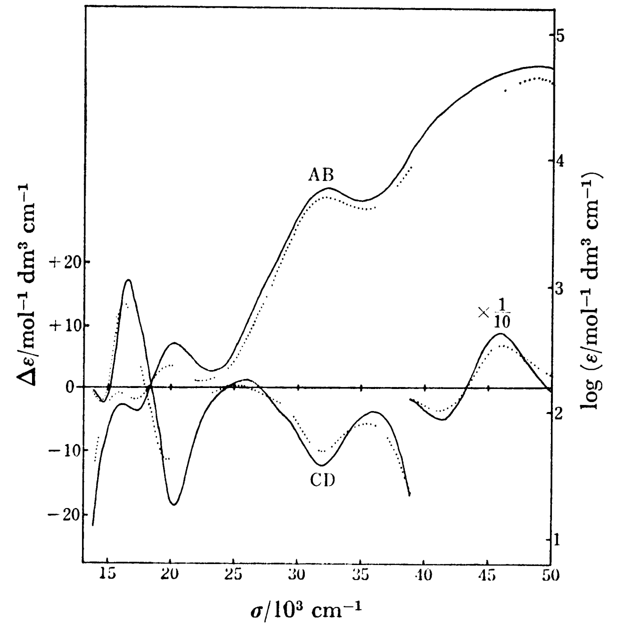

Fig. 2. Absorption (AB) and CD curves of isomer f-7 of $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ (——) and $\mathit{\Lambda}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ (····) in 0.01 M HCl.

Similarly the intensities of the longer or shorter wavelength CD peak of CoO_6 chromophore are almost equal for isomers f-1, f-3, f-5, and f-7: $\Delta\varepsilon_{ext} = -2.3$—$-3.0$ and $+17.1$—$+18.4$ mol^{-1} dm^3 cm^{-1}, respectively. The CD intensity of CoN_4O_2 chromophore band at about 20300 cm^{-1} varies widely: $\Delta\varepsilon_{ext} = -18.7$—$-33.0$ mol^{-1} dm^3 cm^{-1}. The CD patterns in the d-d transition region are similar to each other, while those in the charge transfer transition region differ. From the close similarity (Fig. 2) between the CD spectra of isomers f-1, f-3, f-5, and f-7 and spectrum of $\mathit{\Lambda}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ previously reported,[1] it is concluded that isomers f-1, f-3, f-5, and f-7 have $\mathit{\Lambda}$ configuration and the remaining isomers f-2, f-4, f-6, and f-8 $\mathit{\Delta}$ configuration.

Configurations of CoN_4O_2 Chromophores. Acid hydrolysis of one mole of $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ ion is expected to produce one mole of $[Co(H_2O)_6]^{2+}$ (*via* $[Co(H_2O)_6]^{3+}$) and 3 mol of mononuclear $[Co(en)_2(H_2O)_2]^{3+}$. While the former ion has no chirality, the latter has a configurational chirality, $\mathit{\Delta}$ or $\mathit{\Lambda}$, due to the bis-chelate type structure. The isomers $\mathit{\Delta}(\mathit{\Delta\Delta\Delta})$ or $\mathit{\Lambda}(\mathit{\Delta\Delta\Delta})$ will produce three $\mathit{\Delta}$-$[Co(en)_2(H_2O)_2]^{3+}$ ions, $\mathit{\Delta}(\mathit{\Delta\Delta\Lambda})$ or $\mathit{\Lambda}(\mathit{\Delta\Delta\Lambda})$ two $\mathit{\Delta}$ and one $\mathit{\Lambda}$, $\mathit{\Delta}(\mathit{\Delta\Lambda\Lambda})$ or $\mathit{\Lambda}(\mathit{\Delta\Lambda\Lambda})$ one $\mathit{\Delta}$ and two $\mathit{\Lambda}$, and $\mathit{\Delta}(\mathit{\Lambda\Lambda\Lambda})$ or $\mathit{\Lambda}(\mathit{\Lambda\Lambda\Lambda})$ three $\mathit{\Lambda}$.

Table 2. The $\Delta\varepsilon_{488}$ values after decomposition by 6 M HCl ($\Delta\varepsilon$ values are given in mol^{-1} dm^3 cm^{-1} unit.)

Isomer	$\Delta\varepsilon_{488}$	Ratio	Assignment
f-1	(+1.5)[a]	(+2.0)	($\mathit{\Lambda\Lambda\Lambda}$)
f-3	−2.2	−2.9	($\mathit{\Delta\Delta\Delta}$)
f-5	−0.8	−1.1	($\mathit{\Lambda\Delta\Delta}$)
f-7	+0.7	+0.9	($\mathit{\Lambda\Lambda\Delta}$)

a) The original tetranuclear complex was not isolated in solid salt, but concentration was estimated from the absorbance at 620 nm.

The $\Delta\varepsilon$ values at 488 nm after decomposition in 6 M HCl solution are given in Table 2. Each isomer was dissolved in 6 M HCl and warmed on a water bath at 45 °C for two hours with stirring. The CD intensity of $\mathit{\Lambda}$-$[Co(en)_2(H_2O)_2]^{3+}$ was reported to be 1.0 mol^{-1} dm^3 cm^{-1} at 486 nm.[4] The observed $\Delta\varepsilon_{488}$ values as a whole are smaller than the reported value, which can be attributed to partial racemization, isomerization, and/or decomposition of the generated $[Co(en)_2(H_2O)_2]^{3+}$ in presence of Co^{2+} ions. From the data in Table 2, the absolute configurations of isomers f-1, f-3, f-5, and f-7 are assigned to $\Lambda(\Lambda\Lambda\Lambda)$, $\Lambda(\Delta\Delta\Delta)$, $\Lambda(\Delta\Delta\Lambda)$, and $\Lambda(\Delta\Lambda\Lambda)$, respectively. Thus isomers f-2, f-4, f-6, and f-8 are assigned to the configurations, $\Delta(\Delta\Delta\Delta)$, $\Delta(\Lambda\Lambda\Lambda)$, $\Delta(\Delta\Lambda\Lambda)$, and $\Delta(\Delta\Delta\Lambda)$, respectively.

The CD spectra of Λ-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ might be expected to be more similar to those of the isomers $\Lambda(\Delta\Delta\Lambda)$ and $\Lambda(\Delta\Lambda\Lambda)$ than to those of $\Lambda(\Delta\Delta\Delta)$ and $\Lambda(\Lambda\Lambda\Lambda)$. Isomers f-5 and f-7 show a similar CD pattern (−, −, and +) in the charge transfer transition region, which is similar to that of Λ-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ (Fig. 2). From the order of yields, $\Lambda(\Delta\Delta\Delta) > \Lambda(\Delta\Delta\Lambda) > \Lambda(\Delta\Lambda\Lambda) > \Lambda(\Lambda\Lambda\Lambda)$, the stability of isomers seems to decrease with increase in the number of Λ-configuration for CoN_4O_2 chromophore in the Λ series of CoO_6 chromophore. A molecular model examination shows that the Λ-configuration of CoN_4O_2 chromophore gives a slight repulsion between a proton of ethylenediamine chelate ring and an OH bridge group.

CD Change by Ion-pairing. The absorption peak of the CoO_6 chromophore of isomers f-3 and f-5 shifted to higher energy side in 0.15 M Na_2SeO_3 and then the intensity decreased, the shift being larger for f-3 than f-5. The peak of CoN_4O_2 chromophore shifted to lower energy side and the intensity increased. The intensity change is larger for f-3 than f-5. For the CD spectra, the longer wavelength extremum of CoO_6 chromophore shifted to higher energy side and the intensity increased for both isomers (Fig. 3 and Table 1). The intensity of the shorter wave-length CD extremum of CoO_6 chromophore decreased for both isomers. The CoN_4O_2 chromophore CD band (at 20160 cm^{-1} for both isomers) did not shift, the intensity increasing for f-3 and slightly decreasing for f-5. The difference in CD curves of 0.01 M HCl and 0.15 M Na_2SeO_3 (Fig. 4) show the ion-pairing effect of SeO_3^{2-} ion on the CD of $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$. The curves have six extrema at *ca.* 14200, 16000, 19800, 22400, 24500, and 28000 cm^{-1} in the d-d transition region. The CD spectra of Λ-$[Co(en)_3]^{3+}$ with D_3 symmetry show strong ion-pairing effect[12–14)] in the region of the first d-d absorption band when an oxoanion species such as PO_4^{3-} or SeO_3^{2-} is added to form the so-called Mason type ion-pair,[13–17)] the CD intensity of E_a component of the first d-d transition decreasing and that of A_2 component increasing. Thus the first positive and next negative extrema, at 14200 and *ca.* 16000 cm^{-1}, correspond to the increment of the negative A_2 component and the decrement of the positive E_a component, respectively, of the first d-d transition of CoO_6 chromophore.

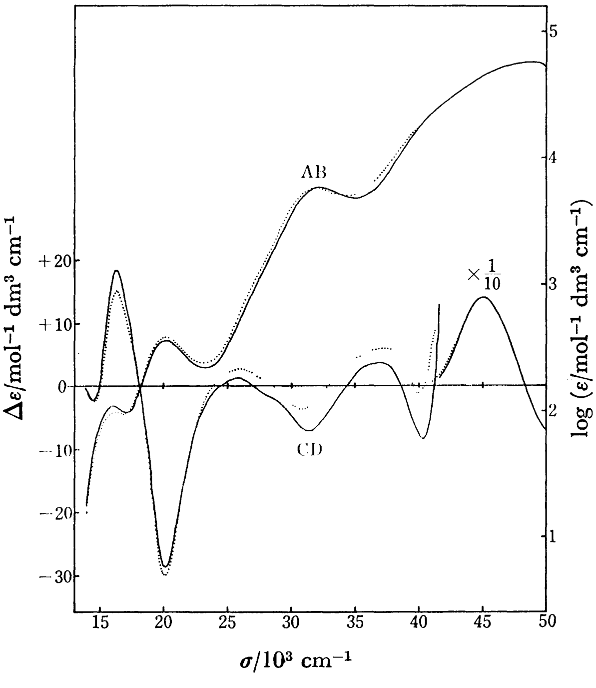

Fig. 3. Absorption (AB) and CD curves of isomer f-3 of $[Co\{(OH)_2Co(en)_{23}]^6\}^+$ in 0.01 M HCl (——) and in 0.15 M Na_2SeO_3 (····).

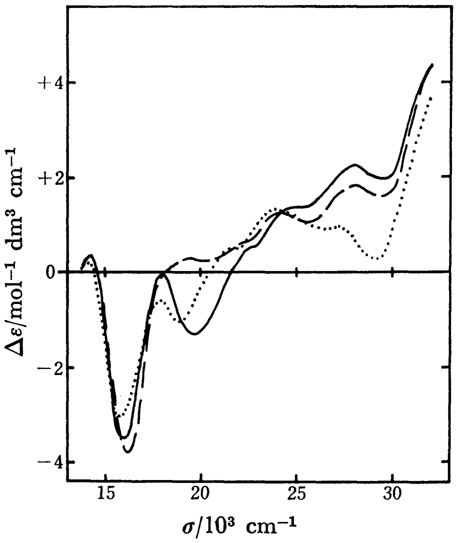

Fig. 4. The ion-pairing effect curves, $\{\Delta\varepsilon_{(\text{in } 0.15\text{ M } Na_2SeO_3)} - \Delta\varepsilon_{(\text{in } 0.01\text{ M HCl})}\}$, of isomer f-3 (——) and f-5 (– – –) of $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$, and Λ-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ (····) (in 0.17 M Na_2SeO_3).

In $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$, hydrogen bond formation occurs between SeO_3^{2-} and the OH bridge groups as for the corresponding dodecaammine complex.[1)] The hydrogen bond formation may occur between the oxoanion and the coordinated $-NH_2$ groups of ethylenediamine of CoN_4O_2 chromophores. Thus chiral oxygen and nitrogen centers are stereospecifically produced by the ion-pair formation. The axial disposition of OH groups in the tetranuclear complex of Λ configuration of CoO_6 chromophore constrains an (*R*) chirality for the "asymmetric" oxygen atoms,[1)] and the axial hydrogen bonding of the NH_2 groups in $\Lambda(\Delta\Delta\Delta)$ configuration constrains an (*S*) chirality for the "asymmetric" nitrogen atoms. The ion-pairing effect curves in Fig. 4 are regarded as having their origin in the vicinal effect of chiral oxygen and/or nitrogen centers stereospecifically produced by the ion-pair formation. A molecular model consideration shows that in the isomer $\Lambda(\Delta\Delta\Delta)$ a set of three OH groups is available each on the upper face and below the downward face (two A sites, 2×3 (*R*) oxygens) and six sets of one OH group and two amino groups (six B sites,

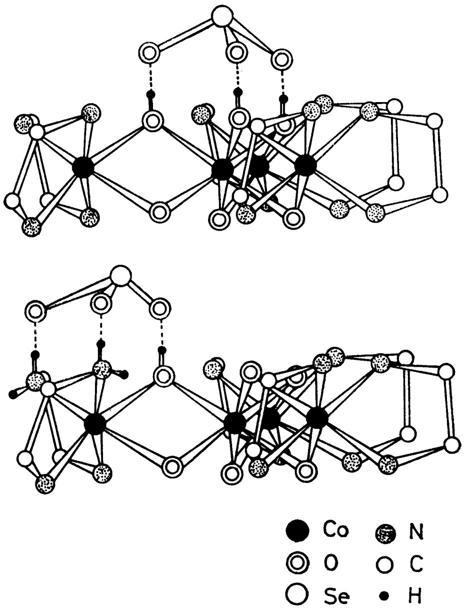

Fig. 5. The possible hydrogen bond formation site for the isomer $\Lambda(\Delta\Delta\Delta)$ with a selenite ion, A site (top) and B site (bottom), viewed normal to the C_3 axis of CoO_6 chromophore.

6×1 (R) oxygens and 6×2 (S) nitrogens) for hydrogen bond formation (Fig. 5). In the isomer $\Lambda(\Delta\Delta\Lambda)$, two A sites with 2×3 ($R$) oxygens and only four B sites with 4×1 (R) oxygens and 4×2 (S) nitrogens are available for hydrogen bonding. As shown in Fig. 4, the ion-pairing effect curve of isomers f-3, $\Lambda(\Delta\Delta\Delta)$, shows a similar CD pattern to that of Λ-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ which has the origin of the effect only in the asymmetric oxygens, which show a negative extremum at *ca.* 19800 cm^{-1}. Thus the ion-pair formation in the present $\Lambda(\Delta\Delta\Delta)$ complex occurs between SeO_3^{2-} and one or two A sites rather than B sites. The ion-pairing effect curve of isomer f-5, $\Lambda(\Delta\Delta\Lambda)$, shows a positive extremum at 19400 cm^{-1} (Fig. 4). The B sites may play a role in this case of ion-pair formation.

Additivity of CD Contributions. If the observed CD curve of $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ can be simply divided into the contributions of CoO_6 and CoN_4O_2 chiralities as has been established for configurational and vicinal chiralities of many other mononuclear cobalt(III) complexes,[18] the following relations are expected to hold:

$$\left.\begin{aligned}\Lambda(\Lambda\Lambda\Lambda) &= \Lambda + 3(\Lambda)\\ \Lambda(\Delta\Lambda\Lambda) &= \Lambda + 2(\Lambda) + (\Delta) = \Lambda + (\Lambda)\\ \Lambda(\Delta\Delta\Lambda) &= \Lambda + (\Lambda) + 2(\Delta) = \Lambda - (\Lambda)\\ \Lambda(\Delta\Delta\Delta) &= \Lambda + 3(\Delta) = \Lambda - 3(\Lambda)\end{aligned}\right\} \qquad (1)$$

where Λ (or Δ) and (Λ) (or (Δ)) are CD contributions of CoO_6 and CoN_4O_2 chiralities, respectively, and $\Lambda = -\Delta$ and $(\Lambda) = -(\Delta)$. The individual Λ and (Λ) can be derived from the observed CD curves from the following relations:

$$\Lambda = [\Lambda(\Lambda\Lambda\Lambda)+\Lambda(\Delta\Delta\Delta)]/2,$$
$$\Lambda = [\Lambda(\Delta\Lambda\Lambda)+\Lambda(\Delta\Delta\Lambda)]/2,$$
$$(\Lambda) = [\Lambda(\Lambda\Lambda\Lambda)-\Lambda(\Delta\Delta\Delta)]/6, \text{ and}$$
$$(\Lambda) = [\Lambda(\Delta\Lambda\Lambda)-\Lambda(\Delta\Delta\Lambda)]/2.$$

However, the calculation (Fig. 6) shows that the separation of Λ and (Λ) (or (Δ)) contributions are very unsatisfactry and that Eq. 1 in this simple form is inadequate for evaluating the CD contributions.

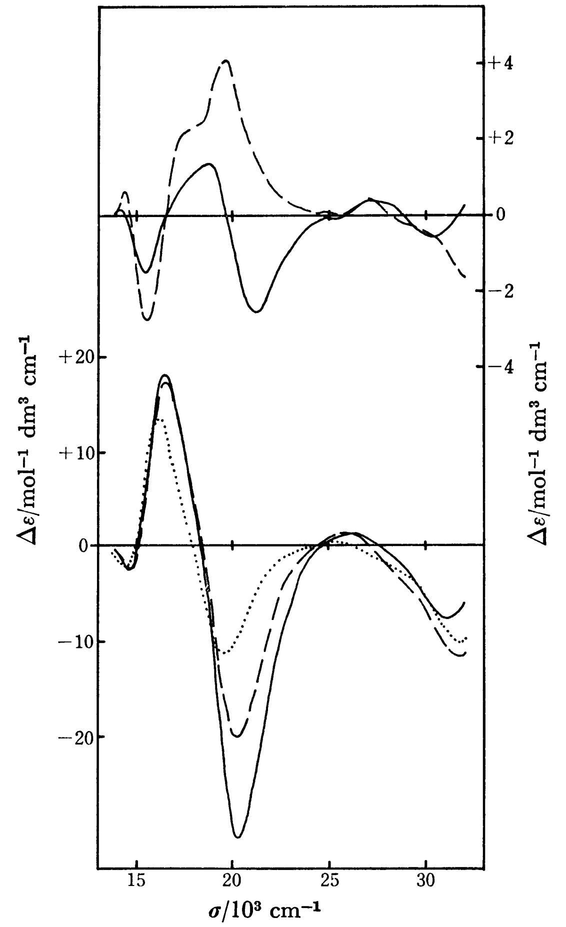

Fig. 6. Inadequacy of Eq. 1 is shown by the calculated curves of (Λ): $[\Lambda(\Lambda\Lambda\Lambda)-\Lambda(\Delta\Delta\Delta)]/6$ (——) and $[\Lambda(\Delta\Lambda\Lambda)-\Lambda(\Delta\Delta\Lambda)]/2$ (---) (upper curves); and of Λ: $[\Lambda(\Lambda\Lambda\Lambda)+\Lambda(\Delta\Delta\Delta)]/2$ (——) and $[\Lambda(\Delta\Lambda\Lambda)+\Lambda(\Delta\Delta\Lambda)]/2$ (---); and observed curve of Λ in the dodecaammine complex (····) (lower curves).

As shown by X-ray analysis of the racemic salts of $\Delta(\Delta\Lambda\Lambda)/\Lambda(\Delta\Delta\Lambda)$[3,5] and $\Delta(\Lambda\Lambda\Lambda)/\Lambda(\Delta\Delta\Delta)$[4] isomers, the four isomers of Λ series $\Lambda(\Delta\Delta\Delta)$, $\Lambda(\Delta\Delta\Lambda)$, $\Lambda(\Delta\Lambda\Lambda)$, and $\Lambda(\Lambda\Lambda\Lambda)$ have different dispositions of three CoN_4O_2 chromophores. The model of the isomer $\Lambda(\Delta\Delta\Delta)$ is rather flat, the pseudo C_3 axes of tris-chelate type CoN_4O_2 chromophores being parallel (p) to the C_3 axis of the CoO_6 one; the structure of $\Lambda(\Delta\Delta\Delta)$ isomer is thus written as $\Lambda(p_\Delta p_\Delta p_\Delta)$. The model of the isomer $\Lambda(\Lambda\Lambda\Lambda)$ is not flat but tall, the pseudo C_3 axes of CoN_4O_2 chromophores being oblique (q) to the C_3 axis of the CoO_6 one. The structure of $\Lambda(\Lambda\Lambda\Lambda)$ isomer is thus written as $\Lambda(q_\Lambda q_\Lambda q_\Lambda)$. The remaining two isomers $\Lambda(\Delta\Delta\Lambda)$ and $\Lambda(\Delta\Lambda\Lambda)$ have a mixed structure, $\Lambda(p_\Delta p_\Delta q_\Lambda)$ and $\Lambda(p_\Delta q_\Lambda q_\Lambda)$, respectively. Kojima *et al.*[19] showed that the CD spectra of the mixed complexes $[Co(en)_x(tn)_y(tmd)_z]^{3+}$ can be expressed by summing up the contributions from three pairs of chelate rings, as has been made in the so-called ring-pairing method[20] (tn = trimethylenediamine and tmd = tetramethylenediamine). By this treatment, Eq. 1 can be rewritten as follows:

$$\left.\begin{aligned} \mathit{\Lambda}(\mathit{\Lambda\Lambda\Lambda}) &= \mathit{\Lambda}(\mathrm{q}_{\Lambda}\mathrm{q}_{\Lambda}\mathrm{q}_{\Lambda}) = 3\mathit{\Lambda}_{\mathrm{qq}} + 3(\mathit{\Lambda}) \\ \mathit{\Lambda}(\mathit{\Delta\Lambda\Lambda}) &= \mathit{\Lambda}(\mathrm{p}_{\Delta}\mathrm{q}_{\Lambda}\mathrm{q}_{\Lambda}) = 2\mathit{\Lambda}_{\mathrm{pq}} + \mathit{\Lambda}_{\mathrm{qq}} + (\mathit{\Lambda}) \\ \mathit{\Lambda}(\mathit{\Delta\Delta\Lambda}) &= \mathit{\Lambda}(\mathrm{p}_{\Delta}\mathrm{p}_{\Delta}\mathrm{q}_{\Lambda}) = \mathit{\Lambda}_{\mathrm{pp}} + 2\mathit{\Lambda}_{\mathrm{pq}} - (\mathit{\Lambda}) \\ \mathit{\Lambda}(\mathit{\Delta\Delta\Delta}) &= \mathit{\Lambda}(\mathrm{p}_{\Delta}\mathrm{p}_{\Delta}\mathrm{p}_{\Delta}) = 3\mathit{\Lambda}_{\mathrm{pp}} - 3(\mathit{\Lambda}) \end{aligned}\right\} \quad (2)$$

where $\mathit{\Lambda}_{\mathrm{pp}}$ *etc.* denote the CD contribution of a ring-pair of two p-oriented $\mathrm{CoN_4O_2}$ chromophores *etc.*

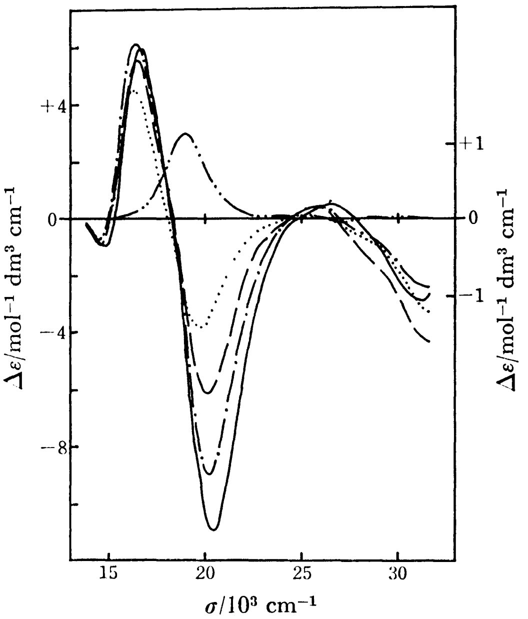

Fig. 7. Calculated curves of $\mathit{\Lambda}_{\mathrm{qq}}$ (——), $\mathit{\Lambda}_{\mathrm{pq}}$ (– – –), $\mathit{\Lambda}_{\mathrm{pp}}$ (–·–·–), and $\mathit{\Lambda}_{\mathrm{aa}}$ (······), and observed curve of $\mathit{\Lambda}$-$[\mathrm{Co(TeO_6H_4)(en)_2}]^+$ (-·····) (the right ordinate).

Equation 2 can be solved by assuming that the CD contribution ($\mathit{\Lambda}$) is equal to the observed CD of $\mathit{\Lambda}$-$[\mathrm{Co(TeO_6H_4)(en)_2}]^+$.[21] The results are shown in Fig. 7. For the dodecaammine complex the CD contribution $\mathit{\Lambda}$ is expressed by $3\mathit{\Lambda}_{\mathrm{aa}}$ which denotes CD contributions of three ring-pairs of two $\mathrm{CoN_4O_2}$ chromophores of tetraammine type. The calculated CD contributions of four kinds of ring-pairs $\mathit{\Lambda}_{\mathrm{pp}}$, $\mathit{\Lambda}_{\mathrm{pq}}$, $\mathit{\Lambda}_{\mathrm{qq}}$, and $\mathit{\Lambda}_{\mathrm{aa}}$ differ from each other in the region of the first d-d absorption band of $\mathrm{CoN_4O_2}$ chromophore. The absolute value of CD intensities in this region is in the order $\mathit{\Lambda}_{\mathrm{qq}} > \mathit{\Lambda}_{\mathrm{pp}} > \mathit{\Lambda}_{\mathrm{pq}} > \mathit{\Lambda}_{\mathrm{aa}}$. The $\mathit{\Lambda}_{\mathrm{pq}}$ contribution can be calculated in two ways from Eq. 2, one from the third formula of the equation (Fig. 7) and the other from the second formula. The results do not differ much, showing the adequacy of Eq. 2.

References

1) Part I of this series: T. Kudo and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **52**, 1648 (1979).

2) A. Werner, *Ber.*, **40**, 2103 (1907).

3) U. Thewalt, *Chem. Ber.*, **104**, 2657 (1971).

4) U. Thewalt and J. Ernst, *Z. Naturforsch., Teil B*, **30**, 818 (1975).

5) D. A. Dixon, R. E. Marsh, and W. P. Schaeffer, *Acta Crystallogr., Sect. B*, **34**, 807 (1978).

6) R. D. Kern and R. A. D. Wentworth, *Inorg. Chem.*, **6**, 1018 (1967).

7) H. A. Goodwin, E. C. Gyarfas, and D. P. Mellor, *Aust. J. Chem.*, **11**, 426 (1958).

8) D. A. Johnson and A. G. Sharpe, *J. Chem. Soc.*, **1966**, 798.

9) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, **1965**, 5094.

10) S. F. Mason and J. W. Wood, *Chem. Commun.*, **1967**, 209.

11) I. Masuda and B. E. Douglas, *J. Coord. Chem.*, **1**, 189 (1971).

12) R. Larsson, S. F. Mason, and B. J. Norman, *J. Chem. Soc., A*, **1966**, 301.

13) S. F. Mason and B. J. Norman, *J. Chem. Soc., A*, **1966**, 307.

14) H. L. Smith and B. E. Douglas, *Inorg. Chem.*, **5**, 784 (1966).

15) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, **1965**, 2883.

16) E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1486 (1971).

17) J. E. Sarneski and F. L. Ulbach, *J. Am. Chem. Soc.*, **93**, 884 (1971).

18) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964); B. E. Douglas, *ibid.*, **4**, 1813 (1965); K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1968); Y. Yamasaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **42**, 119 (1969); N. Matsuoka, J. Hidaka, and Y. Shimura, *Inorg. Chem.*, **9**, 719 (1970); *Bull. Chem. Soc. Jpn.*, **45**, 2491 (1972); **48**, 458 (1975).

19) M. Kojima, H. Yamada, H. Ogino, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 2325 (1977).

20) J. I. Legg and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 2697 (1966).

21) Y. Hosokawa and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **52**, 1051 (1979).