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Preparation and Characterization of Dinuclear Cobalt(III) Complexes Bridged by Quadridentate Ligand with Thioether Donor Atoms

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From the reaction of (2-aminoethanethiolato)bis(ethylenediamine)cobalt(III)(2+) complex with α,ω-dibromoalkanes $Br(CH_2)_nBr$, a series of novel monobridged dinuclear cobalt(III) complexes $[(en)_2Co\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}Co(en)_2]^{6+}$ (n=1, 2, 3, 4, 5, 6, 8, and 10) were prepared and characterized on the basis of their absorption, circular dichroism, and infrared spectra and elemental analyses. In the case of n=2, two geometrical isomers, *meso* and *rac*, were isolated and identified.

Thiolato group retains its strong nucleophilic property even after coordinating to a metal ion. This characteristic has been utilized to prepare a variety of new metal complexes containing coordinated thioether,[1] sulfenato,[2] and sulfinato ligands.[3] In particular, alkylation reactions of dithiolato complexes with difunctional alkylating agents have been known to lead to the concomitant formation of two thioether donor atoms and a chelate ring joining them, that is, the formation of macrocyclic ligands.[4] Similar reactions are applicable to the synthesis of bridged complexes.

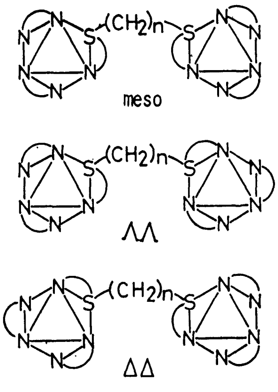

Fig. 1. Three isomers of monobridged dinuclear cobalt(III) complex.

The present report describes the synthesis of monobridged dinuclear cobalt(III) complexes by the reaction of (2-aminoethanethiolato)bis(ethylenediamine)cobalt(III) complex $[Co(aet)(en)_2]^{2+}$ with α,ω-dibromcalkane $Br(CH_2)_nBr$ as bridging agents. As one of advantages of this method, the direct synthesis of optically active bridged complexes becomes possible by starting from the optically active $[Co(aet)(en)_2]^{2+}$ complex.[5] Since the dinuclear complex consists of two optically active octahedral units, a meso (ΔΛ) and two optically active (ΔΔ and ΛΛ) forms are possible (Fig. 1), the latter two of which form a racemate in practice. The isolation of two geometrical isomers of this kind, *meso* and *rac*, has so far been limited to only two cases of $[(en)_2Cr(OH)_2Cr(en)_2]Cl_4\cdot 2H_2O$[6] and $[(en)_2Co(OH)(O_2)Co(en)_2]^{3+}$[7] with double bridged structure, no report being published for the monobridged dinuclear complexes.

Experimental

Preparation and Separation of Complexes. rac- *and/or* meso-*$[(en)_2Co\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}Co(en)_2]Cl_6$ (n= 1, 2, 3, 4, 5, 6, 8, and 10)*: A general procedure was developed by using α,ω-dibromoalkanes $Br(CH_2)_nBr$ and *N*,*N*-dimethylformamide (DMF) as bridging agents and reaction solvent, respectively. To a black solution of four millimoles of *rac*-$[Co(aet)(en)_2](ClO_4)_2$[5] dissolved in 5 cm³ of DMF was added an excess (2.2 mmol) of α,ω-dibromoalkane. The mixture was allowed to stand for about 20 d at room temperature, leading to a deep-red solution. The DMF and unreacted dibromoalkane were extracted into diethyl ether for several times. The resulting dark red oil was dissolved in water, adsorbed on an SP-Sephadex C-25 cation exchange column (Na^+ form), and eluted with a 0.8 M NaCl solution (1 M= 1 mol dm^{-3}). Five colored bands were eluted in the order, a yellow one of $[Co(en)_3]^{3+}$, a dark brown one of $[Co(aet)(en)_2]^{2+}$, and three orange ones A, B, and C. Each of the orange bands was concentrated to a small volume in a rotary evaporator and after repeated removal of NaCl deposited out the solution was treated with a small amount of ethanol to give orange crystals of the desired chloride salt. Analytical data (Table 1) for the complexes A, B, and C corresponded to $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nOH\}]Cl_3$, $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nBr\}]Cl_3$, and $[Co_2(en)_4\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}]Cl_6$, respectively. This characterization is agreed with the column chromatographic behavior; when developed with a 0.3 M NaCl solution, only the last band C remains on the top of Sephadex resin and therefore seems to be the proposed bridge structure with a hexapositive charge.

For the dinuclear complexes prepared from a racemic starting material *rac*-$[Co(aet)(en)_2]^{2+}$, two geometrical isomers, *meso* and *rac*, are possible. In the case of n=2, fractional crystallization of the eluate C produced two different orange crystals: the eluate C was evaporated to a small volume using a rotary evaporator, and the deposit, NaCl, was filtered off. The filtrate was cooled to give first crop of orange crystals (C-1). After filtration the filtrate was further evaporated, a small amount of methanol being added to the concentrated solution, and the deposit, NaCl, was again filtered off. The final filtrate was cooled in an ice bath to give another kind of orange crystals (C-2). Both complexes showed the dinuclear composition, $[Co_2(en)_4\{NH_2(CH_2)_2S(CH_2)_2S(CH_2)_2NH_2\}]Cl_6$, the less soluble C-1 being 3-hydrate and the more soluble C-2 5.5-hydrate.

In order to elucidate the structures, optical resolution was attempted. An aqueous solution containing 0.03 g of the complex C-1 or C-2 was poured into a column of SP-Sephadex C-25 (Na^+ form, 3×80 cm). The adsorbed band was eluted with a mixed solution of 0.5 M NaCl and 0.15 M $Na_2[Sb_2$(*d*-

TABLE 1. ANALYTICAL DATA OF THE COMPLEXES

n	X	C, % Found(Calcd)	H, % Found(Calcd)	N, % Found(Calcd)
$[(en)_2Co\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}Co(en)_2]Cl_6\cdot X$(complex C or C′)				
rac and/or *meso*				
1	$0.25C_2H_5OH$	19.69(19.54)	6.87(6.86)	16.92(16.88)
2	$3H_2O$(C-1)	20.79(20.88)	6.81(6.76)	17.26(17.39)
2	$5.5H_2O$(C-2)	19.74(19.77)	6.81(6.99)	16.20(16.47)
3	$8.5H_2O$	19.45(19.62)	7.30(7.35)	15.20(15.25)
4	$5.5H_2O$	21.91(21.88)	7.27(7.23)	15.95(15.94)
5	$7H_2O$	22.12(22.21)	7.44(7.45)	14.92(15.23)
6	$5.5H_2O$	23.83(23.85)	7.35(7.45)	15.39(15.45)
8	$4.5H_2O$	26.61(26.21)	7.69(7.59)	15.27(15.28)
active($\Delta\Delta$)				
2	$5H_2O$	19.88(19.99)	6.92(6.95)	16.61(16.65)
3	$8H_2O$	19.83(19.81)	7.32(7.31)	15.30(15.40)
4	$5.5H_2O$	21.83(21.88)	7.16(7.23)	15.89(15.95)
5	$5.5H_2O$	22.85(22.89)	7.21(7.34)	15.70(15.69)
6	$5.5H_2O$	23.75(23.85)	7.40(7.45)	15.38(15.45)
8	$5H_2O$	26.08(25.95)	7.57(7.62)	15.15(15.13)
10	$0.75NaCl\cdot 0.75$–$C_2H_5OH\cdot 2.5H_2O$	28.65(28.60)	7.69(7.66)	14.26(14.19)
rac-$[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nBr\}]Cl_3\cdot X$(complex B)				
2	H_2O	19.76(19.71)	5.91(5.79)	14.45(14.36)
3	$2.5H_2O$	20.68(20.45)	6.23(6.29)	12.85(13.25)
4	$2.5H_2O$	22.37(22.13)	6.47(6.50)	12.92(12.91)
5	$0.5H_2O$	25.35(25.37)	6.50(6.39)	13.26(13.45)
6	$1.5H_2O$	26.31(26.08)	6.86(6.75)	12.53(12.67)
8	H_2O	29.61(29.41)	7.12(7.05)	12.42(12.25)
10	$0.5H_2O$	32.38(32.53)	7.45(7.34)	12.06(11.85)
rac-$[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nOH\}]Cl_3\cdot X$(complex A)				
4	$0.5C_2H_5OH\cdot 2H_2O$	26.48(26.76)	7.58(7.76)	14.23(14.18)
5	$2H_2O$	27.20(27.25)	7.37(7.69)	13.63(14.45)
6	$1.5H_2O$	29.79(29.43)	7.56(7.82)	13.96(14.30)
8	H_2O	32.90(33.04)	7.94(8.12)	13.52(13.76)

tart)$_2$]·2H$_2$O, which produced a broad band. The eluate was separated into fractions of 5 cm^3 each. The fractions of complex C-1 showed no optical activity, while the first fractions of complex C-2 exhibited a positive dominant CD band in the first absorption band region which is completely enantiomeric to that of the last fractions. Thus, the two orange complexes are geometrical isomers, C-1 and C-2 corresponding to *meso* and racemic forms, respectively. In all cases other than n=2, the band C could not be splitted into two or more kinds of orange complexes.

Active-$[(en)_2Co\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}Co(en)_2]Cl_6$ *(n=2, 3, 4, 5, 6, 8, and 10)*: Optically active complexes were prepared and separated in the same manner as described above with use of active-[Co(aet)(en)$_2$](ClO$_4$)$_2$[5] instead of the racemic starting material. When eluted with a 0.8 M NaCl solution, the column gave the following five band regardless of the kind of Br(CH$_2$)$_n$Br used; a yellow bands of [Co(en)$_3$]$^{3+}$, a dark brown one of [Co(aet)(en)$_2$]$^{2+}$, and three orange ones A′, B′, and C′. Each orange band was concentrated to a small volume and the chloride salt was crystallized out. Elemental analyses (Table 1) and absorption spectra of the complexes A′, B′, and C′ confirmed their compositions $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nOH\}]Cl_3$, $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nBr\}]Cl_3$, and $[Co_2(en)_4\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}]Cl_6$, respectively.

The distribution of products A′, B′, and C′ under above conditions changed considerably depending upon the number of methylene groups. The yields of the bridged complexes decreased in the following order; n=3 and 4 (*ca.* 75%)>n=5 (*ca.* 70%)>n=6 (*ca.* 65%)>n=8 (*ca.* 50%)>n=10 (*ca.* 40%)>n=2 (*ca.* 20%)≫n=1 (below 5%). The yields of complexes B′ were inversely proportional to those of the corresponding bridged complexes C′ but the total yields of complexes B′ and C′ were almost constant. The yields of complexes A′ were about 5% irrespective of the number of methylene groups, though the products in the case of n=1 were so complicated that the yields of the complexes except the bridged one could not be determined.

Measurements. The electronic absorption spectra were measured on a Shimadzu UV-200 spectrophotometer and CD spectra with a JASCO MOE-1 spectropolarimeter in aqueous solution. The infrared spectra were obtained on a JASCO DS-402G spectrophotometer with NaCl prism nsing Nujol mull or KBr disk. All measurements were made at room temperature.

Results and Discussion

Preparation and Characterization of the Complexes. Several preparative methods have been developed for the alkylation of coordinated thiols. It has been noted that DMF is a superior medium for the alkylation reactions because most alkyl halides and metal perchlorate salts are soluble in this medium.[8] The use of DMF as a reaction solvent in the present study permitted the formation of the alkylated products in a high yield which were not accessible by the use of other solvents such as methanol–water. The formation of $[Co_2(en)_4\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}]^{6+}$ is more favorable in a high concentration of reactants than in a dilute one. The concentration dependence can be elucidated from the following mechanism;[9] the reaction of $[Co(aet)(en)_2]^{2+}$ with $Br(CH_2)_nBr$ gives at first an intermediate $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nBr\}]^{3+}$ species and then an intermolecular reaction leads to the formation of the bridged complex. In fact, when the reaction mixture was diluted twenty times no orange complexes were detectable under the same condition as described above. The yield of the bridged complexes depends upon the number of methylene groups, being especially low in the cases of $n=1$ or 2 (see Experimental). The low yield seems to be ascribed to the steric and electrostatic repulsion between two tripositive

TABLE 2. ABSORPTION AND CD DATA OF THE COMPLEXES

n		Absorption[a] σ_{max}(log ε)		CD[a] σ_{ext}(Δε)
$[(en)_2Co\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}Co(en)_2]^{6+}$				
		rac and/or *meso*	active(ΔΔ)	active(ΔΔ)
1		20.3(2.44)		
		30 (3.5)[b]		
		35.9(4.06)		
		45.7(4.59)		
2	C-1	20.4(2.57)		
		29 (2.8)[b]		
		35.4(4.35)		
		45.7(4.52)		
2	C-2	20.3(2.59)	20.3(2.60)	19.9(−4.83)
				23.5(+0.02)
		29 (2.8)[b]	29 (2.8)[b]	26 (−0.3)[b]
				29 (−1.1)[b]
		35.2(4.33)	35.3(4.34)	34.9(−26.7)
		45.9(4.55)	46.0(4.56)	46.1(+55.7)
3		20.4(2.59)	20.4(2.59)	19.9(−4.52)
				23.5(+0.03)
		29 (2.8)[b]	29 (2.8)[b]	26 (−0.3)[b]
				29 (−1.0)[b]
		35.2(4.33)	35.2(4.33)	34.5(−30.2)
		45.4(4.55)	45.4(4.55)	46.4(+53.6)
4		20.5(2.60)	20.4(2.60)	20.0(−5.19)
		29 (2.8)[b]	29 (2.8)[b]	26.7(−0.17)
				29 (−0.6)[b]
		35.2(4.33)	35.2(4.33)	34.8(−23.0)
		45.1(4.54)	45.0(4.55)	46.1(+50.8)
5		20.5(2.60)	20.5(2.60)	19.9(−4.98)
		29 (2.8)[b]	29 (2.8)[b]	26.2(−0.17)
				29 (−0.7)[b]
		35.2(4.32)	35.2(4.33)	34.8(−21.9)
		45.0(4.54)	44.9(4.54)	45.8(+48.0)
6		20.5(2.61)	20.5(2.61)	20.0(−5.09)
		29 (2.8)[b]	29 (2.8)[b]	26.3(−0.15)
				29 (−0.5)[b]
		35.1(4.33)	35.1(4.32)	34.8(−18.8)
		44.9(4.55)	44.9(4.55)	45.9(+47.4)
8		20.5(2.59)	20.5(2.60)	20.0(−4.91)
		29 (2.8)[b]	29 (2.8)[b]	26.3(−0.07)
				29 (−0.4)[b]
		35.2(4.31)	35.1(4.33)	35.0(−17.5)
		45.0(4.51)	45.1(4.55)	46.1(+43.9)
10			20.5(2.62)	20.1(−5.31)
			29 (2.8)[b]	26.3(−0.07)
				29 (−0.04)[b]
			35.1(4.32)	35.0(−17.9)
			45.1(4.54)	46.1(+45.7)
$[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nBr\}]^{3+}$				
		rac		active (Δ)[c]
2		20.4(2.26)		19.9(−2.63)
		29 (2.4)[b]		26.3(−0.12)
		35.5(3.99)		35.3(−8.68)
		45.9(4.27)		46.5(+22.7)
3		20.5(2.26)		20.0(−2.62)
		29 (2.5)[b]		26.0(−0.08)
		35.5(3.97)		35.3(−8.83)
		45.5(4.24)		46.1(+24.5)
4		20.4(2.29)		
		29 (2.5)[b]		
		35.3(3.96)		
		45.2(4.28)		
5		20.5(2.27)		20.0(−2.83)
		29 (2.5)[b]		26.1(−0.06)
		35.3(3.98)		35.1(−9.43)
		45.1(4.23)		45.8(+25.0)
6		20.5(2.28)		20.0(−2.64)
		29 (2.5)[b]		25.9(−0.07)
		35.2(4.00)		35.1(−8.24)
		45.1(4.24)		45.9(+21.8)
8		20.5(2.30)		
		29 (2.5)[b]		
		35.2(4.01)		
		45.1(4.25)		
10		20.5(2.30)		20.0(−2.95)
		29 (2.5)[b]		25.9(−0.06)
		35.1(4.01)		35.0(−9.64)
		45.0(4.23)		45.9(+25.3)
$[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nOH\}]^{3+}$				
		rac		active (Δ)[c]
4		20.5(2.28)		
		29 (2.5)[b]		
		35.3(3.99)		
		45.1(4.24)		
6		20.5(2.27)		19.9(−2.51)
		29 (2.5)[b]		26.0(−0.06)
		35.2(3.98)		35.0(−7.59)
		45.0(4.22)		46.0(+20.0)
8		20.5(2.27)		
		29 (2.5)[b]		
		35.2(3.97)		
		45.1(4.22)		

a) Wave numbers are given in 10^3 cm^{-1} unit and log ε or Δε values (in parentheses) in mol^{-1} dm^3 cm^{-1}.
b) Shoulder. c) CD intensity was calculated by applying molar absorption coefficient of the corresponding racemate.

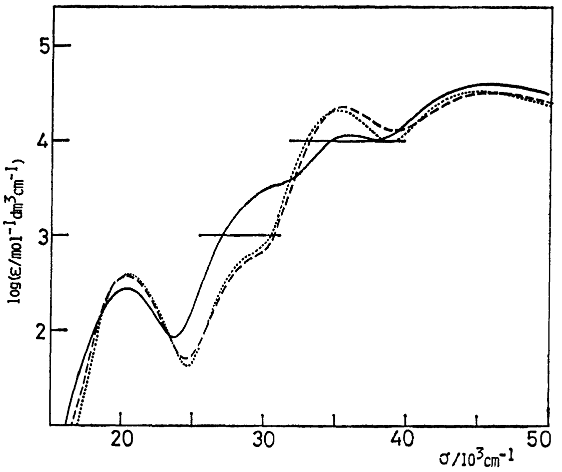

Fig. 2. Absorption spectra of the bridged complexes. $[(en)_2Co\{NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}Co(en)_2]^{6+}$: $n=1$, ——; $n=2$, ----; $n=8$, ------.

groups which must be tied with the shortest methylenic chain.

Absorption Spectra. Figure 2 and Table 2 show the absorption spectra of the present complexes. The bridged complexes exhibit their first d-d absorption bands at about 20400 cm^{-1} which quite agree with those of the $[Co(N)_5(S)]$ type complexes containing a thioether donor atom.5) The first d-d absorption band shifts slightly to higher energy side with increasing the number of methylene groups, while two charge transfer absorption bands in the near-ultraviolet region reversely.

As for the bridged complex of $n=1$, another intense band appears at *ca.* 30000 cm^{-1} with diminishing the intensity of the charge transfer band characteristic of the coordinated sulfur atoms at 35000 cm^{-1}. This new band seems to be also of charge transfer character judging from its intensity ($\log \varepsilon = 3.5$). The other bridged complexes of $n=2$—10 did not show such an intense band but the second d-d absorption band in the same region. Thus, the new band may be due to the *geminal*-sulfur interaction like that observed in organic compounds such as bis(methylthio)methane and 2,2-bis(butylthio)propane,10) because the interaction reduces the promotion energy of lone-pair electrons. A similar absorption band has been reported in a cobalt(III) complex containing a disulfide ligand, $[Co(en)_2\{S\text{-}(SCH_2CH_2NH_3)CH_2CH_2NH_2\}]^{4+}$.11)

Both monomeric complexes, $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nBr\}]^{3+}$ and $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nOH\}]^{3+}$, show almost the same absorption spectra as those of the corresponding bridged complexes except that their molar extinction coefficients are reduced to one-half the values of dinuclear complexes (Table 2).

CD Spectra. In the preparations of optically active bridged complex, the Δ-$[Co(aet)(en)_2]^{2+}$ complex was used as the starting material whose absolute configuration had been assigned on the basis of the CD sign in the first d-d absorption band region.5) As shown in Fig. 3, all the bridged complexes exhibit nearly the same CD spectra irrespective of n values, a negative CD band being dominant in the first absorption band region. The spectral pattern is very analogous to that of Δ-$[Co(en)_2(NH_2CH_2CH_2SR)]^{3+}$ ($R=CH_3$ or C_2H_5).5) Therefore, it is concluded that the alkylation reaction proceeds with retention of the initial absolute configuration and the bridged complexes obtained have the $\Delta\Delta$ absolute configuration.

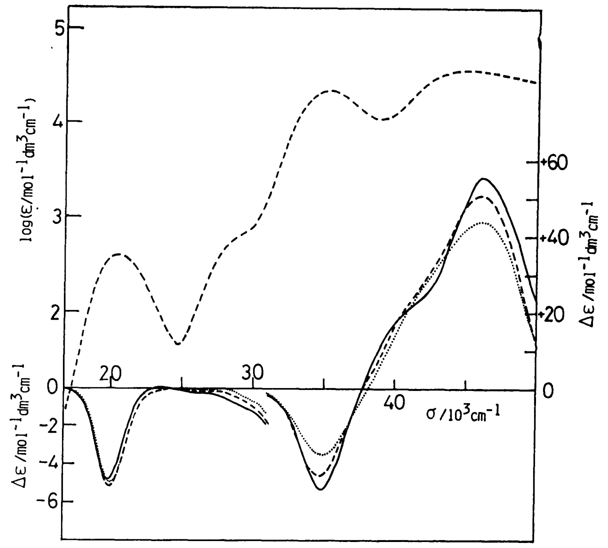

Fig. 3. CD spectra of the bridged complexes $[(en)_2Co\{[NH_2(CH_2)_2S(CH_2)_nS(CH_2)_2NH_2\}Co(en)_2]^{6+}$: $n=2$, ——; $n=4$, ----; $n=8$, ------.

Both monomeric complexes, $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nBr\}]^{3+}$ and $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nOH\}]^{3+}$, show a similar CD pattern to that of the bridged complexes, being also assigned to the Δ absolute configuration.

The CD intensities of the bridged complexes are approximately 2 times larger than those of the monomeric $[Co(en)_2\{NH_2(CH_2)_2S(CH_2)_nBr\}]^{3+}$ complexes in almost all regions. However, the CD intensities of $[Co_2(en)_4\{NH_2(CH_2)_2S(CH_2)_2S(CH_2)_2NH_2\}]^{6+}$ and $[Co_2(en)_4\{NH_2(CH_2)_2S(CH_2)_3S(CH_2)_2NH_2\}]^{6+}$ in the thioether charge transfer band region are 3.1 and 3.4 times larger than those of the corresponding monomeric complexes, respectively. This increase of CD intensity seems to represent an additional chirality which arises on the thioether donor atoms of bridged complexes of only $n=2$ or 3 because of a rather short bridge chain and the resulting unbalance of the R and S chiralities of the asymmetric sulfur atoms. In fact, the CD intensity per one cobalt(III) ion of the dinuclear complex of $n=10$ becomes almost the same as that of the monomeric complex, the increase in the number of methylene groups reducing such interaction between the two coordination centers.

Characterization of Geometrical Isomers. In the case of $n=2$, fractional crystallization of the bridged complex prepared from the racemic starting complex led to the isolation of the two orange crystals, C-1 and C-2. The chromatographic separation with a mixed solution of 0.5 M NaCl and 0.15 M $Na_2[Sb_2(d\text{-tart})_2]\cdot 2H_2O$ as an eluent indicated that only the complex C-2 is resolvable into the optical antipodes. Therefore, it is concluded that the complexes C-1 and C-2 are *meso* and *rac* forms, respectively. As shown in Table

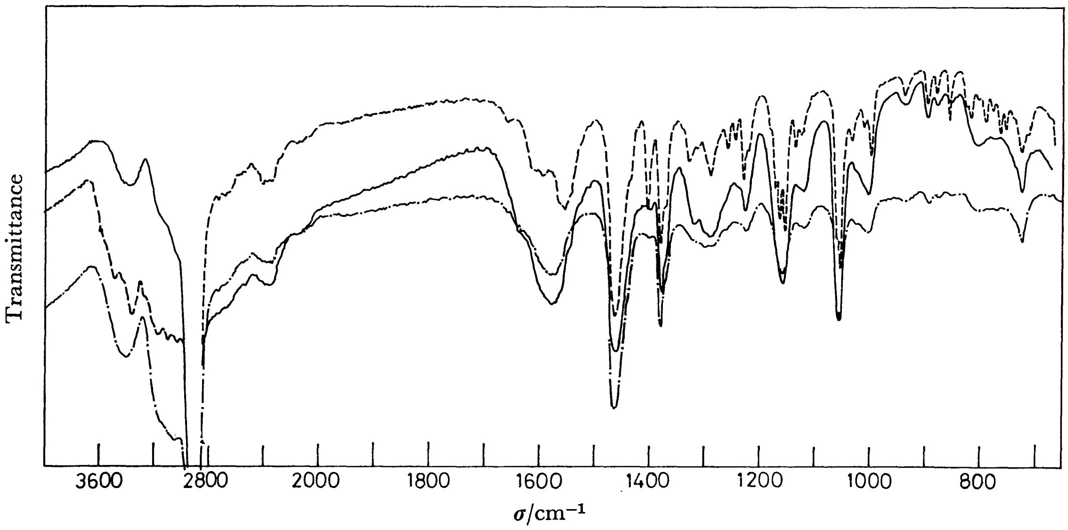

Fig. 4. Infrared spectra of $[(en)_2Co\{NH_2(CH_2)_2S(CH_2)_2S(CH_2)_2NH_2\}Co(en)_2]Cl_6$: C-1, ----; C-2, ——; ΔΔ, -·-·-.

2, the optically active ΔΔ isomer of the bridged complex of $n=2$ exhibits the analogous absorption spectra to that of the racemate C-2 rather than the *meso* form C-1 with respect to both the spectral position and intensity. A similar trend was also observed in the infrared spectra of these complexes (Fig. 4). The chlorides of complexes C-1 and C-2 gave significantly different spectra in the region 4000—400 cm^{-1}. However, the spectrum of active ΔΔ isomer is nearly identical to that of the racemate C-2.

In the case of $n=3$, the complex C obtained from *rac*-$[Co(aet)(en)_2]^{2+}$ showed a similar IR spectrum to that of the optically active ΔΔ isomer in the region 4000—700 cm^{-1}. Since there appear no other absorption peaks besides those of the active isomer, this complex consists of a single species and could be assigned to the racemic form.

References

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