1588 © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* *53,* *1588—1594 (1980)* [Vol. 53, No. 6

Circular Dichroism and Stereochemistry of Tetranuclear Cobalt(III) Complexes of Hexol Type. III.[1] The *meso*-2,3-Butanediamine, (*R*)-1,2-Propanediamine, and (*R,R*)-1,2-Cyclohexanediamine Complexes

Tomikatsu Kudo* and Yoichi Shimura
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

(Received October 24, 1979)

Eight, six, and four optical isomers of diamine hexols $[Co\{(OH)_2Co(diamine)_2\}_3]^{6+}$ containing *meso*-2,3-butanediamine, (*R*)-1,2-propanediamine, and (*R,R*)-1,2-cyclohexanediamine, respectively, were separated by column chromatography. The absorption and CD (circular dichroism) spectra were measured in the visible and ultraviolet regions in 0.01 mol dm^{-3} HCl, the absolute configurations being determined mainly on the basis of the CD spectra. Assuming that the configurational chiralities are identical to those of the corresponding ethylenediamine hexol isomers, it has been established that the *lel* and *ob* orientations of the (*R*)-diamine ligand show different vicinal CD curves due to the asymmetric carbon atom in the ligand.

Eight optical isomers $\Delta(\Delta\Delta\Delta)$, $\Delta(\Delta\Delta\Lambda)$, $\Delta(\Delta\Lambda\Lambda)$, $\Delta(\Lambda\Lambda\Lambda)$, $\Lambda(\Delta\Delta\Delta)$, $\Lambda(\Delta\Delta\Lambda)$, $\Lambda(\Delta\Lambda\Lambda)$, and $\Lambda(\Lambda\Lambda\Lambda)$ are theoretically possible for a hexakis(diamine)-hexa-μ-hydroxo-tetracobalt(III) ion $[Co\{(OH)_2Co(diamine)_2\}_3]^{6+}$. All the eight isomers of $[Co\{OH)_2Co(en)_2\}_3]^{6+}$ (en hexol) were separated by column chromatography,[1] CD (circular dichroism) spectra being studied in comparison with that of the corresponding ammine hexol $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$.[2] Only a few investigations have been reported for hexol complexes containing optically active diamines; for example, Masuda and Douglas[3] reported only two and one of the possible eight optical isomers of $[Co\{(OH)_2Co((S)$- and (R)-1,2-propanediamine$)_2\}_3]^{6+}$, respectively. The present paper deals with the preparation and separation of $[Co\{(OH)_2Co(diamine)_2\}_3]^{6+}$ isomers, assignment of their absolute configurations, and discussion on the so-called vicinal CD curves due to the optically active diamines. (*R*)-(−)-1,2-propanediamine (*R*-pn), (*R,R*)-(−)-1,2-cyclohexanediamine (*R,R*-chxn), and *meso*-2,3-butanediamine (*meso*-2,3-bn) were used as diamine ligands.

Experimental

Preparation and Separation of Isomers. *1)* *$[Co\{(OH)_2Co($meso*-2,3-bn*$)_2\}_3]^{6+}$*: The complex nitrate was prepared by a modification of the method for the corresponding ethylenediamine complex.[4] To 17.4 g of $Co(NO_3)_2 \cdot 6H_2O$ in 20 cm^3 of water was slowly added 40 cm^3 of a 10% ice-cold aqueous solution of *meso*-2,3-butanediamine with stirring in an ice-bath. The mixture was vigorously stirred and oxidized by blowing compressed air on the surface for *ca.* 2h after cooling, the remaining solid being filtered off and washed with a small amount of water. The filtrate and washings were poured into a column (5 × 135 cm) of strong-acid ion-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 a sodium d-tartrate solution (0.17 M in the early stage of elution, and then 0.25 and 0.34 M successively in the later stages). During the course of elution the column was cooled by flushing cold (5 °C) water. The eluted eight brown bands were numbered B-1, B-2, ⋯, and B-8 in the order of elution. Each eluate was diluted about ten times with cold water which had been acidified to pH 4 with $HClO_4$, and the solution was passed through a small amount of strong-acid ion-exchanger (SP Sephadex C-25, Na$^+$ form). The complex on the exchanger was washed with a cold 0.01 M $NaClO_4$ solution and eluted with a cold 5 M $NaClO_4$ solution which had been acidified to pH 4 with $HClO_4$. Powdered sodium perchlorate was added to this eluate, and the solution was kept in a refrigerator. The desired complex was collected by filtration and washed with a cold ethanol–water (1: 1) solution, ethanol, and then ether. The brown crystals were dried in a vacuum desiccator over calcium chloride. Found for isomer B-1: C, 19.20; H, 5.48; N, 11.14%. Calcd for $[Co\{(OH)_2Co($*meso*-2,3-bn$)_2\}_3](ClO_4)_6 \cdot 2H_2O = C_{24}H_{78}N_{12}O_{30}Cl_6Co_4 \cdot 2H_2O$: C, 19.22; H, 5.51; N, 11.21%. Found for isomer B-2: C, 19.22; H, 5.56; N, 11.08%. Calcd for $C_{24}H_{78}N_{12}O_{30}Cl_6Co_4 \cdot 2.5H_2O$: C, 19.11; H, 5.55; N, 11.14%. The other isomers underwent mutarotation in the coures of crystallization, the products obtained showing the same CD pattern as that of the isomer B-1 or B-2 in the region 740—200 nm.

2) *$[Co\{(OH)_2Co(R$-pn$)_2\}_3]^{6+}$*: The isomers were prepared and separated by a similar procedure to that described in *1)* using (*R*)-1,2-propanediamine instead of *meso*-2,3-butanediamine. Eleven brown bands were confirmed on the chromatograph. Measurements of absorption and CD spectra confirmed that the first four and the next three bands give identical CD curves, respectively. Because of their low yields, the first four and the next three bands were combined respectively. They are denoted by P-1 and P-2, the remaining four bands being denoted by P-3, P-4, P-5, and P-6 in the order of elution. Crystallization was carried out as described in *1)*. Found for isomer P-1: C, 14.55; H, 4.89; N, 11.23%. Calcd for $[Co\{(OH)_2Co(R$-pn$)_2\}_3](ClO_4)_6 \cdot 3H_2O \cdot 0.5NaClO_4 = C_{18}H_{66}N_{12}O_{30}Cl_6Co_4 \cdot 3H_2O \cdot 0.5NaClO_4$: C, 14.47; H, 4.89; N, 11.23%. Found for isomer P-2: C, 15.01; H, 4.97; N 11.52%. Calcd for $C_{18}H_{66}N_{12}O_{30}Cl_6Co_4 \cdot 2.5H_2O \cdot 0.25NaClO_4$: C, 14.86; H, 4.92; N, 11.55%. Found for isomer P-3: C, 13.66; H, 5.25; N, 10.61%. Calcd for $C_{18}H_{66}N_{12}O_{30}Cl_6Co_4 \cdot 8H_2O \cdot 0.5NaClO_4$: C, 13.64; H, 5.22; N, 10.61%. Found for isomer P-4: C, 14.22; H, 5,34; N, 11.30%. Calcd for $C_{18}H_{66}N_{12}O_{30}Cl_6Co_4 \cdot 7H_2O$: C, 14.36; H, 5.36; N, 11.17%. Found for isomer P-5: C, 13.93; H, 4.62; N, 10.90%. Calcd for $C_{18}H_{66}N_{12}O_{30}Cl_6Co_4 \cdot 2.5H_2O \cdot NaClO_4$: C, 13.98; H, 4.63; N, 10.87%. Found for isomer P-6: C, 14.67; H, 5.14; N, 11.17%. Calcd for $C_{18}H_{66}N_{12}O_{30}Cl_6Co_4 \cdot 5H_2O \cdot 0.25NaClO_4$: C, 14.41; H, 5.11; N, 11.21%.

3) *$[Co\{(OH)_2Co(R,R$-chxn$)_2\}_3]^{6+}$*: The isomers were prepared and separated by a similar procedure to that described in *1)* using (*R,R*)-1,2-cyclohexanediamine instead of *meso*-2,3-

butanediamine. The four brown bands on the chromatographic column are denoted by C-1, C-2, C-3, and C-4 in the order of elution. Each eluate was diluted *ca.* ten times with cold water which had been acidified to pH 4 with HCl, and was then adsorbed again on a small amount of strong-acid ion-exchanger (SP Sephadex C-25, Na^+ form). This was washed with a cold 0.01 M NaCl solution and eluted with a cold 3 M NaCl solution which had been acidified to pH 4 with HCl. Powdered sodium chloride was added to the eluate, and the solution was kept in a refrigerator. The desired complex was collected by filtration and washed with a cold ethanol–water (1: 2) solution ,ethanol, and then ether. The brown needle crystals were dried in a vacuum desiccator over calcium chloride. Isomer C-3 was obtained in a low yield because of its high solubility. Found for isomer C-1: C, 31.25; H, 7.60; N, 12.06; Cl, 16.79%. Calcd for $[Co\{(OH)_2Co(R,R\text{-chxn})_2\}_3]Cl_6 \cdot 7.5H_2O \cdot 0.5NaCl = C_{36}H_{90}N_{12}O_6Cl_6Co_4 \cdot 7.5H_2O \cdot 0.5NaCl$: C, 30.89; H, 7.56; N, 12.01; Cl, 16.46%. Found for isomer C-2: C, 32.05; H, 7.80; N, 12.13; Cl, 15.96%. Calcd for $C_{36}H_{90}N_{12}O_6Cl_6Co_4 \cdot 7.5H_2O$: C, 31.54; H, 7.72; N, 12.26; Cl, 15.52%. Found for isomer C-3: C, 31.01; H, 7.61, N, 12.07; Cl, 16.64%. Calcd for $C_{36}H_{90}N_{12}O_6Cl_6Co_4 \cdot 7.5H_2O \cdot 0.5NaCl$: C, 30.89; H, 7.56; N, 12.01; Cl, 16.46%. Found for isomer C-4: C, 31.90; H, 7.53; N, 12.30; Cl, 17.17%. Calcd for $C_{36}H_{90}O_6N_{12}Cl_6Co_4$ $6H_2O \cdot 0.5NaCl$: C, 31.49; H, 7.49; N, 12.24; Cl, 16.78%.

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

Results and Discussion

Characterization of Isomers. The absorption and CD data of $[Co\{(OH)_2Co(meso\text{-}2,3\text{-bn})_2\}_3]^{6+}$ isomers are summarized in Table 1. Since isomers B-3 to B-8 were not obtained as solid salt, their CD values were estimated on the basis of concentration which was calculated from the absorbance at 618 nm assuming the molar absorption coefficient $\varepsilon_{618} = 115\ mol^{-1}\ dm^3\ cm^{-1}$, which is the value for B-1 and B-2. The absorption intensities of eight en hexol isomers were almost equal at this wave-length.[1] It is evident from the CD data that B-1 is enantiomeric to B-2, as is B-3 to B-4, B-5 to B-6, and B-7 to B-8. The CD curves of isomers B-1, B-3, B-5, and B-7, all of which have a positive CD band at about 16200 cm^{-1}, are shown in Fig. 1. The data for the isomers of *R*-pn and *R,R*-chxn hexols are summarized in Tables 2 and 3, and the absorption and CD curves are shown in Figs. 2 and 3.

TABLE 1. ABSORPTION AND CD DATA OF $[Co\{(OH)_2Co(meso\text{-}2,3\text{-bn})_2\}_3]^{6+}$ IN 0.01 M HCl

Wave numbers are given in $10^3\ cm^{-1}$ unit, $\log \varepsilon$ or $\Delta\varepsilon$ values (in parentheses) in $mol^{-1}\ dm^3\ cm^{-1}$.

Isomer	Absorption σ_{max} ($\log \varepsilon$)	CD σ_{ext} ($\Delta\varepsilon$)
B-1		14.62 (−2.45)
	16.17 (2.06)	16.34 (+17.9)
	20.14 (2.64)	20.24 (−32.0)
		26.09 (+2.03)
	32.00 (3.78)	31.19 (−4.63)
		37.49 (+11.6)
	48.80 (4.81)	44.31 (+143)
B-2		14.59 (+2.47)
	16.15 (2.06)	16.36 (−18.1)
	20.13 (2.65)	20.24 (+31.8)
		26.16 (−2.01)
	31.98 (3.77)	31.19 (+4.68)
		37.59 (−11.5)
	48.92 (4.81)	44.42 (−148)
B-3		14.41 (−2.27)
	16.19	16.20 (+18.7)
	20.21	20.03 (−29.5)
		25.68 (+1.50)
	32.01	31.37 (−7.51)
		36.19 (+3.33)
		39.78 (−14.3)
	48.32	44.43 (+132)
B-4		14.38 (+2.32)
	16.20	16.23 (−18.5)
	20.21	20.05 (+29.8)
		25.62 (−1.59)
	32.00	31.40 (+7.56)
		36.25 (−3.26)
		39.69 (+14.6)
	48.41	44.53 (−137)
B-5		14.47 (−2.57)
	16.18	16.25 (+17.6)
	20.25	20.04 (−22.8)
		25.59 (+1.10)
	31.99	31.86 (−11.6)
		40.04 (−35.0)
	48.74	44.52 (+78.0)
B-6		14.44 (+2.53)
	16.19	16.28 (−17.6)
	20.23	20.04 (+22.6)
		25.63 (−1.07)
	32.00	31.80 (+11.3)
		40.13 (+35.3)
	48.68	44.62 (−78.4)
B-7		14.51 (−2.64)
	16.21	16.40 (+17.7)
	20.16	20.20 (−20.0)
		25.72 (+1.30)
	32.01	31.68 (−14.7)
		40.67 (−62.1)
	48.62	45.33 (+70.7)
B-8		14.53 (+2.63)
	16.19	16.39 (−17.9)
	20.18	20.21 (+19.7)
		25.72 (−1.34)
	32.00	31.71 (+14.8)
		40.60 (+62.6)
	48.73	45.41 (−71.6)

The absorption and CD spectra of the present hexols remained unchanged in the eluting solution at room temperature for *ca.* 24 h, being the same as those in 0.01 M HCl and in H_2O. All isomers, except for P-5, are fairly stable against mutarotation in 0.01 M HCl, in 0.15 M Na_2SeO_3, and in H_2O. P-5 undergoes mutarotation rather rapidly in 0.15 M Na_2SeO_3 and slowly in H_2O, but is fairly stable in 0.01 M HCl. In the column chromatography, P-1 and P-2 consist of four and three subbands, respectively. The subbands of each isomer show the same CD spectra in 0.01 M HCl. This indicates the occurrence of geometrical isomers due to the difference in arrangements of the asymmetric carbons. MacDermott[5] and Kojima

Table 2. Absorption and CD data of $[Co\{(OH)_2Co(R\text{-pn})_2\}_3]^{6+}$ in 0.01 M HCl
Wave numbers are given in 10^3 cm^{-1} unit, log ε or Δε values (in parentheses) in mol^{-1} dm^3 cm^{-1}.

Isomer	Absorption σ_{max} (log ε)	CD σ_{ext} (Δε)
P-1		14.56 (−2.25)
	16.18 (2.03)	16.39 (+18.5)
	20.22 (2.60)	20.13 (−31.8)
		26.01 (+2.15)
	32.14 (3.78)	31.08 (−6.72)
		37.74 (+10.8)
	49.20 (4.76)	44.58 (+168)
P-2		14.61 (+2.26)
	16.11 (2.07)	16.36 (−22.0)
	20.25 (2.57)	20.16 (+33.9)
		25.86 (−1.15)
	32.06 (3.79)	30.92 (+6.22)
		37.52 (−8.38)
	49.20 (4.79)	44.51 (−137)
P-3		14.58 (−2.53)
	16.18 (2.03)	16.04 (+16.9)
	20.31 (2.55)	20.15 (−24.8)
		25.81 (+2.13)
	32.20 (3.77)	31.39 (−10.3)
		36.52 (+1.96)
		40.32 (−17.8)
	48.97 (4.76)	44.96 (+129)
P-4		14.54 (+2.36)
	16.11 (2.07)	16.34 (−19.5)
	20.30 (2.54)	20.24 (+29.4)
		25.76 (−0.91)
	32.13 (3.77)	31.34 (+7.10)
		36.44 (−2.58)
		40.13 (+13.9)
	48.97 (4.79)	44.90 (−132)
P-5		14.61 (+2.96)
	16.07 (2.11)	16.40 (−18.9)
	20.28 (2.50)	20.23 (+20.5)
		25.64 (−1.19)
	32.20 (3.77)	31.67 (+17.7)
		40.95 (+78.9)
	48.43 (4.76)	45.48 (−57.4)
P-6		14.57 (+2.60)
	16.08 (2.09)	16.36 (−18.1)
	20.29 (2.52)	20.23 (+22.9)
		25.62 (−0.89)
	32.14 (3.78)	31.76 (+11.7)
		40.54 (+41.9)
	48.61 (4.78)	45.02 (−90.3)

Table 3. Absorption and CD data of $[Co\{(OH)_2Co(R,R\text{-chxn})_2\}_3]^{6+}$ in 0.01 M HCl
Wave numbers[a] are given in 10^3 cm^{-1} unit, and log ε or Δε values (in parentheses) in mol^{-1} dm^3 cm^{-1}.

Isomer	Absorption σ_{max}	(log ε)	CD σ_{ext} (Δε)
C-1			14.41 (−2.15)
	16.3^{sh}	(2.00)	16.23 (+17.2)
	20.12	(2.65)	19.96 (−35.8)
			25.73 (+2.70)
	31.90	(3.82)	30.36 (−3.33)
			37.0^{sh} (+22.0)
	46.20	(4.82)	43.29 (+160)
C-2			14.57 (+2.30)
	16.19	(2.08)	16.33 (−20.9)
	20.08	(2.56)	20.02 (+35.4)
			25.63 (−1.11)
	31.80	(3.82)	31.06 (+5.94)
			36.63 (−6.54)
	46.19	(4.84)	43.20 (−93.4)
C-3			14.51 (+2.57)
	16.10	(2.10)	16.30 (−19.9)
	20.10	(2.53)	20.04 (+26.8)
			25.50 (−1.09)
	31.80	(3.81)	31.41 (+12.6)
			39.68 (+33.9)
	45.60	(4.82)	43.60 (−52.2)
C-4			14.52 (−2.22)
	16.19	(2.06)	16.35 (+16.8)
	20.08	(2.56)	19.99 (−24.5)
			25.68 (+2.45)
	31.85	(3.81)	31.06 (−9.58)
			36.40 (+4.77)
			39.06 (−4.33)
	46.30	(4.81)	43.67 (+123)

a) sh=shoulder.

et al.[6−8] separated such geometrical isomers of mononuclear complexes Δ- and Λ-$[Co(R\text{-pn})_3]^{3+}$, Λ-$[Co(i\text{-bn})_3]^{3+}$, and Λ-$[Co(meso\text{-}2,3\text{-bn})_3]^{3+}$ by column chromatography (*i*-bn=2-methyl-1,2-propanediamine), but found their separation to be difficult, the absorption and CD spectra of the separated isomers being nearly identical. A similar kind of geometrical isomerism was expected for the *meso*-2,3-bn hexol, but no band separation was observed in the chromatography.

Absorption and CD Spectra. The absorption and CD spectra of the present hexols are similar to those of $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$.[1] The absorption bands at *ca.* 16200 and 20200 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 *ca.* 32000 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 CD spectra show two extrema (the A_2 and E_a components of approximate D_3 symmetry) in the first d-d transition region of CoO_6 chromophore and one extremum (combined $B_1+A_2+B_2$ components) in the region of CoN_4O_2 chromophore. The CD intensity of CoN_4O_2 chromophore band at *ca.* 20000 cm^{-1} varies widely from isomer to isomer. The CD patterns in the d-d transition region are very similar, while those in the charge transfer transition region somewhat differ (Figs. 1—3).

When the CD spectrum of each isomer of *meso*-2,3-bn hexol is compared with that of the isomer of en hexol with the same fraction-number, *e.g.*, B-1 with E-1, the CD intensity and band shape in the d-d transition region are almost identical but the CD extremum

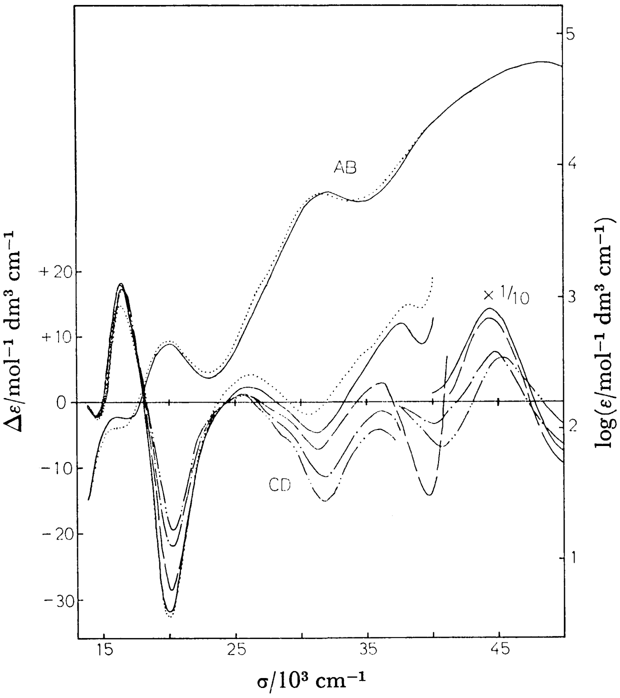

Fig. 1. Absorption (AB) and CD curves of $[Co\{(OH)_2Co(\textit{meso}\text{-}2,3\text{-bn})_2\}_3]^{6+}$.
Isomer B-1 (——), B-3 (– – –), B-5 (–•–•–), and B-7 (–••–••) in 0.01 M HCl and B-1 (------) in 0.15 M Na_2SeO_3.

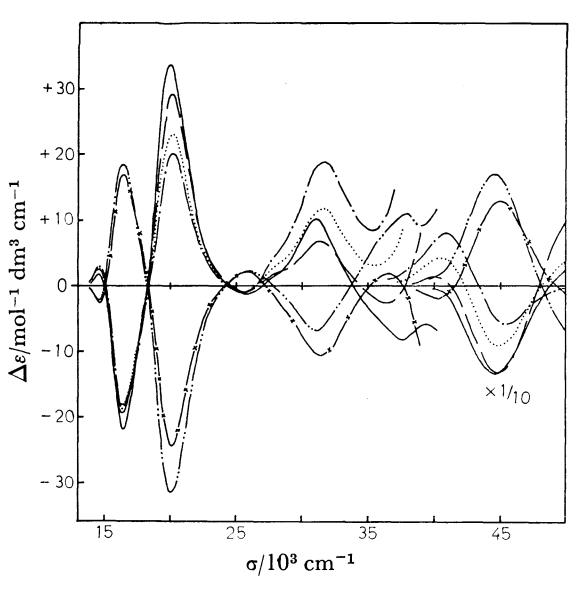

Fig. 2. CD curves of $[Co\{(OH)_2Co(R\text{-pn})_2\}_3]^{6+}$.
Isomer P-1 (–••–••), P-2 (——), P-3 (-x-x-), P-4 (– – –), P-5 (–•–•–), and P-6 (------) in 0.01 M HCl.

positions shift to lower energy side in the isomer of *meso*-2,3-bn hexol. The shift approximately corresponds to the difference between the absorption peaks of *meso*-2,3-bn hexol and en hexol in the CoN_4O_2 chromophore region. The CD bands of not only CoN_4O_2 chromophore but also of CoO_6 chromophore shift to lower energy side. The d-d absorption peak of CoN_4O_2 chromophore varies in the following order of energy: $NH_3$2) $<$ *R*,*R*-chxn $\lesssim$ *meso*-2,3-bn $<$ *R*-pn $\lesssim$ en.1) The order coincides

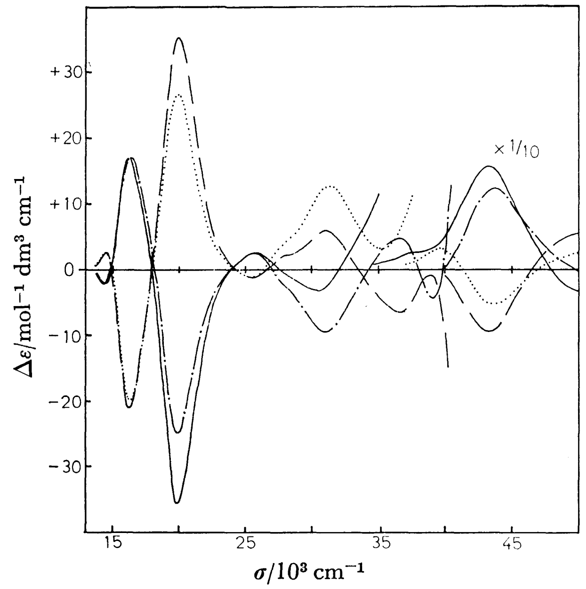

Fig. 3. CD curves of $[Co\{(OH)_2Co(R,R\text{-chxn})_2\}_3]^{6+}$.
Isomer C-1 (——), C-2 (– – –), C-3 (------), and C-4 (–•–•–) in 0.01 M HCl.

approximately with that for mononuclear complexes of CoN_6 type.

Absolute Configuration. From the close resemblance between the CD spectra of $[Co\{(OH)_2Co(\textit{meso}\text{-}2,3\text{-bn})_2\}_3]^{6+}$ and $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$ isomers, isomers B-1, B-3, B-5, and B-7 are assigned to *Λ*(*ΛΛΛ*), *Λ*(*ΔΔΔ*), *Λ*(*ΔΔΛ*), and *Λ*(*ΔΛΛ*), respectively, and B-2, B-4, B-6, and B-8 to *Δ*(*ΔΔΔ*), *Δ*(*ΛΛΛ*), *Δ*(*ΔΛΛ*), and *Δ*(*ΔΔΛ*), respectively. In a similar way, the absolute configurations of isomers P-1 and P-3 of $[Co\{(OH)_2Co(R\text{-pn})_2\}_3]^{6+}$ are assigned to *Λ*(*ΛΛΛ*) and *Λ*(*ΔΔΔ*), respectively, and P-2, P-4, P-5, and P-6 to *Δ*(*ΔΔΔ*), *Δ*(*ΛΛΛ*), *Δ*(*ΔΔΛ*), and *Δ*(*ΔΛΛ*), respectively. Isomer P-5 underwent mutarotation in aqueous solution in a manner similar to that of the corresponding *Δ*(*ΔΔΛ*) isomer of en hexol. Isomers C-1, C-2, C-3, and C-4 of $[Co\{(OH)_2Co(R,R\text{-chxn})_2\}_3]^{6+}$ are assigned to the absolute configurations *Λ*(*ΛΛΛ*), *Δ*(*ΔΔΔ*), *Λ*(*ΔΔΔ*), and *Δ*(*ΔΛΛ*), respectively. C-4 might be assigned alternatively to *Δ*(*ΔΔΛ*) from the CD pattern, particularly in the region of charge transfer transitions. The *Δ*(*ΔΔΛ*) isomers of en, *meso*-2,3-bn, and *R*-pn hexols underwent mutarotation, but not the isomer C-4. In view of vicinal effect, it is not adequate to assign this isomer to the *Δ*(*ΔΔΛ*) configuration. The absolute

TABLE 4. ABSOLUTE CONFIGURATIONS OF $[Co\{(OH)_2Co(diamine)_2\}_3]^{6+}$ ISOMERS

Absolute configuration	en	*meso*-2,3-bn	*R*-pn	*R*,*R*-chxn
Λ(*ΛΛΛ*)	E-1	B-1	P-1	C-1
Δ(*ΔΔΔ*)	E-2	B-2	P-2	C-2
Λ(*ΔΔΔ*)	E-3	B-3	P-3	C-3
Δ(*ΛΛΛ*)	E-4	B-4	P-4	
Λ(*ΔΔΛ*)	E-5	B-5		
Δ(*ΔΛΛ*)	E-6	B-6	P-6	C-4
Λ(*ΔΛΛ*)	E-7	B-7		
Δ(*ΔΔΛ*)	E-8	B-8	P-5	

configurations of all the hexol isomers containing diamines are given in Table 4.

The numbers of isomers of individual hexols obtained decrease in the order of diamines en>*R*-pn>*R*,*R*-chxn, the reverse order of bulkiness of the *C*-substituent groups. The repulsion between the non-bonded atoms seems to exist in the remaining less stable isomers, this being partly confirmed by the construction of molecular models of the missing isomers.

Additivity of CD Contributions. Assuming that the chromophore and configurational chirality of an *R*-pn (or *R*,*R*-chxn) hexol isomer are identical to those of the corresponding en hexol isomer, we get the following equation for the CD of these complexes:

$$\left.\begin{aligned} \Delta(\Delta\Delta\Delta)^{R} &= \Delta(\Delta\Delta\Delta)^{\mathrm{en}} + 6(R) \\ \Delta(\Delta\Delta\Lambda)^{R} &= \Delta(\Delta\Delta\Lambda)^{\mathrm{en}} + 6(R) \\ &\cdots\cdots\cdots\cdots \\ \Lambda(\Lambda\Lambda\Lambda)^{R} &= \Lambda(\Lambda\Lambda\Lambda)^{\mathrm{en}} + 6(R) \end{aligned}\right\} \quad (1)$$

where $\Delta(\Delta\Delta\Delta)^R$ and $\Delta(\Delta\Delta\Delta)^{\mathrm{en}}$ denote the CD of isomers $\Delta(\Delta\Delta\Delta)$ of *R*-pn (or *R*,*R*-chxn) and en hexol, respectively, and (*R*) is the vicinal contribution of an *R*-pn (or *R*,*R*-chxn) ligand. By applying the observed CD curves of *R*-pn (*R*,*R*-chxn) and en hexol isomers to Eq. 1, the vicinal contribution curves (*R*) can be calculated (Figs. 4 and 5). The calculation was performed by using the observed CD curves of en hexol isomers, which were shifted by α (in cm^{-1}) to lower energy side (Table 5). The shift α was estimated from the difference between the CoN_4O_2 absorption peaks of the diamine and en hexol isomers. In the case of *meso*-2,3-bn hexol, the ligand has two asymmetric carbons of opposite chiralities, (*R*) and (*S*), no contribution of vicinal chiralities being expected in total. The calculated vicinal contribution is zero in the region 13800—30000 cm^{-1}.

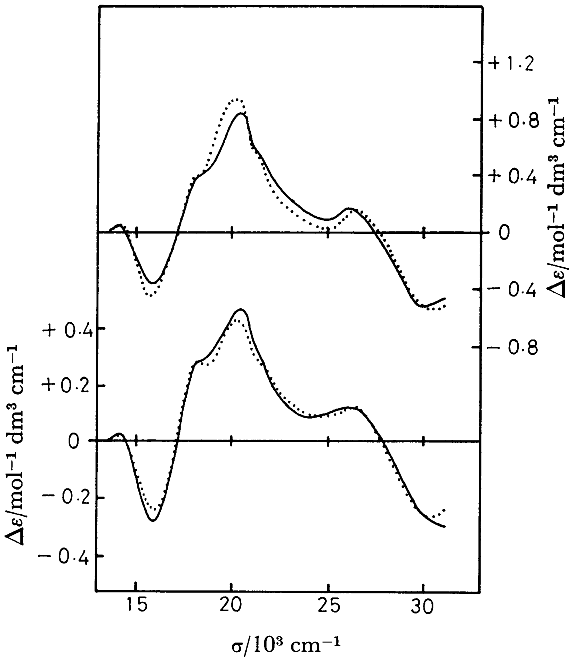

Fig. 4. Calculated vicinal CD curves $(R)_{lel}$. $(R)^{R,R\text{-chxn}}_{\Delta\Delta\Delta} = \Delta\varepsilon\{(\mathrm{C}\text{-}2) - \Delta\varepsilon(\mathrm{E}\text{-}2)\}/6$ (——), and $(R)^{R,R\text{-chxn}}_{\Delta\Delta\Delta} = \{\Delta\varepsilon(\mathrm{C}\text{-}3) - \Delta\varepsilon(\mathrm{E}\text{-}3)\}/6$ (------) (upper curves); and $(R)^{R\text{-pn}}_{\Delta\Delta\Delta} = \{\Delta\varepsilon(\mathrm{P}\text{-}2) - \Delta\varepsilon(\mathrm{E}\text{-}2)\}/6$ (——), and $(R)^{R\text{-pn}}_{\Delta\Delta\Delta} = \{\Delta\varepsilon(\mathrm{P}\text{-}3) - \Delta\varepsilon(\mathrm{E}\text{-}3)\}/6$ (------) (lower curves).

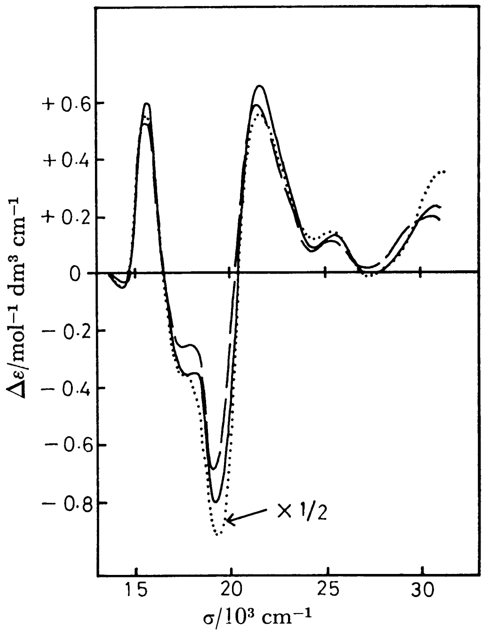

Fig. 5. Calculated vicinal CD curves $(R)_{ob}$. $(R)^{R\text{-pn}}_{\Lambda\Lambda\Lambda} = \{\Delta\varepsilon(\mathrm{P}\text{-}1) - \Delta\varepsilon(\mathrm{E}\text{-}1)\}/6$ (——), $(R)^{R\text{-pn}}_{\Lambda\Lambda\Lambda} = \{\Delta\varepsilon(\mathrm{P}\text{-}4) - \Delta\varepsilon(\mathrm{E}\text{-}4)\}/6$ (-----), and $(R)^{R,R\text{-chxn}}_{\Lambda\Lambda\Lambda} = \{\Delta\varepsilon(\mathrm{C}\text{-}1) - \Delta\varepsilon(\mathrm{E}\text{-}1)\}/6$ (------).

TABLE 5. α VALUES REPRESENTING THE SHIFT OF CD PEAK OF DIAMINE HEXOL ISOMER TO LOWER ENERGY SIDE RELATIVE TO THAT OF THE CORRESPONDING ISOMER OF en HEXOL

Isomer	α/cm^{-1}	Isomer	α/cm^{-1}	Isomer	α/cm^{-1}
B-1	170	P-1	90	C-1	190
B-2	160	P-2	40	C-2	210
B-3	120	P-3	20	C-3	230
B-4	120	P-4	30	C-4	250
B-5	120	P-5	50		
B-6	110	P-6	40		
B-7	120				
B-8	130				

As is seen in Figs. 4 and 5, the calculated vicinal contributions are equal when the isomers have the same absolute configuration in the three CoN_4O_2 chromophores, regardless of the absolute configuration of CoO_6 chromophore. However, the calculated vicinal CD curves are not equal when the absolute configuration of the three CoN_4O_2 chromophores is reversed, *viz.*, $(R)_{\Delta\Delta\Delta} \neq (R)_{\Lambda\Lambda\Lambda}$. The calculated vicinal CD curves of the *R*-pn and *R*,*R*-chxn hexol isomers with the same absolute configuration of CoN_4O_2 chromophores have very similar patterns, the CD intensity of vicinal contribution of *R*,*R*-chxn being about twice that of *R*-pn; thus the intensity is proportional to the number of asymmetric carbons.

The *R*-pn and *R*,*R*-chxn chelate rings have a λ conformation. In the light of the *lel* and *ob* orientations[9] of C–C bonds of diamine chelate rings relative to the pseudo C_3 axis of individual $\mathrm{CoN_4O_2}$ tris(chelate) chromophores, it is evident that the isomer $\{\boldsymbol{\Delta}(\lambda\lambda)\boldsymbol{\Delta}(\lambda\lambda)\boldsymbol{\Delta}(\lambda\lambda)\}$ has the $lel_2lel_2lel_2$ form, $\{\boldsymbol{\Delta}(\lambda\lambda)\boldsymbol{\Delta}(\lambda\lambda)\text{-}\boldsymbol{\Lambda}(\lambda\lambda)\}$ $lel_2lel_2ob_2$, $\{\boldsymbol{\Delta}(\lambda\lambda)\boldsymbol{\Lambda}(\lambda\lambda)\boldsymbol{\Lambda}(\lambda\lambda)\}$ $lel_2ob_2ob_2$, and $\{\boldsymbol{\Lambda}(\lambda\lambda)\boldsymbol{\Lambda}(\lambda\lambda)\boldsymbol{\Lambda}(\lambda\lambda)\}$ $ob_2ob_2ob_2$. Thus, Eq. 1 should be rewritten as follows:

$$\left.\begin{array}{l}
\Delta(\Delta\Delta\Delta)^R = \Delta(\Delta\Delta\Delta)^{\mathrm{en}} + 6(R)_{lel} \\
\Delta(\Delta\Delta\Lambda)^R = \Delta(\Delta\Delta\Lambda)^{\mathrm{en}} + 4(R)_{lel} + 2(R)_{ob} \\
\Delta(\Delta\Lambda\Lambda)^R = \Delta(\Delta\Lambda\Lambda)^{\mathrm{en}} + 2(R)_{lel} + 4(R)_{ob} \\
\Delta(\Lambda\Lambda\Lambda)^R = \Delta(\Lambda\Lambda\Lambda)^{\mathrm{en}} + 6(R)_{ob} \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\boldsymbol{\Lambda}(\Lambda\Lambda\Lambda)^R = \boldsymbol{\Lambda}(\Lambda\Lambda\Lambda)^{\mathrm{en}} + 6(R)_{ob},
\end{array}\right\} \qquad (2)$$

where $(R)_{lel}$ and $(R)_{ob}$ denote the vicinal contribution due to the *lel* and *ob* forms of *R*-pn (or *R*,*R*-chxn) ligand, respectively. Thus, the vicinal CD curves calculated from isomers P-1, P-4, and C-1 are $(R)_{ob}$, and the curves calculated from isomers P-2, P-3, C-2, and C-3 are $(R)_{lel}$. The $(R)_{lel}$ curve differs definitely from the $(R)_{ob}$ one.

The vicinal contributions, $(R)_{lel}$ and $(R)_{ob}$, can be also calculated from the observed CD curves of isomers $\boldsymbol{\Delta}(\Delta\Delta\Lambda)$ and $\boldsymbol{\Delta}(\Delta\Lambda\Lambda)$ by applying Eq. 2:

$$(R)_{lel} = [2\{\Delta(\Delta\Delta\Lambda)^R - \Delta(\Delta\Delta\Lambda)^{\mathrm{en}}\} - \{\Delta(\Delta\Lambda\Lambda)^R - \Delta(\Delta\Lambda\Lambda)^{\mathrm{en}}\}]/6, \text{ and}$$

$$(R)_{ob} = [2\{\Delta(\Delta\Lambda\Lambda)^R - \Delta(\Delta\Lambda\Lambda)^{\mathrm{en}}\} - \{\Delta(\Delta\Delta\Lambda)^R - \Delta(\Delta\Delta\Lambda)^{\mathrm{en}}\}]/6.$$

As is seen in Fig. 6, the vicinal CD curves calculated from isomers $\boldsymbol{\Delta}(\Delta\Delta\Lambda)$ and $\boldsymbol{\Delta}(\Delta\Lambda\Lambda)$ agree with those calculated from $\boldsymbol{\Delta}(\Delta\Delta\Delta)$, $\boldsymbol{\Delta}(\Lambda\Lambda\Lambda)$, $\boldsymbol{\Lambda}(\Delta\Delta\Delta)$ or $\boldsymbol{\Lambda}(\Lambda\Lambda\Lambda)$. This shows that the two vicinal contributions, $(R)_{lel}$ and $(R)_{ob}$, are additive.

Both vicinal contribution curves, $(R)_{lel}$ and $(R)_{ob}$, show rather strong CD even in the absorption region of $\mathrm{CoO_6}$ chromophore which is separated far from the asymmetric carbons.

It was difficult to assign exactly the absolute configuration of the isomer C-4 of $[\mathrm{Co}\{(\mathrm{OH})_2\mathrm{Co}(R,R\text{-chxn})_2\}_3]^{6+}$ only from the CD pattern; it might be assigned to either $\boldsymbol{\Delta}(\Delta\Delta\Lambda)$ or $\boldsymbol{\Delta}(\Delta\Lambda\Lambda)$. If we apply the additivity between $(R)_{lel}^{R,R\text{-chxn}}$ and $(R)_{ob}^{R,R\text{-chxn}}$ obtained from C-1, C-2, or C-3 isomers, it is possible to see which of the following two relations is adequate:

a) $\{\Delta\varepsilon(\text{C-4}) - \Delta(\Delta\Delta\Lambda)^{\mathrm{en}}\}/6 = \{2(R)_{lel}^{R,R\text{-chxn}} + (R)_{ob}^{R,R\text{-chxn}}\}/3$

b) $\{\Delta\varepsilon(\text{C-4}) - \Delta(\Delta\Lambda\Lambda)^{\mathrm{en}}\}/6 = \{(R)_{lel}^{R,R\text{-chxn}} + 2(R)_{ob}^{R,R\text{-chxn}}\}/3.$

We see from Fig. 7 that the calculated curve $\{\Delta\varepsilon(\text{C-4}) - \boldsymbol{\Delta}(\Delta\Lambda\Lambda)_{\mathrm{en}}\}/6$ is very similar to the curve $\{(R)_{lel}^{R,R\text{-chxn}} + 2(R)_{ob}^{R,R\text{-chxn}}\}/3$. The calculated curve in this case is very similar to the curve calculated (intensity was doubled) from P-6 ($\boldsymbol{\Delta}(\Delta\Lambda\Lambda)$). The absolute configuration of the isomer C-4 is therefore exactly assigned to $\boldsymbol{\Delta}(\Delta\Lambda\Lambda)$.

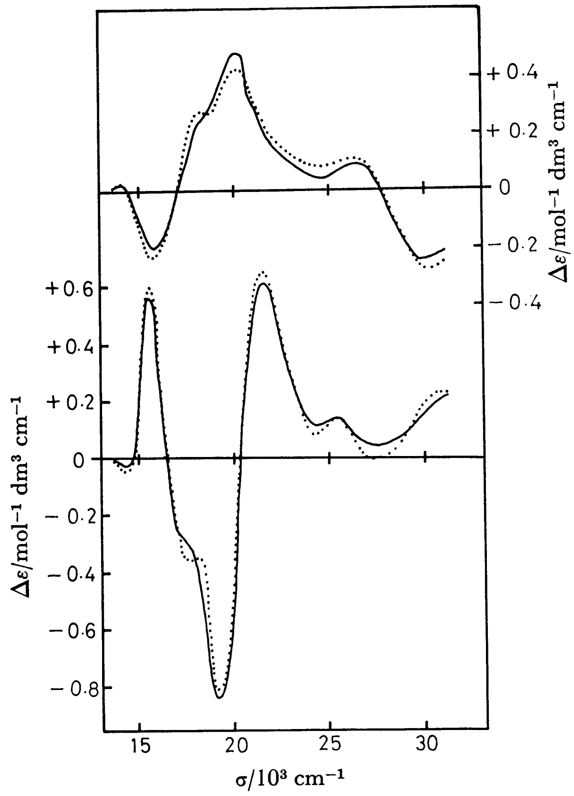

Fig. 6. Calculated vicinal CD curves. $(R)_{lel}^{R\text{-pn}} = [2\{\Delta\varepsilon(\text{P-6}) - \Delta\varepsilon(\text{E-6})\} - \{\Delta\varepsilon(\text{P-5}) - \Delta\varepsilon(\text{E-8})\}]/6$ (——), and $\{\Delta\varepsilon(\text{P-3}) - \Delta\varepsilon(\text{E-3})\}/6$ (------) (upper curves); and $(R)_{ob}^{R\text{-pn}} = [2\{\Delta\varepsilon(\text{P-5}) - \Delta\varepsilon(\text{E-8})\} - \{\Delta\varepsilon(\text{P-6}) - \Delta\varepsilon(\text{E-6})\}]/6$(——), and $\{\Delta\varepsilon(\text{P-1}) - \Delta\varepsilon(\text{E-1})\}/6$ (------) (lower curves).

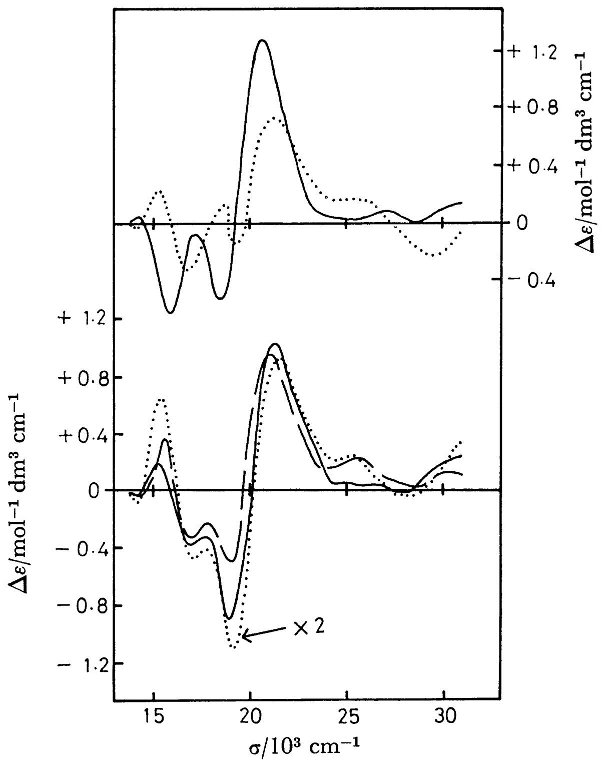

Fig. 7. Calculated CD curves. $\{\Delta\varepsilon(\text{C-4}) - \Delta\varepsilon(\text{E-8})\}/6$ (——) and $\{2(R)_{lel}^{R,R\text{-chxn}} + (R)_{ob}^{R,R\text{-chxn}}\}/3$ (------) (upper curves), and $\{\Delta\varepsilon(\text{C-4}) - \Delta\varepsilon(\text{E-6})\}/6$ (——), $\{(R)_{lel}^{R,R\text{-chxn}} + 2(R)_{ob}^{R,R\text{-chxn}}\}/3$ (– – –), and $\{\Delta\varepsilon(\text{P-6}) - \Delta\varepsilon(\text{E-6})\}/6$ (------) (lower curves).

TABLE 6. EXTREMUM DATA (MEAN VALUES) OF OBTAINED VICINAL CD CONTRIBUTIONS
Wave numbers[a)] are given in 10^3 cm^{-1} unit and $\Delta\varepsilon$ values (in parentheses) in mol^{-1} dm^3 cm^{-1}.

Assignment	$(R)^{R\text{-pn}}_{lel}$	$(R)^{R,R\text{-chxn}}_{lel}$	$(R)^{R\text{-pn}}_{ob}$	$(R)^{R,R\text{-chxn}}_{ob}$
	σ_{ext} $(\Delta\varepsilon)$	σ_{ext} $(\Delta\varepsilon)$	σ_{ext} $(\Delta\varepsilon)$	σ_{ext} $(\Delta\varepsilon)$
A_2 (CoO_6)	14.18 (+0.02)	14.20 (+0.05)	14.41 (−0.05)	14.40 (−0.10)
E_a (CoO_6)	15.92 (−0.26)	15.84 (−0.41)	15.57 (+0.57)	15.61 (+1.11)
B_1 (CoN_4O_2)	18.20 (+0.27)	18.1^{sh} (+0.36)	17.48 (−0.31)	17.5^{sh} (−0.71)
A_2+B_2 (CoN_4O_2)	20.42 (+0.44)	20.34 (+0.90)	19.11 (−0.75)	19.23 (−1.87)
	21.8^{sh} (+0.12)	21.6^{sh} (+0.48)	21.56 (+0.63)	21.60 (+1.11)
2nd d-d transition	26.30 (+0.12)	26.41 (+0.17)	25.43 (+0.12)	25.51 (+0.29)

a) sh=shoulder.

The vicinal contribution of an (R)-diamine ligand consists of the conformational one (λ) and the vicinal one in a limited sence (R) due to the asymmetric carbons. Thus the vicinal contribution of an R-pn or R,R-chxn is presented by $(\lambda)+(R)$, the (R) being proportional to the number of asymmetric carbon atoms, *viz.*, $(R)^{R,R\text{-chxn}}=2(R)^{R\text{-pn}}$. On the other hand, the intensity of vicinal curves calculated by Eq. 2 for R,R-chxn hexol is about twice that of the R-pn hexol. The vicinal contribution due to the asymmetric carbons should be a dominant factor in this case, the conformational contribution hardly contributing at all to the overall vicinal CD. This indicates that the diamine conformation in en hexol is identical to that in R-pn or R,R-chxn hexol. An alternative but more plausible explanation is that the conformational contributions of diamine chelate rings are negligibly small in all the hexol type complexes. In many mononuclear complexes, the conformational effect contributes mainly to the overall vicinal CD.[10,11] In a limited number of mononuclear complexes, however, the vicinal contribution due to asymmetric carbons becomes a dominant factor.[12] The diamine hexols present an interesting example of the latter case.

Numerical data (mean values) of the individual vicinal CD contributions are given in Table 6.

References

1) Part II of this series: T. Kudo and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **52**, 3553 (1979).

2) T. Kudo and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **52**, 1648 (1979).

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

4) A. Werner, *Chem. Ber.*, **40**, 2103 (1907).

5) T. E. MacDermott, *Inorg. Chim. Acta*, **2**, 81 (1968).

6) M. Kojima, Y. Yoshikawa, and K. Yamasaki, *Bull. Chem. Soc. Jpn.*, **46**, 1687 (1973).

7) M. Kojima, Y. Yoshikawa, and K. Yamasaki, *Inorg. Nucl. Chem. Lett.*, **9**, 689 (1973).

8) M. Kojima, Y. Yoshikawa, and K. Yamasaki, *Bull. Chem. Soc. Jpn.*, **48**, 2801 (1975).

9) J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

10) C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

11) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wily-Interscience, New York (1970).

12) H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **40**, 2584 (1967).