  Bull. Chem. Soc. Jpn., 56, 157—164 (1983)

Preparation and Stereochemistry of *Δ-sym*-[(2*S*,2′*S*)-1,1′-Ethylenedipyrrolidine-2,2′-dicarboxylato]cobalt(III) Complexes with Various Bidentate Ligands

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(Received June 29, 1982)

Cobalt(III) complexes containing (2*S*,2′*S*)-1,1′-ethylenedipyrrolidine-2,2′-dicarboxylate (*S,S*-epro) and a bidentate ligand were prepared and characterized. The bidentate ligands were ethylenediamine, trimethylenediamine, oxalate, glycinate, (*R*)- or (*S*)-alaninate, (*R*)- or (*S*)-valinate, (*R*)- or (*S*)-prolinate, (*R*)- or (*S*)-pipecolate, sarcosinate, or *N*-ethylglycinate. The *S,S*-epro ligand coordinates stereoselectively to cobalt(III) ion to take only the *Δ-sym* configuration. The stereochemistry was discussed on the basis of the electronic absorption, CD, and ^{1}H and ^{13}C NMR spectra. The rate constants of isomerization and the Gibbs' free energy difference (*ca.* 0.9 kJ mol^{-1}) between the *R*(*N*) and *S*(*N*) isomers of the sarcosinato or *N*-ethylglycinato complex were investigated in relation to the interligand interaction. The thermodynamics and mechanisms of their isomerization process were little influenced by the *N*-alkyl groups.

For most ethylenediamine-*N,N′*-diacetate (edda) complexes, the symmetric (*sym*) isomer is dominantly formed in comparison with the unsymmetric (*unsym*) one.[1–8] The *unsym* isomer isomerizes to the *sym* one in aqueous solution.[9–11] The formation of the *unsym* isomer for the edda complexes depends mainly on the bidentate ligand coordinated in the remaining two coordination sites,[5,9,12] the geometry of the starting complex,[13] and the reaction temperature.[6] However, the stereospecific formation of the complex with this type of ligand has not been clarified yet.[14]

The optically active quadridentate ligand in this work, (2*S*,2′*S*)-1,1′-ethylenedipyrrolidine-2,2′-dicarboxylate (*S,S*-epro), has two asymmetric carbon atoms and two pyrrolidine rings, although the ligand is an O–N–N–O type similar to the edda. Accordingly, the configurations of the *S,S*-epro ligand are regulated to only two, *Δ*-symmetric and *Λ*-unsymmetric, by coordination to cobalt(III) ion. This selective coordination is suitable for investigation of the stereochemical preference of the amino or cyclic imino carboxylate ligands in the remaining two coordination sites.

In the present paper, some aspects of the stereochemistry of the [Co(*S,S*-epro)(L)] type complexes are dealt with; L denotes ethylenediamine, trimethylenediamine, oxalate, glycinate, (*R*)- or (*S*)-alaninate, (*R*)- or (*S*)-valinate, (*R*)- or (*S*)-prolinate, (*R*)- or (*S*)-pipecolate ((*R*)- or (*S*)-2-piperidinecarboxylate, *R*- or *S*-pipec), sarcosinate (sar), or *N*-ethylglycinate (*N*-et-gly). The *S,S*-epro complexes isolated have been characterized from their electronic absorption, CD, and ^{1}H and ^{13}C NMR spectra. The absolute configurations of the coordinated nitrogen atoms of sar, *N*-et-gly, and *R*- or *S*-pipec were assigned by means of their ^{1}H NMR and CD spectra. The rate constants of isomerizations and the Gibbs' free energy differences are considered for the sar and *N*-et-gly complexes.

Experimental

1) Preparation of Ligands. (2*S*,2′*S*)-1,1′-Ethylenedipyrrolidine-2,2′-dicarboxylic acid was prepared from (*S*)-proline and 1,2-dibromoethane according to the method of Schoenberg *et al.*[15] Found: C, 45.80; H, 7.04; N, 8.82%. Calcd for $C_{12}H_{22}N_2O_4 \cdot 0.75NaCl \cdot H_2O$: C, 45.30; H, 6.97; N, 8.80%.

N-Ethylglycine was prepared by the procedure described previously.[16]

2) Δ-sym-*Ba*[*Co*(S,S-*epro*)(*Cl*)(*OH*)]$_2 \cdot C_2H_5OH$. The complex was prepared and separated by a procedure similar to that used for *Λ-unsym*-[Co(*S,S*-tmpro)(Cl)(OH)]$^-$ (where *S,S*-tmpro denotes (2*S*,2′*S*)-1,1′-trimethylenedipyrrolidine-2,2′-dicarboxylate).[16] The CD spectral pattern in the visible region suggested that the violet complex obtained has the *Δ-sym* configuration. Yield; 0.5 g.

3) Δ-sym-[*Co*(S,S-*epro*)(*en*)]$ClO_4 \cdot 2H_2O$. *Method A*: A solution containing 0.3 g of *trans*-[Co(Cl)$_2$(en)$_2$]Cl[17] and 0.33 g of *S,S*-H$_2$epro·0.75NaCl·H$_2$O in 20 cm^3 of water was adjusted to pH 8.0 by addition of 1 mol dm^{-3} NaOH aqueous solution. After addition of *ca.* 0.1 g of activated charcoal, the mixture was stirred at 50 °C for 30 min. The reaction solution was cooled to room temperature and then filtered. The filtrate was concentrated to a small volume and poured onto a column of SP-Sephadex C-25 (Na$^+$ form, 3 cm × 35 cm). The adsorbed band was separated into two bands, purple-red and yellow in the order of elution, by eluting with 0.05 mol dm^{-3} $NaClO_4$ aqueous solution. The yellow band remained at the top of the column after the purple-red band had been eluted out, and then the band was eluted with a solution saturated with NaCl. It was found, from the absorption and CD spectra, that the purple-red and yellow bands contained *Δ-sym*-[Co(*S,S*-epro)(en)]$^+$ and [Co(en)$_3$]$^{3+}$, respectively. The first eluate was concentrated to a small volume, and to the solution was added ethanol. The resulting crystals were collected and recrystallized from a water–methanol–ethanol (2:1:1) mixture. The needle crystals were collected, washed with ethanol and then ether, and dried in a vacuum desiccator. Yield: 0.24 g.

Method B: The complex was also prepared by the following procedure. A solution containing 0.27 g of $CoCl_2 \cdot 6H_2O$ in 5 cm^3 of water was added to a solution containing 0.06 g of ethylenediamine and 0.32 g of *S,S*-H$_2$epro·0.75NaCl·H$_2$O in 6 cm^3 of water. To the solution was added 0.24 g of PbO_2 and the mixture was stirred at 50 °C for 3 h. The solution was cooled in an ice bath and then filtered. The filtrate was poured onto a column of Dowex

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50W-X8 (200—400 mesh, Na^+ form, 2 cm × 15 cm). The adsorbed band was eluted with 0.2 mol dm^{-3} $NaClO_4$ aqueous solution. It was found that the purple-red band contained only the complex, *Δ-sym*-[Co(*S,S*-epro)(en)]$^+$. The needle crystals were collected by filtration. Yield: 0.09 g.

4) Δ-sym-[*Co*(S,S-*epro*)(*tn*)]$ClO_4 \cdot 0.5C_2H_5OH$. The complex was prepared by the same method as in 3), using trimethylenediamine instead of ethylenediamine.

5) Δ-sym-*K*[*Co*(S,S-*epro*)(*ox*)]$\cdot 4H_2O$. This complex was prepared by a procedure similar to that in Method B of 3), using 1.34 g of $CoCl_2 \cdot 6H_2O$, 0.74 g of oxalic acid, and 1.79 g of *S,S*-H_2epro·0.75NaCl·H_2O. The solution obtained was poured onto a column of QAE-Sephadex A-25 (Cl^- form, 5 cm × 30 cm). The adsorbed band was eluted with 0.07 mol dm^{-3} KCl aqueous solution. The two blue-violet bands were eluted. It was found, from the absorption and CD spectra, that the first eluate contained *Δ-sym*-[Co(*S,S*-epro)(Cl)(OH)]$^-$ and the second one *Δ-sym*-[Co(*S,S*-epro)(ox)]$^-$. The second eluate was concentrated to a small volume with a rotary evaporator. To this solution was added ethanol and it was kept in a refrigerator overnight. The resulted needle crystals were collected and recrystallized from ethanol–water (5:1) mixture. Yield: 0.24 g.

6) Δ-sym-[*Co*(S,S-*epro*)(*gly*)]$\cdot 0.5H_2O$. This complex was prepared and separated by a procedure similar to that used for *Δ-unsym*-[Co(*S,S*-tmpro)(gly)].[16] By the column chromatographic separation, only one band was eluted with water and fractionated into six parts. It was found, from their absorption and CD spectra, that all the fractions contained only *Δ-sym*-[Co(*S,S*-epro)(gly)]. The fractions were combined and concentrated to a small volume. To the solution was added a small amount of ethanol and it was kept in a refrigerator overnight. The needle crystals were collected by filtration, and recrystallized from water by addition of ethanol and then acetone. Yield: 0.43 g.

7) Δ-sym-[*Co*(S,S-*epro*)(S-*ala*)]$\cdot H_2O$, -[*Co*(S,S-*epro*)(R-*ala*)]$\cdot H_2O$, -[*Co*(S,S-*epro*)(S-*val*)]$\cdot 1.5H_2O$, -[*Co*(S,S-*epro*)(R-*val*)], *and* -[*Co*(S,S-*epro*)(S-*pro*)]. These complexes were prepared by the same method as that used for *Δ-sym*-[Co(*S,S*-epro)(gly)].

8) Δ-sym-[*Co*(S,S-*epro*)(R(N)-*sar*)]$\cdot H_2O$ *and* -[*Co*(S,S-*epro*)(S(N)-*sar*)]$\cdot 0.5H_2O$. The solution containing *Δ-sym*-[Co(*S,S*-epro)(Cl)(OH)]$^-$ prepared from 2.4 g of $CoCl_2 \cdot 6H_2O$ was evaporated to dryness in a rotary evaporator below 30 °C, and the complex was extracted with 50 cm^3 of methanol. The methanol solution was added to a solution containing 1.2 g of sarcosine in 150 cm^3 of methanol. After addition of a small amount of activated charcoal, the mixture was stirred at 65 °C for 1 h. The solution was cooled to room temperature and then filtered. The filtrate was concentrated to a pasty cake and *ca.* 20 cm^3 of water was added to it. The solution was passed through columns of Dowex 1-X8 and SP-Sephadex C-25 in order to remove the charged compounds. The concentrated eluate was poured onto a column of QAE-Sephadex A-25 ((*R,R*)-tartrate form, 3.5 cm × 85 cm), and eluted with water. The adsorbed band was separated into three bands: violet, violet, and pink, in this order. It was found, from the absorption and CD spectra, that the first eluate contained *Δ-sym*-[Co(*S,S*-epro)(sar)] (the ratio of the *R*(*N*)-sar and *S*(*N*)-sar isomers was *ca.* 2:3), the second violet one contained *mer*-[Co(sar)$_3$], and the third pink one contained cobalt(II) compound. All the fractions of the first eluate were combined and evaporated to dryness below 30 °C. Yield: 1.1 g. This product was dissolved in methanol. After addition of appropriate volume of ether to it, the solution was kept in a refrigerator overnight. The complex consisted of two kinds of crystalline forms, needle and prism, which could be sorted by hand. It was found, from the absorption and ^{1}H NMR spectra, that the needle and prismatic crystals corresponded to the *R*(*N*)-sar and *S*(*N*)-sar isomers, respectively. Each of them was recrystallized repeatedly from methanol by addition of ether until a constant CD spectrum was obtained.

9) Δ-sym-[*Co*(S,S-*epro*)(R(N)-N-*et-gly*)]$\cdot 0.5H_2O$ *and* -[*Co*(S,S-*epro*)(S(N)-N-*et-gly*)]$\cdot 0.25H_2O$. The complex was prepared and separated into two diastereomers by the same procedure as in 8), using *N*-ethylglycine instead of sarcosine. Yield: 0.59 g. From the CD spectra, the reaction solution also contained the *R*(*N*)-*N*-et-gly and *S*(*N*)-*N*-*et-gly* isomers (the ratio: *ca.* 2:3).

10) Δ-sym-[*Co*(S,S-*epro*)(R-*pro*)]$\cdot 0.5H_2O$. The complex was prepared by the same procedure as in 8), using (*RS*)-proline instead of sarcosine. The complex was chromatographed on a column of QAE-Sephadex A-25 ((*R,R*)-tartrate form, 3.5 cm × 85 cm). The adsorbed band was eluted with water. The two bands, which partially overlapped, were fractionated into eight parts. It was found, from their absorption and CD spectra, that the four earlier fractions contained mainly *Δ-sym*-[Co(*S,S*-epro)(*R*-pro)], and the four later ones contained mainly *Δ-sym*-[Co(*S,S*-epro)(*S*-pro)], which was already prepared in 7). The four eariler fractions were combined and concentrated to a small volume and then chromatographed on the column again. This procedure was repeated several times in order to purify the complex. The eluate was concentrated to a small volume. After addition of ethanol and ether to it, the solution was kept in a refrigerator overnight. The crystals obtained were collected and then recrystallized from an ethanol–acetone (2:1) mixture several times. Yield: 0.09 g. The configuration of the α-carbon atom of the coordinated prolinate was confirmed by the DNP method.[16]

11) Δ-sym-[*Co*(S,S-*epro*)(R-*pipec*)]$\cdot H_2O$ *and* -[*Co*(S,S-*epro*)(S-*pipec*)]. These complexes were prepared and separated by a procedure similar to that in 10). The earlier eluate contained *Δ-sym*-[Co(*S,S*-epro)(*R*-pipec)] and the later one *Δ-sym*-[Co(*S,S*-epro)(*S*-pipec)]. The configuration of the asymmetric carbon atoms of the coordinated pipecolate were also determined by the DNP method.[16] Yields: 0.27 g for the *R*-pipec isomer and 0.015 g for the *S*-pipec one.

Analyses. The analytical results for the complexes obtained are summarized in Table 1.

Measurements. The electronic absorption spectra were recorded with JASCO UVIDEC-1 spectrophotometer and the CD spectra with JASCO J-20 spectropolarimeter in an aqueous solution. These spectra changed very little during the measurements. The ^{1}H NMR spectra were recorded on a JEOL FX-100 NMR spectrometer at probe temperature in three kinds of mixtures: $DClO_4$–CD_3OD, D_2O–$DClO_4$, and $(CD_3)_2SO$–DCl. The ^{13}C NMR spectra were recorded on JEOL FX-90Q NMR spectrometer in the D_2O solution. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal reference for the ^{1}H and ^{13}C NMR measurements.

The isomerization and the equilibrium and kinetic experiments were carried out using both the *R*(*N*) and *S*(*N*) isomers of *Δ-sym*-[Co(*S,S*-epro)(sar)] or -[Co(*S,S*-epro)(*N*-et-gly)]. The rate of CD change with time was measured for a methanol solution of each isomer (*ca.* 1.5×10^{-3} mol dm^{-3}) with JASCO J-500 spectropolarimeter. The runs were carried out in a quartz cell equipped with the water-jacket thermostated at 23.5 °C. The isomerization was followed until equilibrium was reached. The change in the CD intensity was observed at 300—650 nm.

Table 1. Elemental analyses

Complex	C (%)		H (%)		N (%)	
	Found	Calcd	Found	Calcd	Found	Calcd
Δ-sym-Ba[Co(*S,S*-epro)(Cl)(OH)]$_2$·C_2H_5OH	34.54	34.14	4.52	4.85	5.82	6.12
Δ-sym-K[Co(*S,S*-epro)(ox)]·4H_2O	32.48	32.82	4.98	5.11	5.47	5.47
Δ-sym-[Co(*S,S*-epro)(en)]ClO_4·2H_2O	32.88	33.05	5.93	5.94	11.02	11.01
Δ-sym-[Co(*S,S*-epro)(tn)]ClO_4·0.5C_2H_5OH	37.73	37.69	6.15	6.13	10.45	10.99
Δ-sym-[Co(*S,S*-epro)(gly)]·0.5H_2O	42.34	42.43	5.87	5.60	10.61	10.60
Δ-sym-[Co(*S,S*-epro)(*S*-ala)]·H_2O	43.22	42.97	6.32	6.25	10.43	10.02
Δ-sym-[Co(*S,S*-epro)(*R*-ala)]	44.85	44.89	6.07	6.03	10.71	10.47
Δ-sym-[Co(*S,S*-epro)(*S*-val)]·1.5H_2O	44.97	44.74	6.44	6.85	9.06	9.21
Δ-sym-[Co(*S,S*-epro)(*R*-val)]	48.22	47.56	6.51	6.57	9.97	9.79
Δ-sym-[Co(*S,S*-epro)(*R*(*N*)-sar)]·H_2O	42.69	42.97	6.07	6.25	9.94	10.02
Δ-sym-[Co(*S,S*-epro)(*S*(*N*)-sar)]·0.5H_2O	43.70	43.91	6.28	6.14	10.10	10.24
Δ-sym-[Co(*S,S*-epro)(*R*(*N*)-*N*-et-gly)]·0.5H_2O	45.39	45.29	6.74	6.41	9.75	9.90
Δ-sym-[Co(*S,S*-epro)(*S*(*N*)-*N*-et-gly)]·0.25H_2O	45.88	45.77	6.41	6.30	10.28	10.01
Δ-sym-[Co(*S,S*-epro)(*R*-pipec)]·H_2O	47.37	47.06	6.67	6.58	9.21	9.15
Δ-sym-[Co(*S,S*-epro)(*S*-pipec)]	48.92	48.98	6.52	6.39	9.46	9.52
Δ-sym-[Co(*S,S*-epro)(*R*-pro)]·0.5H_2O	46.99	46.79	6.13	6.24	9.49	9.63
Δ-sym-[Co(*S,S*-epro)(*S*-pro)]	47.41	47.78	6.01	6.13	9.79	9.83

Results and Discussion

Structural Assignments. Only two isomers, *Δ-sym* and *Δ-unsym*, are possible for [Co(*S,S*-epro)(en, tn, or ox)]$^{+\text{ or }-}$, because the *S,S*-epro ligand has two asymmetric carbon atoms, *S*(*C*) and *S*(*C*), and two pyrrolidine rings (Fig. 1). In the ^{13}C NMR spectra of the en and ox complexes, the seven peaks are expected for the *Δ-sym* isomer (C_2 symmetry), whereas fourteen peaks are expected for the *Δ-unsym* one (C_1 symmetry).

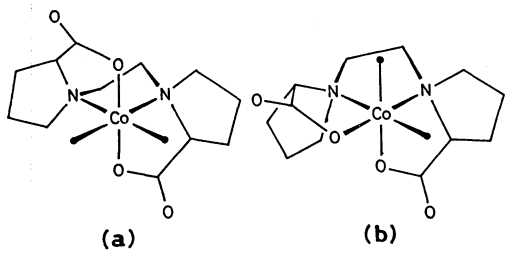

Fig. 1. Two possible configurations of coordinated *S,S*-epro ligand: (a) *Δ-sym* and (b) *Δ-unsym*.

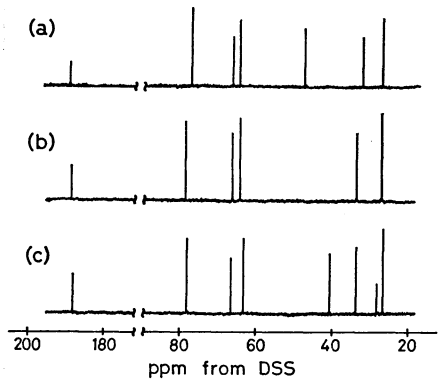

Fig. 2. ^{13}C NMR spectra of *Δ-sym*-[Co(*S,S*-epro)(L)]: L; (a) en, (b) ox, and (c) tn.

As shown in Fig. 2, however, the spectra of the en and ox isomers isolated show seven peaks and indicate that both the isomers are the *Δ-sym*. Similarly, the tn isomer is also the *Δ-sym* type, because it shows eight peaks (C_2 symmetry) (Fig. 2).

The absorption and CD spectra of the en and ox complexes are shown in Fig. 3. The first absorption band of the en and tn complexes have a shoulder at the higher energy side of the major peak (Table 2),

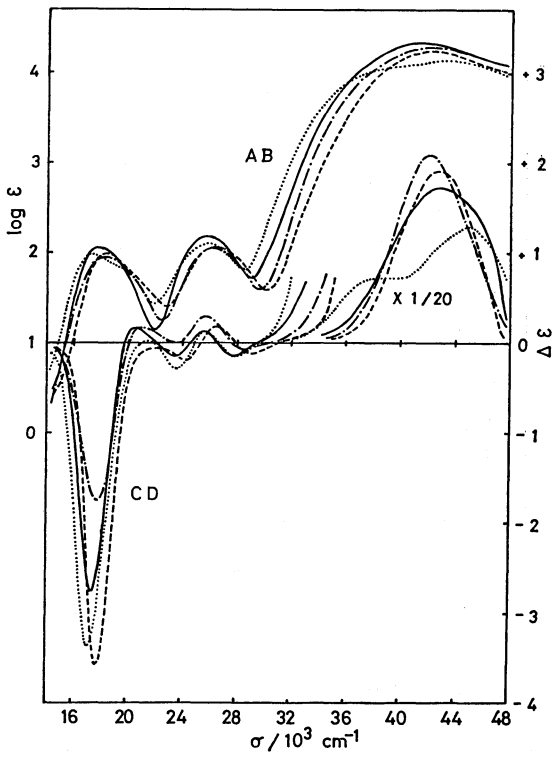

Fig. 3. Absorption and CD spectra of *Δ-sym*-[Co(*S,S*-epro)(L)]: L; ox (——), en (----), (Cl)(OH) (·····), and gly (—·—).

Table 2. Absorption data of *Δ-sym*-[Co(*S,S*-epro)(L)] type complexes

Complex (L)	First band	Second band	Charge transfer band
[Co(*S,S*-epro)(Cl)(OH)]$^-$	17.33(1.98)	25.71(2.11)	40.06(4.1 sh)
	19.42(1.8 sh)		
[Co(*S,S*-epro)(ox)]$^-$	17.78(2.07)	25.74(2.19)	41.67(4.33)
[Co(*S,S*-epro)(en)]$^+$	18.35(1.99)	26.32(2.06)	42.37(4.25)
	20.00(1.8 sh)		
[Co(*S,S*-epro)(tn)]$^+$	18.18(1.92)	26.32(2.07)	41.32(4.43)
	20.00(1.8 sh)		
[Co(*S,S*-epro)(gly)]	18.35(1.95)	26.32(2.05)	42.55(4.29)
[Co(*S,S*-epro)(*R*-ala)]	18.32(1.98)	26.25(2.12)	42.37(4.32)
[Co(*S,S*-epro)(*S*-ala)]	18.25(1.96)	26.32(2.10)	42.55(4.35)
[Co(*S,S*-epro)(*R*-val)]	18.28(1.98)	26.25(2.11)	42.19(4.29)
[Co(*S,S*-epro)(*S*-val)]	18.25(2.00)	26.32(2.11)	42.55(4.31)
[Co(*S,S*-epro)(*R*(*N*)-sar)]	18.08(2.06)	25.91(2.12)	41.67(4.31)
[Co(*S,S*-epro)(*S*(*N*)-sar)]	18.08(2.00)	25.91(2.09)	41.67(4.32)
[Co(*S,S*-epro)(*R*(*N*)-*N*-et-gly)]	18.05(2.09)	25.74(2.13)	41.67(4.28)
[Co(*S,S*-epro)(*S*(*N*)-*N*-et-gly)]	18.05(2.01)	25.97(2.11)	41.49(4.34)
[Co(*S,S*-epro)(*R*-pipec)]	17.86(2.10)	25.61(2.22)	40.65(4.28)
[Co(*S,S*-epro)(*S*-pipec)]	17.95(2.01)	25.84(2.17)	40.65(4.28)
[Co(*S,S*-epro)(*R*-pro)]	18.18(2.05)	26.04(2.15)	41.49(4.26)
[Co(*S,S*-epro)(*S*-pro)]	18.18(1.98)	26.11(2.11)	41.67(4.25)

Wave numbers and log ε values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1}, respectively. sh denotes a shoulder.

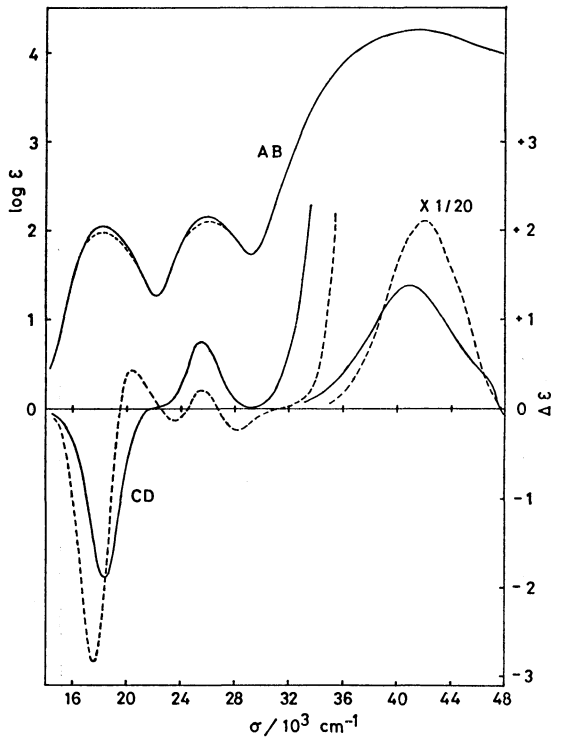

Fig. 4. Absorption and CD spectra of *Δ-sym*-[Co(*S,S*-epro)(L)]: L; R-pro (——) and S-pro (----).

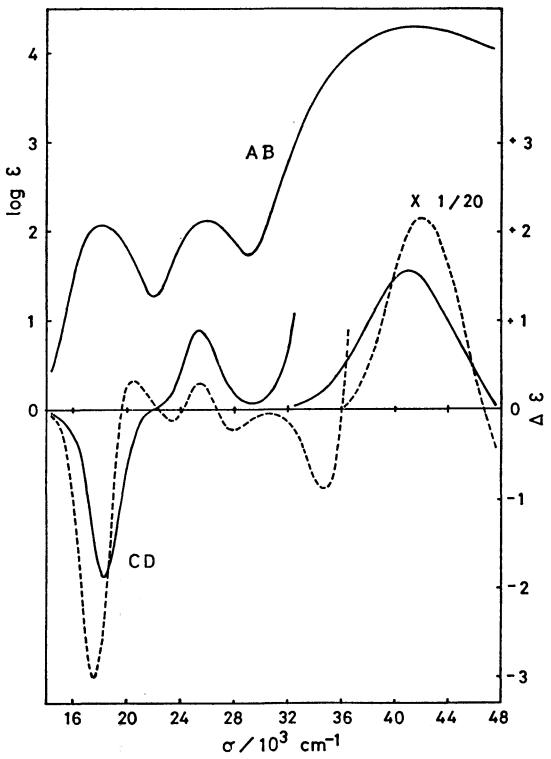

Fig. 5. Absorption and CD spectra of *Δ-sym*-[Co(*S,S*-epro)(L)]: L; *R*(*N*)-sar (——) and *S*(*N*)-sar (----).

indicating the trans(O) structure.[1,6,7,11,18,19] The CD spectra of the en, tn, and ox complexes show the negative major band in the first absorption band region (Table 3). These absorption and CD spectral behaviors suggest that the en, tn and ox complexes commonly take *Δ* configuration.[4,19–21] From these results, the en, tn, and ox complexes isolated can be assigned to the *Δ-sym* configuration.

Of three possible isomers, *Δ-sym*, *Δ-unsym-mer*, and *Δ-unsym-fac*, for [Co(*S,S*-epro)(amino carboxylato)], only one isomer was selectively isolated for each of

TABLE 3. CD DATA OF *Δ-sym*-[Co(*S,S*-epro)(L)] TYPE COMPLEXES

Complex (L)	First band region	Second band region	Charge transfer band region
[Co(*S,S*-epro)(Cl)(OH)]$^-$	17.06(−3.38)	23.58(−0.29)	38.46(+14.6 sh)
	21.19(+0.02)	25.64(+0.13)	45.25(+24.89)
		27.93(−0.14)	
[Co(*S,S*-epro)(ox)]$^-$	17.48(−2.76)	23.47(−0.15)	42.74(−34.67)
	20.49(+0.17)	25.64(+0.15)	
		27.78(−0.13)	
[Co(*S,S*-epro)(en)]$^+$	17.92(−3.57)	24.27(−0.19)	42.74(+38.21)
		26.60(+0.19)	
		29.07(−0.12)	
Co(*S,S*-epro)(tn)]$^+$	18.41(−2.12)	26.32(+0.32)	34.25(−0.22)
	21.37(+0.21)		42.19(+34.89)
[Co(*S,S*-epro)(gly)]	17.85(−1.76)	23.47(−0.01)	42.19(+41.67)
	21.01(+0.18)	25.77(+0.29)	
		28.74(−0.07)	
[Co(*S,S*-epro)(*R*-ala)]	17.92(−1.64)	25.77(+0.33)	42.02(+36.45)
	20.92(+0.35)	28.74(−0.06)	
[Co(*S,S*-epro)(*S*-ala)]	17.85(−2.12)	23.64(−0.04)	42.37(+39.03)
	21.74(+0.02)	26.04(+0.26)	
		28.74(−0.10)	
[Co(*S,S*-epro)(*R*-val)]	17.85(−1.30)	25.77(+0.43)	42.02(+33.38)
	20.75(+0.50)	28.90(−0.04)	
[Co(*S,S*-epro)(*S*-val)]	17.85(−2.52)	23.81(−0.09)	42.74(+36.36)
		25.91(+0.25)	
		28.57(−0.11)	
[Co(*S,S*-epro)(*R*(*N*)-sar)]	18.38(−1.90)	25.45(+0.89)	40.98(+31.45)
[Co(*S,S*-epro)(*S*(*N*)-sar)]	17.61(−3.02)	23.36(−0.13)	34.97(−0.88)
	20.49(+0.34)	25.38(+0.30)	42.02(+42.23)
		27.93(−0.23)	
[Co(*S,S*-epro)(*R*(*N*)-*N*-et-gly)]	18.38(−2.02)	25.32(+1.06)	40.32(+28.21)
[Co(*S,S*-epro)(*S*(*N*)-*N*-et-gly)]	17.54(−3.06)	23.26(−0.12)	34.84(−0.96)
	20.24(+0.48)	25.32(+0.30)	42.02(+41.00)
		27.78(−0.26)	
[Co(*S,S*-epro)(*R*-pipec)]	18.18(−3.82)	25.13(+1.26)	40.00(+25.33)
[Co(*S,S*-epro)(*S*-pipec)]	17.57(−3.20)	23.09(−0.01)	41.67(+38.14)
	20.28(+0.59)	25.25(+0.55)	
		27.93(−0.18)	
[Co(*S,S*-epro)(*R*-pro)]	18.25(−0.89)	25.51(+0.76)	40.98(+27.78)
[Co(*S,S*-epro)(*S*-pro)]	17.61(−2.84)	23.47(−0.13)	42.02(+42.02)
	20.49(+0.45)	25.58(+0.22)	
		28.09(−0.24)	

Wave numbers and $\Delta\varepsilon$ values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1}, respectively. sh denotes a shoulder.

the seven amino carboxylato complexes (Table 1). These isomers commonly show the broad first absorption band (Figs. 3—5 and Table 2). This absorption spectral pattern points out that the isomers are mer form, namely, *Δ-sym* and *Δ-unsym-mer*.[11,18] Furthermore, all the isomers exhibit a negative major CD band in the first absorption band region (Figs. 3—5 and Table 3). These facts suggest that the complexes isolated are only the *Δ-sym* configuration.[22]

The selective formation for the *Δ-sym* configuration was also observed for the [Co(*S,S*-epro)(L)] complexes (L: $(H_2O)_2$, CO_3, and $(Cl)(H_2O)$).[20] Molecular models reveal that the backbone ethylenediamine ring of the *S,S*-epro ligand takes a gauche form for the *Δ*-symmetric coordination, and an envelope form for the *Δ*-unsymmetric case. These results mean that the *Δ*-symmetric preference of the *S,S*-epro complexes depends mainly on the more stable conformation of the backbone ethylenediamine ring.[23]

^{1}H NMR and CD Spectra. When the *N*-alkyl substituted amino or cyclic imino carboxylate ligand coordinates to the cobalt(III) ion, the nitrogen atom of the ligand becomes chiral, *R*(*N*) or *S*(*N*). Accordingly, two additional isomers, *R*(*N*) or *S*(*N*), are possible for each of the *Δ-sym*-[Co(*S,S*-epro)(am)] complexes (am: sar, *N*-et-gly, *R*- or *S*-pro, and *R*- or *S*-pipec).

In the ^{1}H NMR spectra of the *Δ-sym*-[Co(*S,S*-epro)-

(am)] complexes, the resonance lines due to the *N*-bonded protons of the needle crystalline isomers appear at lower field than those of the prismatic crystalline ones (Fig. 6). The asymmetric nitrogen atom of the coordinated (*S*)-prolinate ligand is fixed to the *S*(*N*) configuration and that of the (*R*)-prolinate one is fixed to the *R*(*N*) one.[24] The *N*-bonded protons of the *S*(*N*) isomer for the *Δ-sym*-[Co(*S*,*S*-epro)(*S*-pro)] complex lies above the carbonyl group of the *S*,*S*-epro ligand (Fig. 7a-2), while that of the *R*(*N*) one lies in the plane involving the other carbonyl group of the ligand (Fig. 7a-1). In the region of the *N*-bonded protons, the resonance line of the *S*-pro complex (at 6.17 ppm) is observed at higher field than that of the *R*-pro one (at 6.40 ppm).[25] The *N*-bonded protons of the *R*(*N*) isomer of the sar, *N*-et-gly, or pipec complex are similar in environment to that of the (*R*)-prolinate, and those of the *S*(*N*) one to that

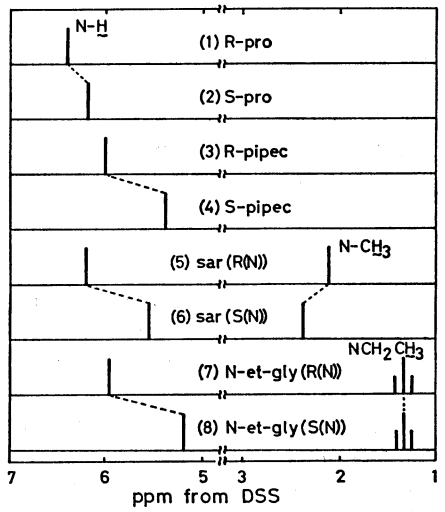

Fig. 6. The distribution of the chemical shifts due to the *N*-bonded and *N*-alkyl protons of *Δ-sym*-[Co(*S*,*S*-epro)(am)]. (1), (2), (7), and (8) were recorded in $DClO_4$–CD_3OD, (3) and (4) in $(CD_3)_2SO$–DCl, and (5) and (6) in D_2O–$DClO_4$.

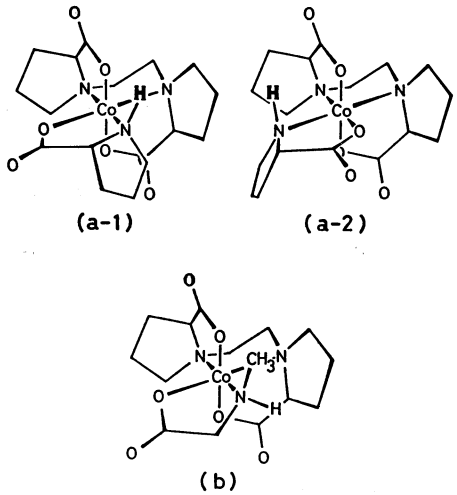

Fig. 7. Probable chiral configurations of the prolinate and sarconsinate ions in *Δ-sym*-[Co(*S*,*S*-epro)(L)]: L; (a-1) *R*-pro, (a-2) *S*-pro, and (b) *S*(*N*)-sar.

of the (*S*)-prolinate. Accordingly, it is suggested for the *Δ-sym*-[Co(*S*,*S*-epro)(am)] complexes that the needle crystalline isomers showing the signal at the lower field are the *R*(*N*) configuration and the prismatic crystalline ones at the upper field the *S*(*N*) one. Contrary to the case of the *N*-bonded protons, the resonance lines of the methyl group for the *R*(*N*) isomer of the *Δ-sym*-[Co(*S*,*S*-epro)(sar)] complex are observed at higher field than that of the *S*(*N*) one. This observation is also explained on the basis of the difference of the magnetic and steric environments of the methyl group.[25] Namely, the methyl group of the *R*(*N*) isomer lies above the carbonyl group of the *S*,*S*-epro ligand, whereas that of the *S*(*N*) one lies in the plane involving the other carbonyl group of the ligand (Fig. 7b).

In order to estimate the CD contribution of the asymmetric nitrogen atoms in the *Δ-sym*-[Co(*S*,*S*-epro)-(am)] complexes, the vicinal CD curves are calculated in the same manner as that for the cobalt(III) complexes with the *S*,*S*-tmpro ligand (Figs. 8 and 9).[16] The vicinal CD curves for the needle crystalline isomers for the sar, *N*-et-gly, and *R*-pipec complexes are similar to that of the *R*-pro complex and the curves of the prismatic ones for the sar, *N*-et-gly, and *S*-pipec complexes are similar to that of the *S*-pro one. Furthermore, the curves for the *R*-pro and *S*-pro complexes show an antipodal relationship in the first absorption band region (Figs. 8 and 9). These results also support the conclusion that the asymmetric nitrogen atoms of the needle and prismatic crystalline isomers take the *R*(*N*) and *S*(*N*) configurations, respectively.

Mutarotation and Equilibrium Distribution. The *R*-(*N*) and *S*(*N*) isomers of the *Δ-sym*-[Co(*S*,*S*-epro)(sar)] complex show a change of the CD spectra with time in methanol at ambient temperature (23.5 °C), as shown in Fig. 10. When either of the isomers was used as a starting substance, the identical CD curve with two distinct isodichroic points at 512 and 570

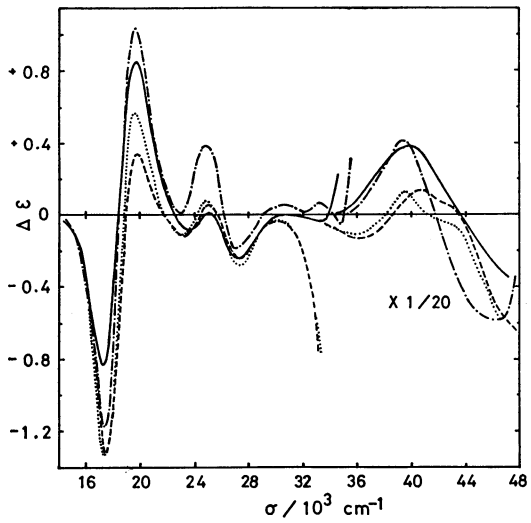

Fig. 8. Calculated vicinal CD curves due to the nitrogen atom of the bidentate ligand in *Δ-sym*-[Co(*S*,*S*-epro)(am)]: am; *S*(*N*)-sar (----), *S*(*N*)-*N*-et-gly (·····), *S*-pro (——), and *S*-pipec (—·—).

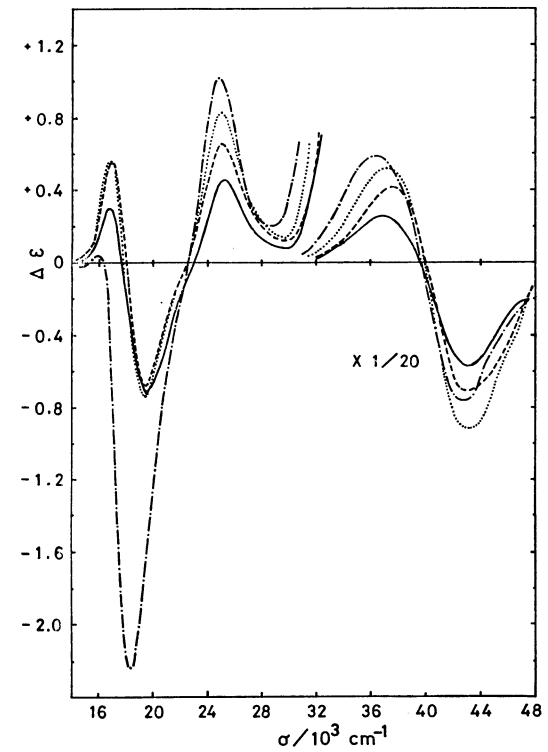

Fig. 9. Calculated vicinal CD curves due to the nitrogen atom of the bidentate ligand in *Δ-sym*-[Co(*S,S*-epro)(am)]: am; *R*(*N*)-sar (----), *R*(*N*)-*N*-et-gly (·····), *R*-pro (——), and *R*-pipec (—·—).

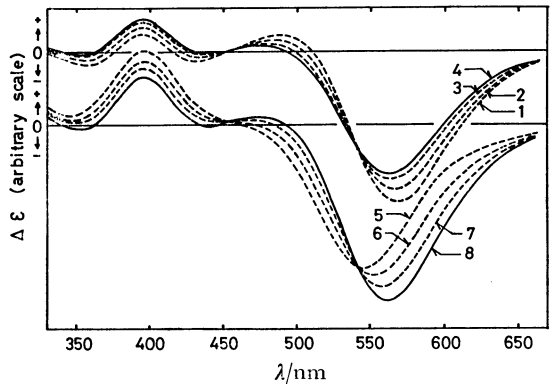

Fig. 10. Change of the CD spectra with time for the *S*(*N*)-sar (upper) and *R*(*N*)-sar (lower) isomers of *Δ-sym*-[Co(*S,S*-epro)(sar)] in methanol at 23.5 °C. The curves 1—4 were measured at 0, 465, 1265, and 3200 min, respectively, and the curves 5—8 at 0, 495, 1295, and 3300 min, respectively.

nm was obtained at equilibrium. No change was noticed with time in the absorption spectra for the two isomers; this fact indicates that mutarotation took place for the two isomers of the sar complex. Similar behavior was also observed for the *R*(*N*) and *S*(*N*) isomers of the *Δ-sym*-[Co(*S,S*-epro)(*N*-et-gly)] complex with two isodichroic points at 516 and 580 nm. These CD spectral characteristics show that epimerization takes place for these isomers at the asymmetric nitrogen atoms as follows:

$$R(N) \underset{k_{SR}}{\overset{k_{RS}}{\rightleftharpoons}} S(N),$$

where k_{RS} and k_{SR} denote the rate constants for the epimerization of the *R*(*N*) isomer to the *S*(*N*) one and of the *S*(*N*) isomer to the *R*(*N*) one, respectively.

The equilibrium constant, K_{eq}, for the epimerization reaction was determined by the CD spectral measurements to be 1.43±0.01 for the sar complex and 1.47±0.01 for the *N*-et-gly one. From these results, the free energy difference, $-\Delta G^\circ$, between the *R*(*N*) and *S*(*N*) isomers could be estimated to be 0.88±0.02 kJ mol^{-1} for the sar complex and 0.95±0.02 kJ mol^{-1} for the *N*-et-gly one, respectively.

The rate constants for the epimerization are calculated from the equilibrium constant and the observed rate constant, k_{obsd}.

$$k_{obsd} = k_{RS} + k_{SR},$$

$$K_{eq} = k_{RS}/k_{SR}.$$

The k_{obsd} was obtained, using each of the two isomers as a starting substance, by the first-order kinetic study:

$$\ln X_e/(X_e - X_t) = k_{obsd} \cdot t,$$

where X_t and X_e stand for concentrations of the isomerized species at any time, *t*, and at equilibrium respectively. The values of k_{RS} and k_{SR}, therefore, were $(1.58\pm0.54)\times10^{-5}$ s^{-1} and $(1.11\pm0.39)\times10^{-5}$ s^{-1} for the sar complex, and $(0.96\pm0.45)\times10^{-5}$ s^{-1} and $(0.65\pm0.31)\times10^{-5}$ s^{-1} for the *N*-et-gly one, respectively.

Both the equilibrium and the kinetic results of the sar complex are in fair agreement with those of the *N*-et-gly one. This fact suggests that the thermodynamics and mechanisms of the isomerization process are little influenced by the size of the *N*-alkyl group on the asymmetric nitrogen atom. The $-\Delta G^\circ$ value of *ca.* 0.9 kJ mol^{-1} for the sar and *N*-et-gly complexes is consistent with that of 1.72 kJ mol^{-1} for the *trans, cis*(*RR*) and *trans,cis*(*SS*) isomers of dichlorobis((*S*)-2-(methylaminomethyl)pyrrolidine)cobalt(III),[26] having two asymmetric nitrogen atoms.

It is interesting to point out from the equilibrium constant value (*ca.* 1.45) that the *N*-alkyl group prefers the *S*(*N*) configuration to the *R*(*N*) one. Inspection of models for the *R*(*N*) and *S*(*N*) isomers of the sar and *N*-et-gly complexes reveal that the *N*-alkyl groups of the *R*(*N*) isomer are in more close proximity to the quadridentate moiety than that of the *S*(*N*) one. It is inferred, therefore, that the preference of the *S*(*N*) configuration over the *R*(*N*) one can be related to an interligand interactions between the *N*-alkyl group and the *S,S*-epro ligand.

Steric Interaction. It was reported that the coordinated *R*- or *S*-pipec have an intrinsic tendency for the stereoselective coordination and take the *S*(*N*), *R*(*C*) and *R*(*N*),*S*(*C*) configurations, respectively.[16,27,28] In the *Δ-sym*-[Co(*S,S*-epro)(pipec)] complex, however, the *R*-pipec takes the *R*(*N*),*R*(*C*) configuration and the, *S*-pipec takes the *S*(*N*),*S*(*C*) one. This selective coordination can be explained in terms of the interligand interaction between the piperidine ring of the pipecolate and the pyrrolidine ring of the *S,S*-epro ligand. Namely, an inspection of the models suggests that the order of the interligand crowd for the possible isomers of the *Δ-sym*-[Co(*S,S*-epro)(*R*- or *S*-pipec)] complex is *S*(*N*),*R*(*C*)>*R*(*N*),*S*(*C*)>*S*(*N*),*S*(*C*)>*R*(*N*),*R*(*C*). This

consideration is supported by X-ray analysis results which show that the *Λ-sym*-[Co(*S*,*S*-epro)(*R*-pipec)], which is the major product, takes the *R*(*N*),*R*(*C*) configuration.[29]

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