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Circular Dichroism Spectra and Stereochemistry of Dicyanotetrakis(diamine)-tetra-μ-hydroxo-tricobalt(III)(3+) Complexes

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The chiral tetra-μ-hydroxo-trinuclear complexes, *cis*-$[Co(CN)_2\{(OH)_2Co(NH_3)_4\}_2]^{3+}$ and *cis*-$[Co(CN)_2\{(OH)_2Co(diamine)_2\}_2]^{3+}$ have been prepared and separated into their optical isomers and/or diastereomers by column chromatography (diamine: ethylenediamine, (*R*)-1,2-propanediamine, and (*S*,*S*)-1,2-cyclohexanediamine). The absolute configurations of isomers have been assigned on the basis of their CD and ^{13}C NMR spectra and the characterization of mononuclear complex produced by decomposition of the trinuclear isomers of ethylenediamine ligands. It has been proved that the main CD contributions due to the two chiral $Co(OH)_4(CN)_2$ and $Co(N)_4(OH)_2$ centers are additive for the present systems.

Octaamminedicyano-tetra-μ-hydroxo-tricobalt(III) complex salts have been prepared from the reaction of "hexol" complex[1,2] $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ with excess cyanide by Siebert and Schiedermaier,[3] the composition of the trinuclear(3+) ion being comfirmed by X-ray crystal structure analysis.[4] The complex ion has a chiral structure with two cyano ligands in *cis* positions. Thus the *cis*-$[Co(CN)_2\{(OH)_2Co(NH_3)_4\}_2]^{3+}$ ion should be optically resolved. However, no attempt has been reported to resolve this complex.

The present paper deals with the optical resolution of the *cis*-$[Co(CN)_2\{(OH)_2Co(NH_3)_4\}_2]^{3+}$ complex, and the preparation and the separation of isomers of the corresponding diamine complexes, *cis*-$[Co(CN)_2\{(OH)_2Co(diamine)_2\}_2]^{3+}$, where diamine stands for en (ethylenediamine), *R*-pn ((*R*)-1,2-propanediamine), or *S*,*S*-chxn ((*S*,*S*)-1,2-cyclohexanediamine). The isomers were characterized from UV-VIS absorption, circular dichroism (CD), and ^{13}C NMR spectra and from the identification of the decomposition products. The trinuclear isomers are composed of two kinds of chromophore, a *cis*-$Co(OH)_4(CN)_2$ and two *cis*-$Co(N)_4(OH)_2$, as shown in Fig. 1. The central $Co(OH)_4(CN)_2$ chromophore has a configurational chirality, Δ or Λ, due to the skew arrangement of two $Co(OH)_2Co$ four-membered rings. In the cases of the diamine complexes, each $Co(N)_4(OH)_2$ chromophore also has a configurational chirality, Δ or Λ, due to the tris-chelate type arrangement of two diamine and a $Co(OH)_2Co$ rings. Thus six optically active isomers are possible for the diamine complexes in total: $\Delta(\Delta\Delta)$, $\Delta(\Delta\Lambda)$, $\Delta(\Lambda\Lambda)$, $\Lambda(\Delta\Delta)$, $\Lambda(\Delta\Lambda)$, and $\Lambda(\Lambda\Lambda)$, where the chirality symbols in parentheses denote the configurations of the peripheral $Co(N)_4(OH)_2$ chromophores. The six optical isomers of en analogue can be classified into three geometrical isomers, since each of them finds its enantiomer in themselves. Two of these geometrical isomers, $\Delta(\Delta\Delta)$ or $\Lambda(\Lambda\Lambda)$, and $\Delta(\Lambda\Lambda)$ or $\Lambda(\Delta\Delta)$, possess a C_2 axis, whereas another one geometrical isomer $\Delta(\Delta\Lambda)$ or $\Lambda(\Delta\Lambda)$ possesses no symmetry element other than C_1 axis.

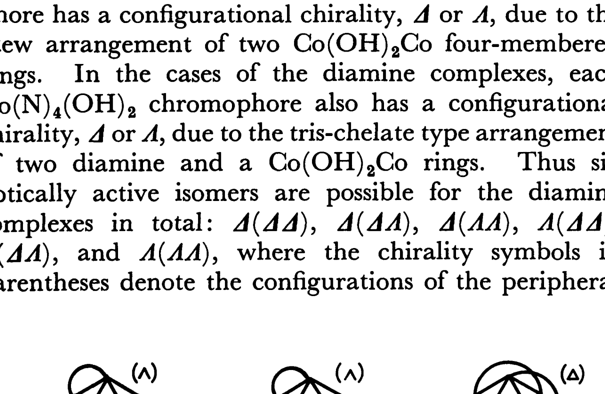

Fig. 1. Three geometrical isomers of the Δ configuration of $Co(OH)_4(CN)_2$ chromophore.

Experimental

Preparation and Optical Resolution of cis-$[Co(CN)_2\{(OH)_2Co(NH_3)_4\}_2]^{3+}$. The racemic sulfate salt was prepared by a modification of the procedure of Siebert and Schiedermaier.[3] To 5 g of "hexol" sulfate[5] $[Co\{(OH)_2Co(NH_3)_4\}_3](SO_4)_3\cdot 4H_2O$ suspended in 30 cm^3 of water was added 1.5 g of sodium cyanide dissolved in 15 cm^3 of water with stirring. A red precipitate was obtained immediately. After continued stirring for a few hours, the precipitate was filtered off and washed with water, ethanol, and ether.

Four-tenths grams of $Ba(CH_3CO_2)_2$ was added to 0.6 g of the red racemic sulfate salt suspended in 20 cm^3 of water and, after stirring for a few hours, the precipitated $BaSO_4$ was removed by filtration. To the filtrate was added 0.36 g of $Na_2(d\text{-}C_4H_4O_6)\cdot 2H_2O$. A pale-red precipitate appeared as the less-soluble diastereomer, which was filtered and purified by washing with water until the washings showed a constant CD value at *ca.* 500 nm. The less-soluble diastereomer was added to an aqueous solution containing ion exchanger resin QAE-Sephadex A-25 ($CH_3CO_2^-$ form, *ca.* 10 times excess) and stirred for a few hours. The resin was removed by filtration and $(NH_4)_2SO_4$ was added to the filtrate to give the optically active salt (Δ isomer), which was washed with water, ethanol, and ether, and dried in air. Found: C, 4.28; H, 4.92; N, 23.81%. Calcd for $[Co(CN)_2\{(OH)_2Co(NH_3)_4\}_2](SO_4)_{3/2}$: C, 4.16; H, 4.89; N, 24.27%.

Preparation and Separation of Isomers of cis-$[Co(CN)_2\{(OH)_2Co(diamine)_2\}_2]^{3+}$. *1)* cis-$[Co(CN)_2\{(OH)_2Co(en)_2\}_2]^{3+}$: A solution of the "en hexol" complex $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ prepared in the one-tenth scale of the Ref. 6 was poured onto a short column of SP-Sephadex C-25 (Na$^+$ form) and eluted with a NaCl solution. To the collected brown eluate of the en hexol (3.76×10^{-3} mol) was added 1.1 g of NaCN (*ca.* 6 times excess). The solution became red within a few hours. After the precipitated solid had been filtered off, the filtrate was poured onto a column (5×60 cm) of SP-Sephadex C-25 (Na$^+$ form). The adsorbed band was eluted with a 0.2 mol dm^{-3} $Na_2(d\text{-}C_4H_4O_6)$ solution. Succeeding a broad pink band (chemically unidentified) two red ones were eluted. The earlier- and later-eluted portions of each band showed the opposite CD signs; that is, each band consists of a couple of enantiomers. Each of the enantiomers was named E1(−), E1(+), E2(+), or E2(−) after its sign of the CD extremum at *ca.* 500 nm. Each combined eluate E1 or E2 was diluted to about 5 times the volume with water, poured onto a short column of SP-Sephadex C-25 (Na^+ form), and eluted with a NaCl aqueous solution. The eluate was evaporated to a small volume at a temperature below 30 °C. After repeated removal of NaCl, the resulting solution was treated with an adequate amount of ethanol and kept standing in a refrigerator. Red crystals (the chloride salt) deposited in a few days were collected with suction, recrystallized from a water–ethanol solution, washed with ethanol and ether, and dried in air. The perchlorate salt was obtained in a similar way. Found for the racemic chloride of E1: C, 16.60; H, 6.06; N, 19.49%. Calcd for $[Co(CN)_2\{(OH)_2Co(en)_2\}_2]Cl_3 \cdot 4.5H_2O$: C, 16.57; H, 6.26; N, 19.33%. Found for the racemic perchlorate salt of E1: C, 14.33; H, 4.40; N, 16.74%. Calcd for $[Co(CN)_2\{(OH)_2Co(en)_2\}_2](ClO_4)_3$: C, 14.37; H, 4.34; N, 16.76%. Found for the racemic chloride salt of E2: C, 16.18, H, 6.33; N, 18.88%. Calcd for $[Co(CN)_2\{(OH)_2Co(en)_2\}_2]Cl_3 \cdot 5.5H_2O$: C, 16.17; H, 6.38; N, 18.86%. Found for the racemic perchlorate salt of E2: C, 13.48; H, 4.76; N, 15.77%. Calcd for $[Co(CN)_2\{(OH)_2Co(en)_2\}_2](ClO_4)_3 \cdot 3H_2O$: C, 13.50; H, 4.76; N, 15.74%.

In cases in which the optically active $\Lambda(\Delta\Delta\Delta)$ isomer[6] of hexol complex $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ was used as starting material, also two red bands were characterized on the chromatographic column. The CD measurements indicated that the band eluted firstly was E1(−) and that the one eluted afterward a new isomer, which was denoted as E3(+). Each eluate was reloaded on a short column of SP-Sephadex C-25 (Na^+ form) to remove the d-$C_4H_4O_6^{2-}$ ion, and eluted with a NaCl aqueous solution. After repeated removal of NaCl, the E1(−) solution was poured onto a short column of QAE-Sephadex A-25 (Br^- form) and eluted with water, and the eluate was evaporated to a small volume. The resulting solution was treated with an adequate amount of ethanol and kept standing in a refrigerator. Red crystals of E1(−) deposited in a few days were collected with suction, washed with ethanol and ether, and dried in air. E3(+) isomer was obtained in a similar manner using acetone in place of ethanol. Found for E1(−): C, 14.35; H, 5.15; N, 16.40%. Calcd for $[Co(CN)_2\{(OH)_2Co(en)_2\}_2]Br_3 \cdot 4H_2O$: C, 14.15; H, 5.22; N, 16.50%. Found for E3(+): C, 14.00; H, 5.06; N, 16.04%. Calcd for $[Co(CN)_2\{(OH)_2Co(en)_2\}_2]Br_3 \cdot 3.5H_2O \cdot 1/5\,NaBr$: C, 13.96; H, 5.15; N, 16.28%.

The isomer E2(−) was separated as follows. The eluate E2 was diluted with water and reloaded on a column of SP-Sephadex C-25 (Na^+ form). The adsorbed band was eluted with 0.2 mol dm^{-3} $Na_2(d$-$C_4H_4O_6)$ and some later fractions which showed the same CD spectrum of (−) sign at *ca.* 500 nm were collected together. This procedure was repeated until the CD values became constant and then the solution was stored for CD measurements after the chromatographic removal of d-$C_4H_4O_6^{2-}$ ion.

2) cis-*$[Co(CN)_2\{(OH)_2Co(S,S\text{-}chxn)_2\}_2]^{3+}$*: The isomers were prepared and separated by the same procedure as in *1)* except for the use of *S,S*-chxn instead of en. Four red bands were observed on the chromatographic column. The CD measurements showed that the second and the third bands were each composed of two isomers. The separation of these two isomers was accomplished by the way described for E2(−). The resulting six bands were denoted as C1, C2, C3, C4, C5, and C6 in the elution order. The isolation as solid crystalline salts was successful only for the C4 and C6 eluate. Found for C4: C, 29.83; H, 6.21; N, 13.27%. Calcd for $[Co(CN)_2\{(OH)_2Co(S,S\text{-}chxn)_2\}_2]Br_3 \cdot 3H_2O$: C, 29.82; H, 6.35; N 13.37%. Found for C6: C, 33.51; H, 7.24; N, 14.89%. Calcd for $[Co(CN)_2\{(OH)_2Co(S,S\text{-}chxn)_2\}_2]Cl_3 \cdot 4H_2O$: C, 33.50; H, 7.35; N, 15.03%. The eluates C1, C2, C3, and C5 were stored for CD measurements.

3) cis-*$[Co(CN)_2\{(OH)_2Co(R\text{-}pn)_2\}_2]^{3+}$*: The isomers were prepared and separated by the same procedure as in *1)* except for the use of *R*-pn instead of en. Three red bands were observed on the column. From the measurements of CD spectra, it turned out that the third band was composed of four isomers. Their separation was carried out by a similar procedure as described for E2(−). The resulting six bands were denoted as P1, P2, P3, P4, P5, and P6 in the elution order. No crystalline salt was isolated in this system as yet. Each eluate was stored for CD measurements after chromatographic removal of d-$C_4H_4O_6^{2-}$ ion.

Measurements: The visible and ultraviolet absorption spectra were measured on a Hitachi 330 spectrophotometer and CD spectra recorded on a JASCO MOE-1 spectropolarimeter. The absorption and CD measurements were made in aqueous solutions at room temperature. The ^{13}C NMR spectra were measured with a JEOL FX-90Q NMR spectrometer in D_2O containing dioxane as an internal standard.

Results and Discussion

Preparation and Characterization of Isomers. In the preparation of trinuclear complexes with diamine ligands, the purity of the starting "hexol" complex was of primary importance and therefore its separation was carried out cautiously. An unidentified brown band was observed just before the desired hexol band on the chromatographic column. If the starting hexol solution includes this unknown brown species, the reaction with NaCN gave an insoluble pale-brown precipitate as a main product. Infrared spectra of the precipitate showed two sharp bands at 2160 and 2240 cm^{-1} in the region of the CN stretching vibration mode, which indicated the coodination of CN^-. The N/C ratio was 1 for the en system and 0.8 for the *R*-pn system. These data suggest that the precipitate is a di- or polynuclear complex $Co_2(CN)_4(\mu\text{-}OH)_2(diamine)_2$, which was insoluble in most solvents.

The yields of isomers were in the order of E2>E1 for en series, P2>P4≃P6>P5>P3>P1 for the *R*-pn series, and C1≃C3≃C4≃C6>C2≃C5 for the *S,S*-chxn series. The isomers P5 and P6 underwent mutarotation during the separation by the column chromatography. In the course of attempted crystallization of C1 isomer, it was C6 isomer that appeared as crystals.

The first spin-allowed d-d absorption band of *cis*-$[Co(CN)_2\{(OH)_2Co(NH_3)_4\}_2]^{3+}$ appears at 19420 cm^{-1} and seems to be composed of those of *cis*-$CoN_4(OH)_2$ and *cis*-$Co(OH)_4(CN)_2$ chromophores, since the first absorption band of $[Co(CO_3)(NH_3)_4]^+$ appears[7] at 19100 cm^{-1} and the two components[8] of first absorption band of *cis*-$[Co(CO_3)_2(CN)_2]^{3-}$ at 18300 and 22500 cm^{-1}. In the corresponding region of CD curve there are two extrema at 16860 and 19380 cm^{-1} (Fig. 2). The absorption shoulder at 23500 cm^{-1} may be assigned to the higher wavenumber component of the split first band of $Co(OH)_4(CN)_2$ moiety. Since the second d-d transition bands of both the chromophores are expected to have about the same energies, the absorption shoulder

TABLE 1. ABSORPTION DATA of *cis*-$[Co(CN)_2\{(OH)_2Co(NH_3)_4\}_2]^{+3}$ AND *cis*-$[Co(CN)_2\{(OH)_2Co(diamine)_2\}_2]^{3+}$ IN WATER
(Position of a shoulder is presented by a rough value of wave number with a sign sh)

Complex	$\sigma_{max}/10^3$ cm^{-1} and $\log(\varepsilon/mol^{-1}\,dm^3\,cm^{-1})$ in parentheses			
(Ammine)	19.42 (2.36) 23.5 sh (2.32)	26.7 sh (2.63)	35.7 sh (3.61)	
E1(ClO_4)	19.80 (2.50)	26.3 sh (2.70)	35.7 sh (3.76)	47.00 (4.64)
E1(Cl)	19.80 (2.50)	26.3 sh (2.70)	35.1 sh (3.68)	46.00 (4.64)
E2(ClO_4)	19.80 (2.54)	26.3 sh (2.74)	35.7 sh (3.81)	46.00 (4.66)
E2(Cl)	19.80 (2.49)	26.3 sh (2.70)	35.1 sh (3.69)	46.00 (4.62)
E1(−)	19.80 (2.48)	27.0 sh (2.75)	35.7 sh (3.67)	45.5 sh (4.63)
E2(−)	19.80 (2.50[a])			
E3(+)	19.80 (2.49)	26.3 sh (2.74)	35.1 sh (3.68)	46.5 sh (4.62)
P1—P6	19.80 (2.50[a])			
C1, C2, C3, C5	19.61 (2.55[a])			
C4	19.61 (2.54)	25.6 sh (2.70)	33.9 sh (3.71)	44.6 sh (4.68)
C6	19.61 (2.55)	25.3 sh (2.68)	34.5 sh (3.72)	45.00 (4.66)

a) Estimated value (See text).

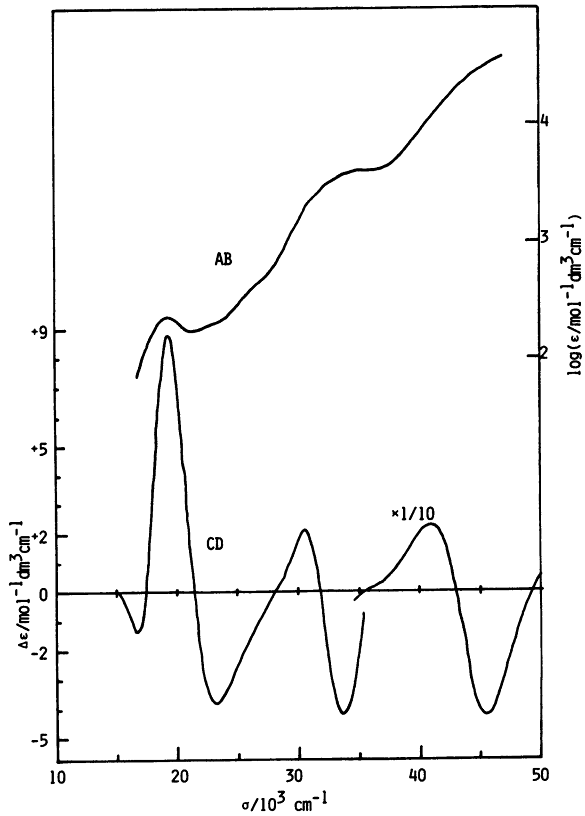

Fig. 2. The absorption (AB) and CD curves of *cis*-$[Co(CN)_2\{(OH)_2Co(NH_3)_4\}_2]^{3+}$.

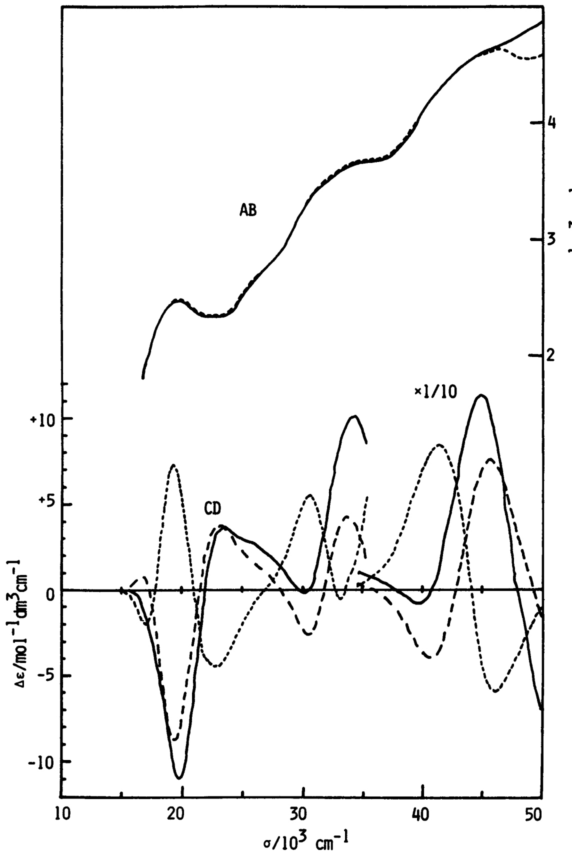

Fig. 3. The absorption (AB) and CD curves of *cis*-$[Co(CN)_2\{(OH)_2Co(en)_2\}_2]^{3+}$ isomers: E1(−) (——) and E2 (------) (AB); E1(−) (——), E2(−) (- - -), and E3(+) (------) (CD).

at 26700 cm^{-1} is assigned to their overlap. The intense band at 35700 cm^{-1} can be assigned to the charge-transfer transition from the OH bridging group to the central metal, $e_g(Co) \leftarrow p_\pi(O)$. The CD pattern is very similar to that of the parent "hexol" $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ in the regions of around 20000 and 35000—50000 cm^{-1} (Fig. 2), and the CD intensity being about two-thirds of the "hexol."[2] Therefore, the absolute configuration of the present trinuclear complex is assigned on the basis of the CD signs in these regions: Δ configuration for (+) CD around 20000 cm^{-1} and for (+) and (−) bands from the lower energy side in the region of 35000—50000 cm^{-1}. Thus the isomer obtained from the less-soluble diastereomer of *d*-tartrate salt has the Δ absolute configuration.

All complexes containing diamine ligands showed similar absorption spectra to one another (Table 1). The first d-d absorption maxima become more intense and shift to the higher wave number than that of the corresponding ammine complex. Therefore, the CD

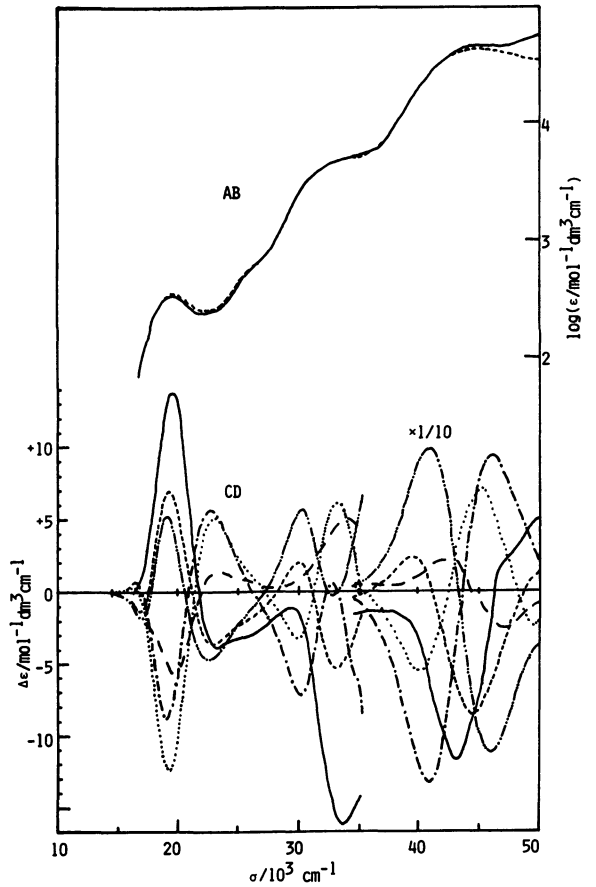

Fig. 4. The absorption (AB) and CD curves of *cis*-[Co-$(CN)_2\{(OH)_2Co(S,S\text{-chxn})_2\}_2]^{3+}$ isomers: C4 (——) and C6 (------) (AB); C1 (——), C2 (– – –), C3 (------), C4 (······), C5 (–··–), and C6 (—·—) (CD).

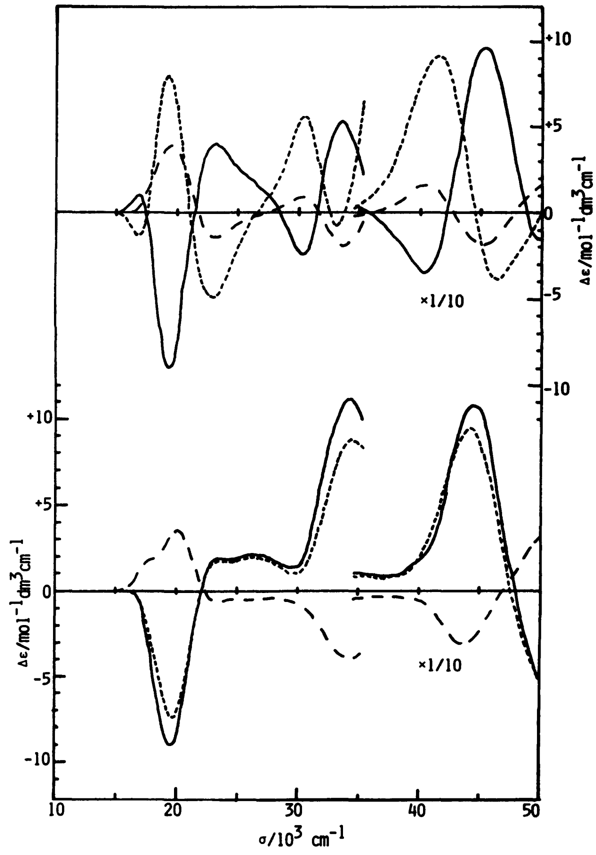

Fig. 5. The CD curves of *cis*-$[Co(CN)_2\{(OH)_2Co(R\text{-}pn)_2\}_2]^{3+}$ isomers: P1 (——), P2 (------), and P3 (– – –) (lower curves); P4 (——), P5 (— —), and P6 (------) (upper curves).

intensities of the isomers which were not obtained as solid salt, were calculated on the basis of the assumption that E2(−) and all *R*-pn isomers have the molar absorption coefficient log (ε/mol⁻¹ dm³ cm⁻¹) = 2.50 at 19800 cm⁻¹ and C1, C2, C3, and C5 isomers 2.55 at 19610 cm⁻¹. The $|\Delta\varepsilon|$ values at *ca.* 20000 cm⁻¹ are in the range of 7—12 (Figs. 3, 4, and 5), being comparable with that for the ammine complex. The absolute configuration of $Co(OH)_4(CN)_2$ moiety can be assigned by the sign of this band; that is, Λ configuration for negative sign and Δ for positive. The CD pattern in the region of 35000—50000 cm⁻¹ are also similar to that of the ammine analogue, though their intensities about 2—3 times stronger (Table 2). The intensity and sign of the CD band at *ca.* 45000 cm⁻¹ of the diamine complex are comparable with those of the hexol complex of corresponding diamine.[9] The absolute configuration of $Co(OH)_4(CN)_2$ moiety can be assigned also on the basis of the sign of this band as was done for the $Co(OH)_6$ moiety of hexol: Δ configuration for a negative sign and Λ for positive. The assignments are in good agreement to those from the CD sign of the first d-d absorption band.

Configuration of cis-$[Co(CN)_2\{(OH)_2Co(en)_2\}_2]^{3+}$. ¹³C NMR spectra showed four signals (45.89, 45.19, 44.97, and 43.29 ppm) for E3(+), also four (46.16, 45.02, 44.64, and 43.89 ppm) for E1(rac), and six (46.27, 46.05, 45.08, 44.64, 44.00, and 42.86 ppm) for E2(rac) in the methylene region of en. This result confirms that the isomer E2(rac) has no symmetry and that the configuration of its two $Co(N)_4(OH)_2$ moieties are ($\Delta\Lambda$).

Acid hydrolysis of one mole of *cis*-$[Co(CN)_2\{(OH)_2Co(en)_2\}_2]^{3+}$ ion is expected to produce one mole of $[Co(CN)_2(H_2O)_4]^+$ and two moles of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$. Since the former tetraaqua ion has no chirality, only latter bis(ethylenediamine) complex will contribute to the CD spectrum. The isomer $\Delta(\Delta\Delta)$ or $\Lambda(\Delta\Delta)$ will produce two Δ-$[Co(en)_2(H_2O)_2]^{3+}$ ions, and $\Delta(\Lambda\Lambda)$ or $\Lambda(\Lambda\Lambda)$ two Λ-$[Co(en)_2(H_2O)_2]^{3+}$ ions, whereas $\Delta(\Delta\Lambda)$ or $\Lambda(\Delta\Lambda)$ will produce an equal amount of Δ- and Λ-$[Co(en)_2(H_2O)_2]^{3+}$, namely rac-$[Co(en)_2(H_2O)_2]^{3+}$. The isomer E1(−) was decomposed by adding a 6.0 mol dm⁻³ HCl solution to give a negative CD band at 483 nm ($\Delta\varepsilon = -0.81$), which corresponds to that of Δ-$[Co(en)_2(H_2O)_2]^{3+}$ ($\Delta\varepsilon_{485} = -1.05$).[10] Similarly, the isomer E3(+) also showed a negative CD band ($\Delta\varepsilon = -0.56$). These results indicate that the isomers E1(−) and E3(+) prepared from $\Lambda(\Delta\Delta\Delta)$-hexol have the $\Lambda(\Delta\Delta)$ and $\Delta(\Delta\Delta)$ configurations, respectively.

Thus, from the CD and ¹³C NMR spectra and the acid decomposition experiment it is concluded that the absolute configurations of E1(−), E1(+), E2(−), E2(+), and E3(+) isomers are $\Lambda(\Delta\Delta)$, $\Delta(\Lambda\Lambda)$, $\Lambda(\Delta\Lambda)$,

TABLE 2. CD DATA OF *cis*-$[\mathrm{Co(CN)_2\{(OH)_2Co(NH_3)_4\}_2}]^{3+}$ AND *cis*-$[\mathrm{Co(CN)_2\{(OH)_2Co(diamine)_2\}_2}]^{3+}$ IN WATER (σ_{ext} value is given in $10^3\ \mathrm{cm^{-1}}$ and $\Delta\varepsilon$ in $\mathrm{mol^{-1}\ dm^3\ cm^{-1}}$ in parentheses)

Complex	d-d transition region	charge-transfer region	Complex	d-d transition region	charge-transfer region
(Ammine, Δ)	16.86 (−1.41)	30.58 (+2.17)	C5[a]	17.09 (−1.92)	30.40 (+5.78)
	19.38 (+8.88)	33.67 (−4.26)		19.14 (+5.38)	32.89 (−0.34)
	23.20 (−3.87)	40.82 (+23.1)		22.62 (−4.76)	40.98 (+99.7)
		45.45 (−42.9)			45.98 (−115)
E1(−)	19.82 (−11.1)	30.21 (−0.26)	C6	16.67 (+0.64)	30.30 (−7.21)
	23.47 (+3.68)	34.31 (+10.2)		19.16 (−8.94)	32.84 (+0.62)
		39.68 (−8.12)		22.73 (+5.65)	40.82 (−134)
		45.05 (+114)			46.08 (+93.4)
E2(−)[a]	16.75 (+0.83)	30.65 (−2.61)	P1[a]	19.69 (−9.10)	34.25 (+11.1)
	19.42 (−8.79)	33.79 (+4.33)		23.7 sh (+1.87)	44.44 (+109)
	23.19 (+3.79)	40.82 (−39.3)		26.53 (+2.17)	
		45.66 (+76.6)	P2[a]	19.80 (−7.46)	34.48 (+8.78)
E3(+)	17.05 (−2.13)	30.58 (+5.57)		23.53 (+1.71)	44.25 (+94.7)
	19.29 (+7.35)	33.33 (−0.48)		26.53 (+1.96)	
	22.83 (−4.51)	41.32 (+86.4)	P3[a]	20.08 (+3.53)	34.19 (−3.97)
		46.08 (−63.0)		23.53 (−0.67)	43.48 (−30.8)
C1[a]	19.63 (+13.9)	33.90 (−16.2)		25.97 (−0.53)	
	23.36 (−3.90)	43.20 (−116)	P4[a]	16.84 (+1.09)	30.30 (−2.48)
C2[a]	19.80 (−5.66)	34.19 (+5.04)		19.38 (−9.09)	33.74 (+5.41)
	23.36 (+1.36)	42.46 (+22.0)		23.15 (+3.97)	40.32 (−34.1)
		47.17 (−25.2)			45.45 (+96.3)
C3[a]	16.95 (−1.41)	30.21 (+2.06)	P5[a]	19.57 (+3.97)	30.30 (+0.97)
	19.34 (+7.00)	33.33 (−5.33)		23.20 (−1.46)	33.67 (−1.91)
	22.99 (−3.63)	39.60 (+24.5)			40.49 (+16.3)
		44.64 (−85.9)			45.45 (−18.2)
C4	16.39 (+0.24)	30.12 (−3.30)	P6[a]	16.92 (−1.35)	30.49 (+5.64)
	19.34 (−12.5)	33.33 (+6.25)		19.23 (+8.04)	33.22 (−0.72)
	23.09 (+5.12)	40.00 (−55.9)		22.99 (−4.92)	41.15 (+93.1)
		45.35 (+70.9)			46.08 (−39.8)

[a] The CD intensities were calculated by the method described in text.

TABLE 3. THE FORMATION RATIOS OF OPTICAL ISOMERS OF *cis*-$[\mathrm{Co(CN)_2\{(OH)_2Co(en)_2\}_2}]^{3+}$ IN THE REACTION OF THE OPTICALLY ACTIVE HEXOL ISOMERS WITH EXCESS CYANIDE

(The ratio was determined from the absorbance at 505 nm.)

Absolute configuration of the starting hexol isomer[4]	Formation ratios of derivatives				
$\Lambda(\Delta\Delta\Delta)$	Calcd	$\Lambda(\Delta\Delta)$ only			
	Obsd	$\Lambda(\Delta\Delta)$	3	$\Delta(\Delta\Delta)$	1
$\Lambda(\Delta\Delta\Lambda)$	Calcd	$\Lambda(\Delta\Delta)$	1	$\Lambda(\Lambda\Delta)$	2
	Obsd	$\Lambda(\Delta\Delta)$	1	E2*	5

* E2: $\Lambda(\Lambda\Delta)+\Delta(\Lambda\Delta)$.

$\Delta(\Delta\Lambda)$, and $\Delta(\Delta\Delta)$, respectively.

The preparation of en trinuclear complexes was achieved from the two optical isomers of en "hexol" instead of a mixture of several isomers. If the trinuclear complex is formed without racemization nor isomerization, that is, each of the $\mathrm{Co(en)_2(OH)_2}$ moiety in the starting complex is replaced statistically by two cyano ligands, it is possible to predict the yields and the absolute configurations of the derivatives. However, the observed ratios are somewhat different from the estimated ones (Table 3), which are related with the partial racemization and/or isomerization.

Characterization of cis-$[\mathit{Co(CN)_2\{(OH)_2Co(}\mathrm{R}\mathit{\text{-}pn)_2\}_2}]^{3+}$ *and* cis-$[\mathit{Co(CN)_2\{(OH)_2Co(}\mathrm{S,S}\mathit{\text{-}chxn)_2\}_2}]^{3+}$ *Complexes.* The trinuclear complex of optically active diamine has six diastereomers. In the *R*-pn series, six isomers were found in the chromatographic separation. The isomers P1 and P2, however, showed almost the same CD spectra in all of the region measured. It appears that these isomers correspond to the geometrical ones due to the different spacial arrangements of the asymmetric carbons of four *R*-pn ligands. A similar kind of isomerism was observed for the hexol complex.[9] The six isomers of *R*-pn series are assigned in comparison of the CD spectra (Table 2) with those of the en series as follows: $\Lambda(\Delta\Delta)$ for P1 and P2, $\Delta(\Lambda\Lambda)$ for P3, $\Lambda(\Delta\Lambda)$ for P4, $\Delta(\Delta\Lambda)$ for P5, and $\Delta(\Delta\Delta)$ for P6 (Table 4).

For the *S*,*S*-chxn series, all the six diastereomers were completely identified. Since an *S*,*S*-chxn chelate ring take a δ conformation, the *ob* or *lel* orientation[11] should be fixed for Δ- or Λ-configuration of the $\mathrm{Co(N)_4(OH)_2}$ moiety, respectively. It is generally accepted that the *lel* orientation is more stable than the *ob* one. The isomers C2 and C5 were less stable than the others in addition to their low yield. Therefore, their configurations of $\mathrm{Co(N)_4(OH)_2}$ moiety are expected to be $(\Delta\Delta)$, that is they have *ob*$_4$ form. Taking this expectationinto account, the absolute configurations of all the isomers are estimated on the CD spectra (Table 2) as follows:

TABLE 4. ABSOLUTE CONFIGURATIONS OF *cis*-$[Co(CN)_2\{(OH)_2Co(diamine)_2\}_2]^{3+}$ ISOMERS

Absolute configuration	en series	Absolute configuration	*R*-pn series	Absolute configuration	*S*,*S*-chxn series
$\Lambda(\Delta\Delta)$	E1(−)	$\Lambda(\Delta lel_2\cdot\Delta lel_2)$	P1, P2	$\Lambda(\Delta ob_2\cdot\Delta ob_2)$	C2
$\Delta(\Lambda\Lambda)$	E1(+)	$\Delta(\Lambda ob_2\cdot\Lambda ob_2)$	P3	$\Delta(\Lambda lel_2\cdot\Lambda lel_2)$	C1
$\Delta(\Delta\Lambda)$	E2(+)	$\Delta(\Delta lel_2\cdot\Lambda ob_2)$	P5	$\Delta(\Delta ob_2\cdot\Lambda lel_2)$	C3
$\Lambda(\Delta\Lambda)$	E2(−)	$\Lambda(\Delta lel_2\cdot\Lambda ob_2)$	P4	$\Lambda(\Delta ob_2\cdot\Lambda lel_2)$	C4
$\Delta(\Delta\Delta)$	E3(+)	$\Delta(\Delta lel_2\cdot\Delta lel_2)$	P6	$\Delta(\Delta ob_2\cdot\Delta ob_2)$	C5
$\Lambda(\Lambda\Lambda)$	—	$\Lambda(\Lambda ob_2\cdot\Lambda ob_2)$	—	$\Lambda(\Lambda lel_2\cdot\Lambda lel_2)$	C6

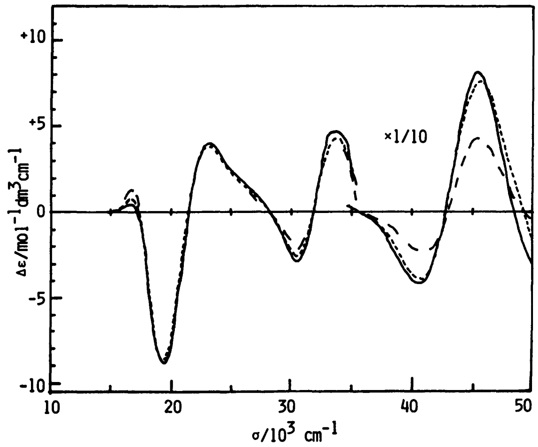

Fig. 6. Configurational CD curves of $Co(OH)_4(CN)_2$ chromophore for en.
$\Lambda=\{E1(-)-E3(+)\}/2$ (——), $\Lambda=\Lambda(\Lambda\Delta)=E2(-)$ (------), and Λ configuration of ammine series (— —).

$\Delta(\Lambda\Lambda)$ for C1, $\Lambda(\Delta\Delta)$ for C2, $\Delta(\Delta\Lambda)$ for C3, $\Lambda(\Delta\Lambda)$ for C4, $\Delta(\Delta\Delta)$ for C5, and $\Lambda(\Lambda\Lambda)$ for C6. The estimation are completely confirmed by the CD curve analysis discussed below and summarized in Table 4.

Additivity of CD Contributions. If the observed CD curves of *cis*-$[Co(CN)_2\{(OH)_2Co(en)_2\}_2]^{3+}$ can be simply divided into each contribution due to $Co(OH)_4(CN)_2$ and $Co(N)_4(OH)_2$ chiralities as has been established for configurational and vicinal chiralities of many mononuclear cobalt(III) complexes,[12] the following relations are expected to hold for the observed CD curves $\Lambda(\Lambda\Lambda)$, $\Lambda(\Delta\Lambda)$, or $\Lambda(\Delta\Delta)$:

$$\Lambda(\Lambda\Lambda) = \Lambda + 2(\Lambda),$$
$$\Lambda(\Delta\Lambda) = \Lambda + (\Lambda) + (\Delta) = \Lambda,$$
$$\Lambda(\Delta\Delta) = \Lambda + 2(\Delta),$$

where Λ and Δ, and (Λ) and (Δ) are CD contributions due to the central $Co(OH)_4(CN)_2$ and the peripheral $Co(N)_4(OH)_2$ chiralities, respectively. Then the individual Λ and (Δ) contributions can be derived from the observed CD curves by the following relations:

$$\Lambda = [\Lambda(\Delta\Delta)-\Delta(\Delta\Delta)]/2,$$
$$(\Delta) = [\Lambda(\Delta\Delta)-\Lambda(\Delta\Lambda)]/2,$$
$$(\Delta) = [\Lambda(\Delta\Lambda)+\Delta(\Delta\Delta)]/2.$$

Figure 6 shows the calculated CD contribution Λ due to the $Co(OH)_4(CN)_2$ moiety. This is quite similar to the observed CD curve $\Lambda(\Delta\Lambda)=\Lambda$ of the E2(−) isomer and also in good agreement with that of the Λ isomer of ammine series. The calculated Δ CD curves due to the $Co(N)_4(OH)_2$ moiety are also similar to one another (Fig. 7) and the CD sign at *ca.* 20000 cm^{-1} is compatible with that of the main component in the region of the first d-d transition of the $[Co(en)_2(O\text{–}O)]$ complexes having the same configuration.[10] These facts mean that the simple additivity rule assumed above is adequate for the present system. It is recognized evidently that the chirality of the central $Co(OH)_4(CN)_2$ moiety induces the dominant CD contribution. In the case of the en hexol isomers, this kind of additivity of CD spectra was unsatisfactory.[6]

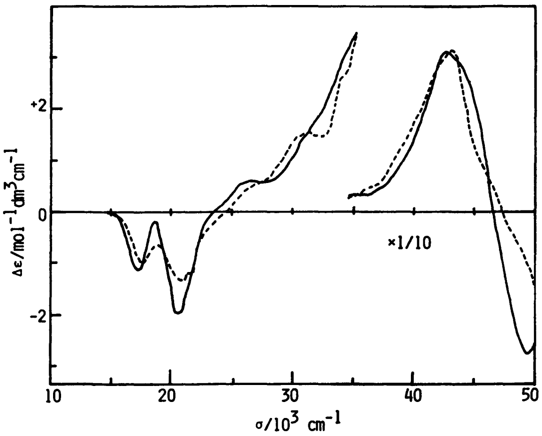

Fig. 7. Configurational CD curves of $Co(N)_4(OH)_2$ chromophore for en.
$(\Delta)=\{E1(-)-E2(-)\}/2$ (——) and $\{E2(-)+E3(+)\}/2$ (---).

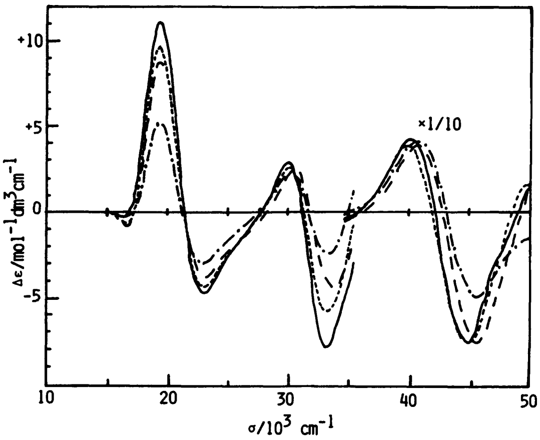

Fig. 8. Configurational CD curves of $Co(OH)_4(CN)_2$ chromophore for *S*,*S*-chxn. $\Delta=(C1-C6)/2$ (——), $(C5-C2)/2$ (—·—), and $(C3-C4)/2$ (------), and E2(+) (— —) for comparison.

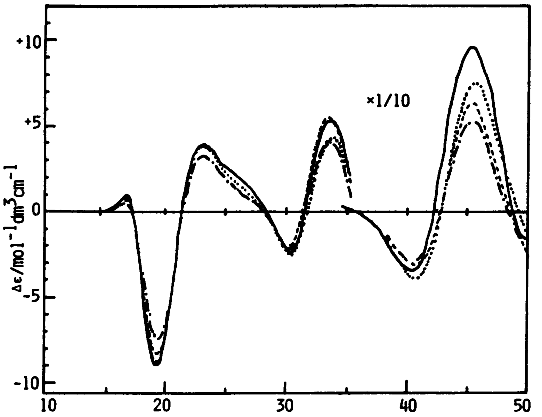

Fig. 9. Configurational CD curves of $Co(OH)_2(CN)_2$ chromophore for *R*-pn. Λ=P4 (——), (P1−P6)/2 (------), and (P2—P6)/2 (—·—), and E2(−)(······) for comparison.

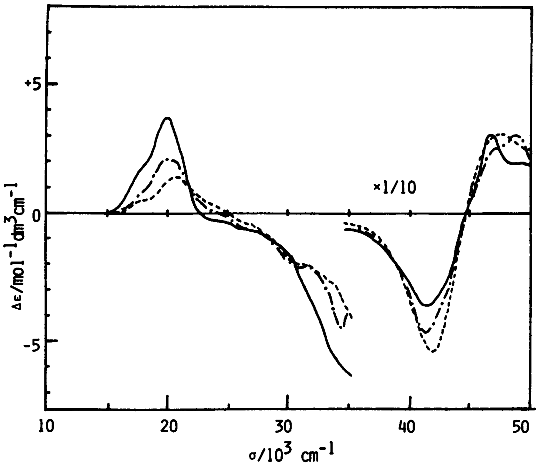

Fig. 10. Configurational CD curves of $Co(N)_4(OH)_2$ chromophore for *S*,*S*-chxn. (Λ)=(C1−C3)/2 (——), (C3−C5)/2 (------), and (C6—C4)/2 (—·—).

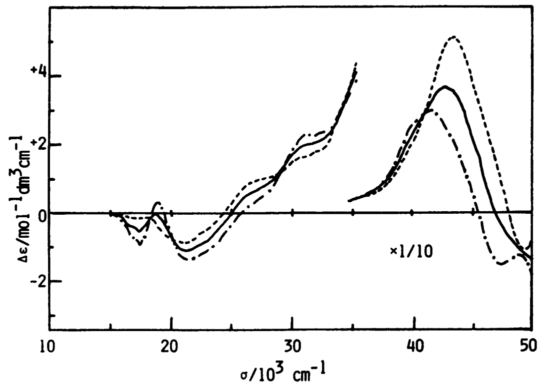

Fig. 11. Configurational CD curves of $Co(N)_4(OH)_2$ chromophore for *R*-pn. (Δ)=(P1+P6)/4 (——), (P4+P6)/2 (------), and (P1−P4)/2 (—·—).

As for the *R*-pn series, we get the following relations:

$$\Delta(\Delta R_2\cdot\Delta R_2) = \Delta + 2(\Delta) + 4(R),$$
$$\Delta(\Delta R_2\cdot\Lambda R_2) = \Delta + (\Delta) + (\Lambda) + 4(R) = \Delta + 4(R),$$
$$\Lambda(\Lambda R_2\cdot\Lambda R_2) = \Lambda + 2(\Lambda) + 4(R),$$

where (R) is the vicinal contribution of an *R*-pn ligand. The individual Δ (or Λ) and (Λ) (or (Δ)) can be derived from the observed CD curves from the following relations:

$$\begin{aligned}\Delta &= [\Delta(\Lambda R_2\cdot\Lambda R_2)-\Lambda(\Lambda R_2\cdot\Lambda R_2)]/2\\ &= [\Delta(\Delta R_2\cdot\Delta R_2)-\Lambda(\Delta R_2\cdot\Delta R_2)]/2\\ &= [\Delta(\Delta R_2\cdot\Lambda R_2)-\Lambda(\Delta R_2\cdot\Lambda R_2)]/2,\\ (\Lambda) &= [\Delta(\Lambda R_2\cdot\Lambda R_2)-\Delta(\Delta R_2\cdot\Lambda R_2)]/2\\ &= [\Delta(\Delta R_2\cdot\Lambda R_2)-\Delta(\Delta R_2\cdot\Delta R_2)]/2\\ &= [\Lambda(\Lambda R_2\cdot\Lambda R_2)-\Lambda(\Delta R_2\cdot\Lambda R_2)]/2.\end{aligned}$$

Figures 8 and 9 show the calculated CD curves due to the central $Co(OH)_4(CN)_2$ moiety in the *S*,*S*-chxn(Δ) and *R*-pn(Λ) trinuclear complexes, respectively, as well as the observed Δ or Λ CD curves of the en isomer E2(+) or E2(−) for comparison. The vicinal contribution of *R*-pn ligands is neglected in the calculation for *R*-pn series. However, the curves are in fair agreement with one another except for that obtained from the unstable C2 and C5 isomers. Figures 10 and 11 show the calculated (Λ) and (Δ) CD curves due to the peripheral $Co(N)_4(OH)_2$ moiety. The curves are relatively in good agreement with one another. The vicinal CD contributions due to the coodinated optically active diamine (*R*) and (*S*) can not be calculated clearly because they are negligibly small compared with the CD contributions Δ, Λ, (Λ), or (Δ).

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