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Stereochemistry of *Λ-uns*-(2*S*,2*S*′)-1,1′-Trimethylenedipyrrolidine-2,2′-dicarboxylato Cobalt(III) Complexes with *N*-Alkyl Substituted Amino or Cyclic Imino Acids

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((2*S*,2*S*′-1,1′-Trimethylenedipyrrolidine-2,2′-dicarboxylato)(α-amino carboxylato)cobalt(III) complexes were prepared and characterized, where the α-amino carboxylate ligand is glycinate, (*R*)- or (*S*)-alaninate, (*R*)- or (*S*)-valinate, sarcosinate, *N*-ethylglycinate, (*R*)-prolinate, or (*S*)-pipecolate((*S*)-2-piperidinecarboxylate). Of the three possible isomers, only the *Λ-uns-mer* form was prepared for each of the complexes except for the glycinato complex. The (*R*)-prolinato and (*S*)-pipecolato complexes were stereoselectively prepared by using (*RS*)-proline or (*RS*)-pipecolic acid. The pipecolate ion coordinated selectively was assigned to *S*(*C*) configuration on the basis of the CD measurement of the 2,4-dinitrophenyl-pipecolic acid. The nitrogen atom of the sarcosinate, *N*-ethylglycinate, (*R*)-prolinate, or (*S*)-pipecolate ion, which coordinated stereoselectively to Co(III) ion, took the *R*(*N*) configuration. The stereoselectivity in this work was discussed on the basis of the electronic absorption, CD, and PMR spectra.

When the ethylenediamine-*N*,*N*′-diacetate ion (edda) coordinated to Co(III) ion to form [Co(edda)(am)]-type complex (am: α-amino carboxylate ion), the edda preferred to take a symmetric coordination rather than an unsymmetric one,[1–3] while the trimethylenediamine-*N*,*N*′-diacetate ion (tmdda) preferred the unsymmetric one.[4–6] It was assumed that the preference depends mainly on the probable conformation of the backbone diamine chelate ring of the linear O–N–N–O-type ligand.[4] The linear quadridentate ligand in this work, the (2*S*,2*S*′)-1,1′-trimethylenedipyrrolidine-2,2′-dicarboxylate ion (*S*,*S*-tmpro), has two chiral centers, *S*(*C*)*S*(*C*), and two pyrrolidine rings. By coordination to Co(III) ion, therefore, the possible configurations are regulated to only two, *Δ*-symmetric and *Λ*-unsymmetric. This is useful for investigations of the stereochemical preference of the quadridentate ligand and of the selective coordination of the bidentate ligand, α-amino carboxylate, for the remaining two coordination sites.

In the present paper, some aspects of the stereochemistry of the [Co(*S*,*S*-tmpro)(am)]-type complexes are dealt with, where am denotes glycinate, (*S*)- or (*R*)-alaninate, (*S*)- or (*R*)-valinate, (*R*)-prolinate, (*S*)-pipecolate ((*S*)-2-pipelidinecarboxylate, *S*-pipec), sarcosinate (sar), and *N*-ethylglycinate (*N*-et-gly). The *S*,*S*-tmpro complexes obtained have been characterized from their electronic absorption, CD, and PMR spectra. The stereoselective coordination of the *S*,*S*-tmpro and bidentate ligands are discussed in relation to the conformational preference and their steric interaction. The absolute configurations of the coordinated pipecolate ion and of the coordinated nitrogen atoms of the sar, *N*-et-gly, *R*-pro, and *S*-pipec were assigned by means of their CD and PMR spectra.

Experimental

1) Preparation of Ligands. (2*S*,2*S*′)-1,1′-Trimethylenedipyrrolidine-2,2′-dicarboxylic acid was prepared from (*S*)-proline and 1,3-dibromopropane according to the method of Schoenberg *et al.*[7] The needle crystals obtained were recrystallized from ethanol. Found: C, 39.74; H, 6.05; N, 7.05%. Calcd for $C_{13}H_{22}N_2O_4 \cdot 2NaCl \cdot 0.5H_2O$: C, 39.40; H, 5.86; N, 7.07%.

N-Ethylglycine was prepared by the ethylation of glycine using ethyl iodie.[8] Found: C, 34.77; H, 7.24; N, 10.12%. Calcd for $C_4H_9NO_2 \cdot HCl$; C, 34.41; H, 7.17; N, 10.04%.

2) Λ-uns-*Ba*[*Co*(S,S-*tmpro*)*Cl*(*OH*)]$_2 \cdot H_2O$. To a solution containing 1.6 g of tmpro$H_2 \cdot 2NaCl \cdot 0.5H_2O$ and 1.0 g of $CoCl_2 \cdot 6H_2O$ in 20 cm^3 of water was gradually added 1.0 g of PbO_2 by means of vigorous stirring at 65 °C for 10 min. The color of the solution changed from pale red to blue. The solution was cooled to room temperature and then filtered. The filtrate was poured into an anion-exchange column (Dowex 1-X8, 200—400 mesh, Cl^- form, 5×15 cm). The absorbed band was eluted with an 1 mol dm^{-3} $BaCl_2$ aqueous solution, and the eluate was evaporated to dryness. The complex was extracted from the solid with methanol, and the blue complex was obtained by the addition of ether. The complex was recrystallized from methanol by adding a small amount of ether. The CD spectral pattern in the visible region suggested that the *S*,*S*-tmpro has a *Λ-uns* form, but the geometrical arrangement with respect to Cl^- and OH^- is still unknown.

3) Λ-uns-[*Co*(S,S-*tmpro*)(*gly*)]. To the solution of *Λ-uns*-[Co(*S*,*S*-tmpro)Cl(OH)]$^-$ in *2)* was added a solution containing 0.3 g of glycine in 10 cm^3 of water. The pH of the solution was then adjusted to 7.0 by the addition of an 1 mol dm^{-3} NaOH aqueous solution. After the addition of a small amount of activated charcoal, to the mixture was added 1.0 g of PbO_2 at 65 °C for 30 min. The reaction solution was cooled to room temperature and then filtered. The filtrate was passed through the anion-exchange column as in *2)* in order to remove the unreacted anion, *Λ-uns*-[Co(*S*,*S*-tmpro)Cl(OH)]$^-$. The eluate was evaporated to a small volume with a rotary evaporator and then chromatographed on an anion-exchange column (QAE-Sephadex A-25, (*R*,*R*)-tartrate form, 3.5×85 cm). The adsorbed band was separated into five bands: yellow, violet, violet, violet, and red, in the order of elution, by eluting with water. The first yellow band contained cationic compounds, because it was adsorbed by a cation-exchange resin (SP-Sephadex C-25, Na^+ form). It was found, from the absorption and CD spectra, that the second band contained *Λ-uns-mer*-[Co(*S*,*S*-tmpro)(gly)]; the third one, *mer*-[Co(gly)$_3$]; the fourth one, *Λ-uns-fac*-[Co(*S*,*S*-tmpro)(gly)], and the fifth one, *fac*-[Co(gly)$_3$] (the earlier-eluted part of the fifth band consists of the *Δ-fac* isomer, and the later-eluted part, the *Λ-fac* isomer). The fourth band contained a very small amount of the complex in comparison

with the second band.

4) *Λ*-uns-mer-[*Co*(S,S-*tmpro*)(*gly*)]·H_2O. The second eluted band in *3)* was evaported to a small volume, and to the concentrated solution was added ethanol and then acetone. The solution was kept in a refrigerator overnight. The needle crystals thus precipitated were collected and recrystallized from water by the addition of ethanol and acetone. The pure crystals were collected, washed with ethanol and then ether, and dried in the air. Yield: 0.125 g.

5) *Λ*-uns-fac-[*Co*(S,S-*tmpro*)(*gly*)]·$3H_2O$. The fourth eluate in *3)* was evaporated to dryness. The violet solid was suspended in ethanol and collected by filtration. The crude complex was purified as in *4)*. Yield: 0.01 g.

6) *Λ*-uns-mer-[*Co*(S,S-*tmpro*)(S-*ala*)]·H_2O, [*Co*(S,S-*tmpro*)(R-*ala*)]·H_2O, [*Co*(S,S-*tmpro*)(S-*val*)]·H_2O, *and* [*Co*(S,S-*tmpro*)(R-*val*)]·H_2O. These complexes were prepared and isolated in the same method as that used for *Λ-uns-mer*-[Co(*S*,*S*-tmpro)(gly)]. The *Λ-uns-fac* isomer was not detected in these complexes.

7) *Λ*-uns-mer-[*Co*(S,S-*tmpro*)(*sar*)]. The complex was prepared by the same procedure as that used for [Co(*S*,*S*-tmpro)(gly)] using 0.37 g of sarcosine. The reaction mixture being passed through the columns (Dowex 1-X8 and SP-Sephadex C-25) in order to remove the negative and positive charged compounds was chromatographed on a column (QAE-Sephadex A-25, Cl^- form, 3.5×85 cm). The only band was eluted with water and fractionated into eight parts. It was found from their absorption and CD spectra that all eight fractions contained *Λ-uns-mer*-[Co(*S*,*S*-tmpro)(sar)]. Yield: 0.15 g.

8) *Λ*-uns-mer-[*Co*(S,S-*tmpro*)(N-*et-gly*)]·$0.5H_2O$. The complex was prepared and isolated using the same procedure as had been used for *Λ-uns-mer*-[Co(*S*,*S*-tmpro)(sar)]. Yield: 0.10 g.

9) *Attempt to Prepare* [*Co*(S,S-*tmpro*)(S-*pro*)]. The preparation of the [Co(*S*,*S*-tmpro)(*S*-pro)] was attempted by a procedure similar to that used for the glycinato complex, but using (*S*)-proline instead of glycine. After the removal of the charged compounds as in *7)*, a small amount of the violet complex was obtained. Chromatography behavior and the absorption and CD spectra showed that the eluate contained *mer*- and *fac*-[Co(*S*-pro)$_3$], while the desired [Co(*S*,*S*-tmpro)-(*S*-pro)] was not detected.

10) *Λ*-uns-mer-[*Co*(S,S-*tmpro*)(R-*pro*)]·$2.5H_2O$. This complex was prepared by the same procedure as that used for [Co(*S*,*S*-tmpro)(gly)] using 1 g of (*RS*)-proline. The reaction mixture having been removed the negative and positive charged compounds as in *7)* was chromatographed on the column (QAE-Sephadex A-25, Cl^- form). The complex was separated into three bands: blue-violet, violet, and red, in the order of elution. The absorption and CD spectra showed that the first adsorbed band contained *Λ-uns-mer*-[Co(*S*,*S*-tmpro)(*R*-pro)], and the second and third bands, *mer*- and *fac*-[Co(*RS*-pro)$_3$] respectively. The needle crystals were isolated from the first eluate by a procedure similar to that used for *4)*. Yield: 0.15 g. The complex was recrystallized from ethanol by adding ether and dried in a vacuum desiccator.

11) *Λ*-uns-mer-[*Co*(S,S-*tmpro*)(S-*pipec*)]·$0.5H_2O$. This complex was prepared and isolated by the same procedure as in *10)* using 0.60 g of (*RS*)-pipecolic acid. The complex was chromatographed on the column (QAE-Sephadex A-25, (*R*,*R*)-tartrate form); the CD spectra of the eight fractionated eluates were identical. The crude complex was recrystallized twice from an ethanol–methanol (1:1) mixture by the addition of ether without any change in the CD spectrum. Yield: 0.14 g. The absolute configuration of the coordinated (*R*)- and/or (*S*)-pipecolate ion was determined by the following method.

A solution containing 0.033 g of [Co(*S*,*S*-tmpro)(pipec)]·$0.5H_2O$ in 20 cm^3 of a 0.6 mol dm^{-3} $NaHCO_3$ aqueous solution was warmed at 55 °C. To the solution was added 6 cm^3 of a 0.1 mol dm^{-3} NaOH solution, whereupon the color of the solution immediately changed from blue-violet to colorless. The colorless solution was cooled to room temperature as soon as possible, neutralized by the addition of 6 mol dm^{-3} HCl, and then evaporated to dryness with a rotary evaporator. The pipecolic acid thus released was dinitrophenylated by the method reported by Yonetani *et al.*[9] The resulting dinitrophenylated pipecolic acid (DNP-pipec) showed the same CD spectrum as that of DNP-pipecolic acid described in the literature.[10] Thus, it was determined that the coordinated pipecolate ion has *S* configuration.

12) uns-mer-[*Co*(*tmdda*)(*sar*)]·$0.5H_2O$. This complex was prepared by the method described in a previous paper.[4] Only the *uns-mer* isomer was obtained, without the *uns-fac* one being formed.

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

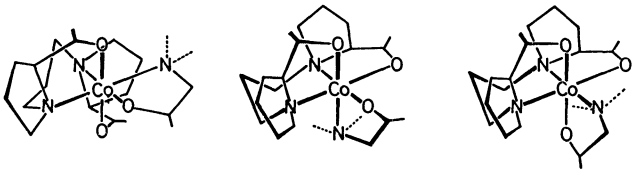
Measurements. The electronic absorption spectra were recorded with a JASCO UVIDEC-1 spectrophotometer, and the CD spectra, with a JASCO J-20 spectropolarimeter. The PMR spectra were recorded on a JEOL JNM-MH-100 NMR spectrometer at the probe temperature in a D_2O solvent. Sodium 2,2-dimethyl-2-silapentanesulfonate (DSS) was used as the internal reference.

Table 1. Elemental analyses (%)

Complex	C		H		N	
	Found	Calcd	Found	Calcd	Found	Calcd
Λ-uns-Ba[Co(*S*,*S*-tmpro)Cl(OH)]$_2$·H_2O	33.96	34.13	4.64	4.86	5.88	6.13
Λ-uns-mer-[Co(*S*,*S*-tmpro)(gly)]·H_2O	42.78	42.96	6.22	6.26	10.24	10.02
Λ-uns-fac-[Co(*S*,*S*-tmpro)(gly)]·$3H_2O$	39.41	39.56	6.22	6.65	9.21	9.23
Λ-uns-mer-[Co(*S*,*S*-tmpro)(*S*-ala)]·H_2O	44.67	44.33	6.55	6.53	9.99	9.70
Λ-uns-mer-[Co(*S*,*S*-tmpro)(*R*-ala)]·H_2O	44.02	44.33	6.32	6.53	9.85	9.70
Λ-uns-mer-[Co(*S*,*S*-tmpro)(*S*-val)]·H_2O	46.72	46.85	6.98	7.00	9.05	9.11
Λ-uns-mer-[Co(*S*,*S*-tmpro)(*R*-val)]·H_2O	46.36	46.85	6.84	7.00	9.26	9.11
Λ-uns-mer-[Co(*S*,*S*-tmpro)(sar)]	45.93	46.26	6.29	6.32	10.26	10.12
Λ-uns-mer-[Co(*S*,*S*-tmpro)(*N*-et-gly)]·$0.5H_2O$	46.67	46.60	6.54	6.68	9.62	9.59
Λ-uns-mer-[Co(*S*,*S*-tmpro)(*R*-pro)]·$2.5H_2O$	44.74	44.44	6.73	6.85	8.33	8.64
Λ-uns-mer-[Co(*S*,*S*-tmpro)(*S*-pipec)]·$0.5H_2O$	49.64	49.13	6.65	6.52	9.04	9.05
uns-mer-[Co(tmdda)(sar)]·$0.5H_2O$	35.07	34.89	5.44	5.57	12.17	12.21

Results and Discussion

Structural Assignments. The (2S,2S')-1,1'-trimethylenedipyrrolidine-2,2'-dicarboxylate anion is an O–N–N–O-type ligand similar to the trimethylenediamine-*N,N'*-diacetate anion,[4-6] while the *S,S*-tmpro has two chiral centers, (*S*(*C*) and *S*(*C*)), and two pyrrolidine rings. Accordingly, only three chiral configurations, *Δ-s*, *Λ-uns-fac*, and *Λ-uns-mer*, are possible for the [Co(*S,S*-tmpro)(am)] complex (Fig. 1).



(a) (b) (c)

Fig. 1. Three possible isomers of [Co(*S,S*-tmpro)(am)] type complex, (a) *Δ-s*, (b) *Λ-uns-fac*, and (c) *Λ-uns-mer*.

The absorption and CD spectral data of the isolated *S,S*-tmpro complexes are summarized in Tables 2 and 3, while the representative curves are shown in Figs. 2 and 3. Of the nine complexes in this work, only the glycinato complex gave two kinds of isomers, though the later-eluted glycinato isomer formed a trace amount. The absorption curves of the nine complexes resemble each other remarkably except for the later-eluted glycinato isomer, and their CD curves all show a positive

Table 2. Absorption data of *Λ-uns*-[Co(*S,S*-tmpro)(am)], *Λ-uns*-[Co(*S,S*-tmpro)Cl(OH)]$^-$, and *uns*-[Co(tmdda)(sar)]

Complex	First band	Second band	Charge-transfer band
mer-[Co(*S,S*-tmpro)(gly)]	18.18(2.20)	25.64(2.31)	41.32(4.26)
fac-[Co(*S,S*-tmpro)(gly)]	17.99(2.26)	25.38(2.25)	40.82(3.99)
mer-[Co(*S,S*-tmpro)(*S*-ala)]	18.21(2.22)	25.71(2.33)	41.49(4.29)
mer-[Co(*S,S*-tmpro)(*R*-ala)]	18.25(2.23)	25.77(2.33)	41.32(4.35)
mer-[Co(*S,S*-tmpro)(*S*-val)]	18.08(2.22)	25.58(2.34)	40.98(4.30)
mer-[Co(*S,S*-tmpro)(*R*-val)]	18.18(2.24)	25.71(2.33)	41.32(4.29)
mer-[Co(*S,S*-tmpro)(sar)]	17.86(2.25)	25.38(2.34)	40.65(4.27)
mer-[Co(*S,S*-tmpro)(*N*-et-gly)]	17.70(2.26)	25.32(2.34)	40.16(4.27)
mer-[Co(*S,S*-tmpro)(*R*-pro)]	17.89(2.22)	25.38(2.29)	40.32(4.27)
mer-[Co(*S,S*-tmpro)(*S*-pipec)]	17.86(2.28)	25.25(2.41)	39.84(4.44)
mer-[Co(tmdda)(sar)]	18.87(2.03)	26.46(2.21)	44.25(4.32)
[Co(*S,S*-tmpro)Cl(OH)]$^-$	17.18(2.22)	24.69(2.24)	39.68(4.15)

The wave numbers and log ε values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 cm^{-1} respectively.

Table 3. CD data of *Λ-uns*-[Co(*S,S*-tmpro)(am)] and *Λ-uns*-[Co(*S,S*-tmpro)Cl(OH)]$^-$

Complex	First-band region	Second-band region	Charge-transfer-band region
mer-[Co(*S,S*-tmpro)(gly)]	16.23(−1.05)	25.38(−1.80)	39.37(−16.49)
	18.38(+5.74)		42.02(sh)
fac-[Co(*S,S*-tmpro)(gly)]	18.12(+2.98)	25.38(−1.05)	40.98(−13.70)
mer-[Co(*S,S*-tmpro)(*S*-ala)]	16.23(−0.94)	25.38(−1.70)	39.06(−16.42)
	18.38(+6.01)		43.86(sh)
mer-[Co(*S,S*-tmpro)(*R*-ala)]	16.29(−1.05)	25.51(−1.90)	39.37(−15.34)
	18.52(+6.38)		43.86(sh)
mer-[Co(*S,S*-tmpro)(*S*-val)]	16.23(−1.43)	25.51(−1.88)	38.76(−18.22)
	18.32(+6.77)		44.64(− 9.76)
mer-[Co(*S,S*-tmpro)(*R*-val)]	16.10(−0.52)	25.51(−1.59)	41.32(−15.20)
	18.38(+6.40)		
mer-[Co(*S,S*-tmpro)(sar)]	16.18(−2.14)	25.13(−1.86)	38.17(−14.40)
	18.15(+5.40)		45.25(−12.52)
mer-[Co(*S,S*-tmpro)(*N*-et-gly)]	16.18(−2.31)	25.13(−1.67)	37.88(+12.58)
	18.12(+5.06)		45.25(−11.10)
mer-[Co(*S,S*-tmpro)(*R*-pro)]	16.16(−1.49)	25.13(−1.56)	37.88(−14.34)
	18.25(+4.37)		45.25(− 9.30)
mer-[Co(*S,S*-tmpro)(*S*-pipec)]	16.13(−1.94)	25.25(−1.80)	38.17(−13.36)
	18.12(+5.69)		45.05(−11.58)
[Co(*S,S*-tmpro)Cl(OH)]$^-$	15.63(−0.43)	24.27(−0.79)	39.68(−13.52)
	17.67(+4.18)		45.45(sh)

The wave numbers and $\Delta\varepsilon$ values (in parentheses) are given in 10^3 cm^{-1} and mol^{-1} dm^3 dm^{-1} respectively. Sh denotes the shoulder of the peak.

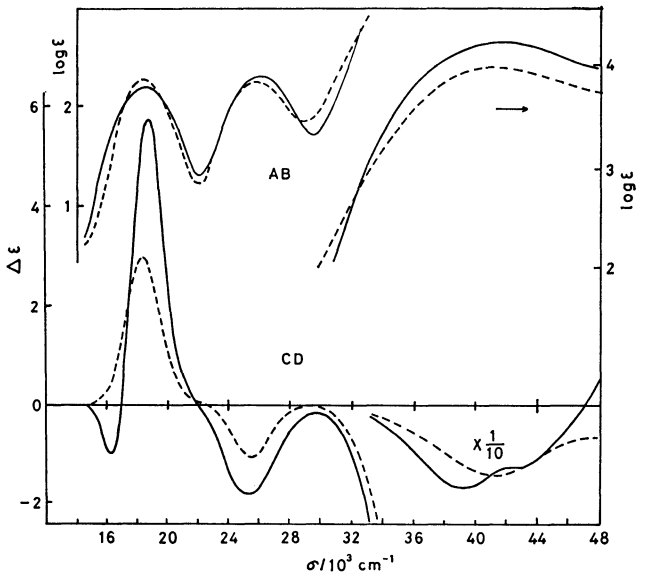


Fig 2. Absorption and CD spectra for the isomers of [Co(*S,S*-tmpro)(gly)], *Λ-uns-mer* (——) and *Λ-uns-fac* (----).

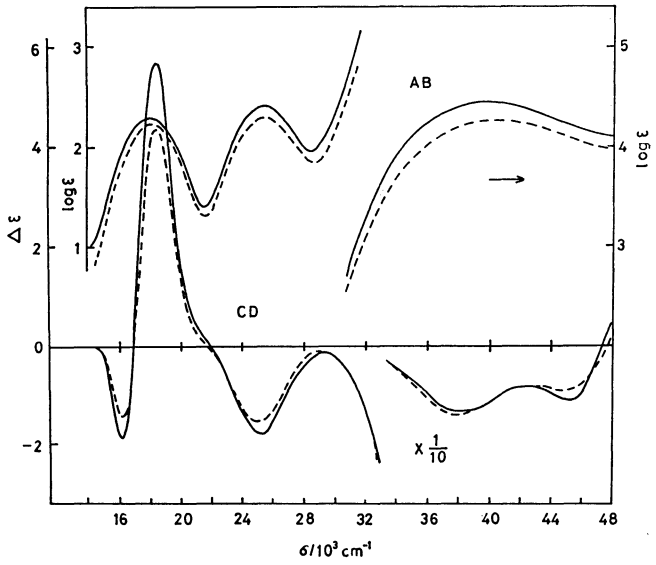


Fig. 3. Absorption and CD spectra of *Λ-uns-mer*-[Co(*S,S*-tmpro)(*R*-pro)] (——) and *Λ-uns-mer*-[Co(*S,S*-tmpro)(*S*-pipec)] (——).

dominant CD band in the first absorption band region, such as those of *Λ-uns-mer*-[Co(tmdda)(am)].[4] The later-eluted glycinato isomer, the absorption spectral pattern of which differs from those of the earlier-eluted isomer and the other eight complexes, also shows a positive dominant CD band in the corresponding region. This CD behavior suggests that all of the complexes isolated commonly take *Λ* configuration, namely, *Λ-uns-mer* or *Λ-uns-fac* (Fig. 1).

As is shown in Fig. 2, the first absorption band of the earlier-eluted glycinato isomer is broad, whereas that of the later one is sharp. These absorption spectral patterns indicate that the earlier-eluted isomer is *mer*(N_3O_3), and the later one, *fac*(N_3O_3).[11] The absorption spectra of the other complexes coincide with that of the earlier-eluted glycinato isomer (Figs. 2 and 3 and Table 2). Therefore, the later-eluted glycinato isomer is assigned to the *Λ-uns-fac* form, and the earlier-eluted isomer and the eight complexes, the *Λ-uns-mer* form.

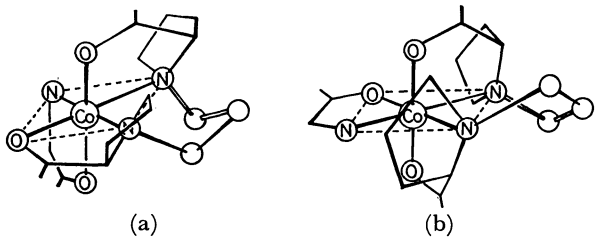


Fig. 4. Chair (a) and skew-boat (b) conformations for the trimethylenediamine chelate ring of *Λ-uns-mer*- and *Λ-s*-[Co(*S,S*-tmpro)(am)], respectively.

Stereospecificity. For all of the present complexes, the coordinated *S,S*-tmpro ligand takes the *Λ*-unsymmetric form. Furthermore, the CD spectrum of the starting complex, [Co(*S,S*-tmpro)Cl(OH)]$^-$, suggests that the chiral configuration is *Λ*-unsymmetric (Table 3). Molecular models reveal that the backbone trimethylenediamine ring of *S,S*-tmpro takes a symmetrical chair form for the *Λ*-unsymmetric coordination, while a skew-boat is most probable for the *Δ*-symmetric one (Fig. 4). From the present results, accordingly, it is possible to say that the *Λ*-unsymmetric preference of the *S,S*-tmpro depends mainly on the more stable conformation of the backbone trimethylenediamine ring.[12,13]

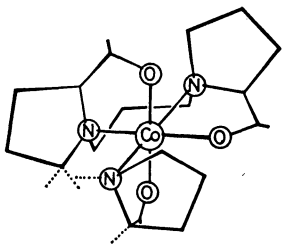


Fig. 5. Probable chiral configuration, *R*(*N*), of the (*R*)-prolinate ion in *Λ-uns-mer*-[Co(*S,S*-tmpro)(*R*-pro)].

The *Λ-uns-mer* and *Λ-uns-fac* isomers were obtained only for the glycinato complex. For both the sarcosinato and *N*-ethylglycinato complexes, however, the *mer* isomer was obtained, and no *fac* isomer was detected. It seems that this preference for the *Λ*-unsymmetric *mer* is attributable to the proximity between the *N*-alkyl group of the sarcosinate or *N*-ethylglycinate ring and the chair-conformed trimethylenediamine ring of the *S,S*-tmpro (Fig. 1). A similar trend was also observed for the [Co(tmdda)(sar)] complex (Tables 2 and 3). Another steric factor is found between the axial pyrrolidine ring of the *S,S*-tmpro and *N*-alkyl group of the bidentate ligand. A typical example of this interaction is found in the *Λ-uns-mer*-[Co(*S,S*-tmpro)(*S*-pro)] complex (Fig. 5). The prolinato complex could not be formed by using (*S*)-proline as the bidentate ligand, though the (*R*)-prolinato complex was selectively

formed, without the forming of the (*S*)-prolinato complex, by using (*RS*)-proline. This selectivity is due to the fact that the *N* atom of (*S*)-proline is regulated to the *S* configuration by coordinating to Co(III). That is, the *S*(*N*) coordination can not be realized in the *Λ-uns-mer S,S*-tmpro complex because of the proximity between the pyrrolidine rings of (*S*)-prolinate and *S,S*-tmpro (Fig. 5). In the *R*(*N*) coordination of (*R*)-prolinate, on the contrary, the pyrrolidine ring of the (*R*)-prolinate chelate avoids that of *S,S*-tmpro. A similar selectivity can also be expected for the pipecolato, sarcosinato, and *N*-ethylglycinato complexes of the *Λ*-unsymmetric configuration. The pipecolato complex, *Λ-uns-mer*-[Co(*S,S*-tmpro)(*S*-pipec)], was selectively prepared by using (*RS*)-pipecolic acid, as in the case of *Λ-uns-mer*-[Co(*S,S*-tmpro)(*R*-pro)]. The absolute configuration of the selected pipecolate ion was determined to be *S*(*C*) by the 2,4-dinitrophenyl (DNP) method.[9,10]

From model constructions, the order of the interligand crowd for the possible isomers of *Λ-uns-mer*-[Co(*S,S*-tmpro)(*R*- or *S*-pipec)] is $S(N)S(C) \gg S(N)R(C) > R(N)S(C) \approx R(N)R(C)$. Of the four isomers, the *R*(*N*)*S*(*C*) isomer is most probable for the pipecolato complex, since the *S*(*N*)*R*(*C*) and *R*(*N*)*R*(*C*) isomers are eliminated on the basis of the DNP method described above. In the $[Co(R\text{-pipec})(NH_3)_4]^+$ complex, the pipecolate ion coordinated to Co(III) with the *S*(*N*) configuration and the piperidine ring conformation took the chair form.[14] In the *Λ-uns-mer*-[Co(*S,S*-tmpro)(*S*-pipec)] complex, therefore, it is probable that the (*S*)-pipecolate ion coordinates to Co(III) to take the *R*(*N*) configuration. This suggests that the repulsion between the pyrrolidine ring and the chair-conformed piperidine one is relaxed by the *R*(*N*) preference of the pipecolate chelate.

The *R*(*N*) preference in the sarcosinato and *N*-ethylglycinato complexes is vague in comparison with that in the (*S*)-pipecolato one, and so their PMR spectra were measured in D_2O. The singlet (at 2.28 ppm) due to the *N*-methyl group is observed for the sarcosinato complex, and the triplet (at 1.32 ppm) due to the *N*-ethyl group for the *N*-ethylglycinato complex. These spectral patterns indicate that, for both of the complexes, the nitrogen atom of the bidentate ligand takes either the *R* or *S* configuration. However, no further information was obtained. In order to estimate the configuration of the nitrogen atoms of the complexes, the vicinal CD curves due to the nitrogen atom were estimated for the (*R*)-prolinato, (*S*)-pipecolato, sarcosinato, and *N*-ethylglycinato complexes, namely, $\Delta\varepsilon(R\text{-pro}) - \Delta\varepsilon(R\text{-val})$ for *R*-pro, $\Delta\varepsilon(S\text{-pipec}) - \Delta\varepsilon(S\text{-val})$ for *S*-pipec, $\Delta\varepsilon(\text{sar}) - \Delta\varepsilon(\text{gly})$ for sar, and $\Delta\varepsilon(N\text{-et-gly}) - \Delta\varepsilon(\text{gly})$ for *N*-et-gly (Fig. 6). The vicinal CD curves are quite similar to each other. These results suggest that the nitrogen atoms of the (*S*)-pipecolate, sarcosinate, and *N*-ethylglycinate ions of the *Λ-uns-mer* type

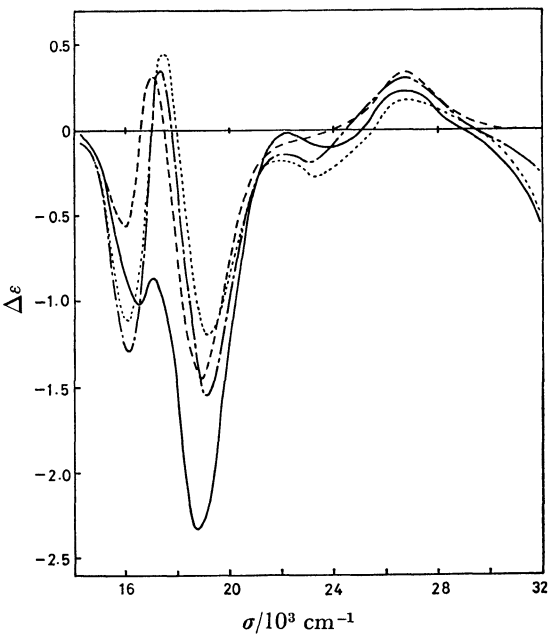


Fig. 6. Calculated vicinal CD curves of *Λ-uns-mer*-[Co(*S,S*-tmpro)(am)] complexes, *R*-pro (——), *S*-pipec (– – –) *N*-et-gly (–·–·–), and sar (------).

complexes coordinate selectively to Co(III) by means of the *R*(*N*) configuration.

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