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# Cobalt(III) Complexes with Tripodlike Quadridentate Ligands. I. Circular Dichroism Spectra of Quasi-enantiomeric Geometrical Isomers of [Co(tripod)(chiral bidentate)]-type Complexes

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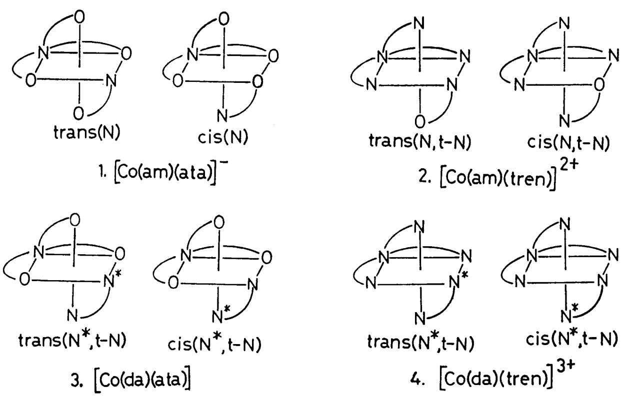
Cobalt(III) complexes containing a tripodlike quadridentate ligand, tris(2-aminoethyl)amine or nitrilotriacetate, and a chiral bidentate, L-amino carboxylate or (*R*)-propylenediamine, are prepared and separated into their respective geometrical isomers. The two geometrical isomers have mutually quasi-enantiomeric configurations. Circular dichroism spectra in the d-d absorption band region are discussed in connection with this novel type of geometrical isomerism.

Two geometrical isomers, *trans*(*N*) and *cis*(*N*), of (L-amino carboxylato)(nitrilotriacetato)cobaltate(III) ion [Co(L-am)(ata)]$^{-}$ [1)] which has been prepared by Koine *et al.*[2)] show vicinal CD (circular dichroism) due to the coordinated chiral amino carboxylate ligand in the d-d absorption band region. But it has remained puzzling why the intensity of vicinal CD is much stronger than those of other simple (L-amino carboxylato)cobalt(III) complexes which have no tripodlike quadridentate ligand.

The present paper deals with CD spectra of several mixed cobalt(III) complexes of a tripodlike quadridentate ligand, ata$^{3-}$ or tren[1)] and a chiral bidentate one, α-amino carboxylate or 1,2-diamine. For each of these complexes two geometrical isomers are possible, which are denoted as in Fig. 1.



1. [Co(am)(ata)]$^{-}$  2. [Co(am)(tren)]$^{2+}$  3. [Co(da)(ata)]  4. [Co(da)(tren)]$^{3+}$

Fig. 1. Two geometrical isomers of [Co(tripod)(chiral bidentate)]type complex: tripod=ata$^{3-}$ or tren, chiral bidentate=am$^{-}$ or da, and *N** and *t-N* mean the nitrogen atoms adjacent to the asymmetric carbon atom of the ligand and that of the tertiary amine of tripod ligand, respectively.

## Experimental

*Preparations.* *(1) [Co(*L*-ala)(tren)]$^{2+}$ Salts*: To a solution of [CoCl$_2$(tren)]ClO$_4$·0.5H$_2$O[3)] (1 g) in 10 cm$^3$ of water was added an aqueous solution of L-alanine (0.3 g) neutralized with an equimolar amount of NaOH and the mixture was mechanically stirred for 2 h at 60 °C. The resulting red solution was poured into a cation-exchanger column (SP Sephadex C-25, Na$^+$ form) and the adsorbed band was eluted with a 0.07 M NaCl aqueous solution (1 M=1 mol dm$^{-3}$). The band split into three; orange, red, and purple one in the elution order. The third band turned out to be a trivalent complex cation, [Co(tren)(H$_2$O)$_2$]$^{3+}$, from the absorption spectrum and the column chromatographic behavior. The first and second eluates were evaporated almost to dryness on a rotary evaporator below 40 °C. A small amount of methanol was added to the residue to precipitate NaCl, which was filtered off. The repetition of this procedure enabled one to remove most of the sodium chloride. On addition of NaClO$_4$ to the solution the chloride perchlorate salt (orange isomer) or perchlorate (red isomer) deposited. They were recrystallized from warm water, washed with methanol and ether and dried in air. Found for the orange isomer: C, 24.98; H, 5.69; N, 16.50%. Calcd for [Co(L-ala)(tren)]Cl·ClO$_4$: C, 25.25; H, 5.66; N, 16.36%. Found for the red isomer: C, 21.71; H, 5.01; N, 14.37%. Calcd for [Co(L-ala)(tren)](ClO$_4$)$_2$: C, 21.56; H, 5.04; N, 13.98%.

*(2) Other tren Complexes with Amino Carboxylate*: L-val, L-ser, L-phe, D-pgly, and L-cys complexes were prepared in the same way as that described in (1) using the corresponding amino carboxylate ligand instead of L-alaninate. Only orange isomer was isolated for these amino carboxylato complexes except for the L-cys one, for which only a brown isomer was isolated. Found for the L-val complex: C, 24.87; H, 5.50; N, 13.40%. Calcd for [Co(L-val)(tren)](ClO$_4$)$_2$: C, 25.39; H, 5.44; N, 13.46%. Found for the L-ser complex: C, 20.67; H, 5.06; N, 13.34%. Calcd for [Co(L-ser)(tren)](ClO$_4$)$_2$: C, 20.54; H, 4.99; N, 13.31%. Found for the L-phe complex: C, 31.80; H, 5.09; N, 12.51%. Calcd for [Co(L-phe)(tren)](ClO$_4$)$_2$: C, 31.70; H, 4.98; N, 12.33%. Found for the D-pgly complex: C, 30.63; H, 4.67; N, 12.81%. Calcd for [Co(D-pgly)(tren)](ClO$_4$)$_2$: C, 30.33; H, 4.74; N, 12.64%. Found for the L-cys complex: C, 25.04; H, 5.57; N, 16.10%. Calcd for [Co(L-cys)(tren)]ClO$_4$: C, 24.96; H, 5.60; N, 16.19%.

*(3) [Co(ata)(en)] and [Co(ata)(R-pn)]*: One gram of *cis*(*Cl*)-[CoCl$_2$(NH$_3$)$_2$(en)]Cl[4)] was dissolved in 10 cm$^3$ of water and to this blue solution was added a solution (5 cm$^3$) containing nitrilotriacetic acid (1 g) and NaOH (0.46 g) with stirring. The mixture was stirred for 4 h at 70 °C until the evolution of gaseous ammonia ceased. The resulting red-violet solution was then poured into a cation-exchanger column (Dowex 50w-x8, Na$^+$ form) and after the adsorbed band had been eluted with water, the red-violet eluate obtained was evaporated on a rotary evaporator and to the residue was added methanol to precipitate the complex as a powder. It was recrystallized from water, washed with methanol and ether and air-dried. Found: C, 29.63; H, 4.92; N, 12.98%. Calcd for [Co(ata)(en)]·H$_2$O: C, 29.54; H, 4.97; N, 12.92%.

The corresponding *R*-pn complex was prepared using *cis*(*Cl*)-[CoCl$_2$(NH$_3$)$_2$(*R*-pn)]Cl[4)] as a starting meterial. Found: C, 32.62; H, 5.18; N, 12.77%. Calcd for [Co(ata)-

($R$-pn)]$\cdot$0.5$H_2O$: C, 32.72; H, 5.20; N, 12.73%.

*(4) [Co(en)(tren)]$Br_3\cdot$0.5$H_2O$ and [Co(R-pn)(tren)]$Br_3$:* One gram of *cis*(*Cl*)-[$CoCl_2(NH_3)_2$(en)]Cl[4] was dissolved in 10 $cm^3$ of water and to the solution were added a small amount of activated charcoal and a solution (neutralized with NaOH) of tren$\cdot$3HBr (1.4 g) in 10 $cm^3$ of water. The mixture was mechanically stirred for 3 h at 60 °C until the color of the solution turned orange. The resulting mixture was then diluted to 50 $cm^3$ with water and the activated charcoal was filtered off by suction. The filtrate was evaporated in a rotary evaporator almost to dryness. The residue was dissolved in 5 $cm^3$ of water and NaBr (0.5 g) was added to the solution. Yellow crystals deposited were filtered and recrystallized from warm water, washed with methanol and ether and dried in air. For the $R$-pn complex *cis*(*Cl*)-[$CoCl_2(NH_3)_2$($R$-pn)]Cl[4] was used as a starting material. Found for the en complex: C, 18.41; H, 5.05; N, 15.96%. Calcd for [Co(en)(tren)]$Br_3\cdot$0.5$H_2O$: C, 18.69; H, 5.31; N, 16.35%. Found for the $R$-pn complex: C, 20.80; H, 5.50; N, 16.27%. Calcd for [Co($R$-pn)(tren)]$Br_3$: C, 20.82; H, 5.45; N, 16.19%.

*(5) Other Complexes:* The [Co(L-ala)(ata)]$^-$ (*trans*(*N*) and *cis*(*N*)) and [Co(L-ala)$(NH_3)_4$]$^{2+}$ complexes were prepared in the same way as described in the literature.[2,5]

*Measurements.* The visible and ultraviolet absorption measurements were made by a Shimadzu UV-200 spectrophotometer in aqueous solutions. The CD spectra were recorded on a JASCO MOE-1 spectropolarimeter in aqueous solutions and the $^1$H-NMR spectra were obtained in deuterium oxide on Varian XL-100-15 spectrometer using DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as as internal standard.

## Results and Discussion

*(1) [Co(am)(ata)]$^-$ Complexes.* The two isomers of [Co(L-ala)(ata)]$^-$, red-violet and blue-violet, have been assigned[2] to *trans*(*N*) and *cis*(*N*) structures, respectively, from the splitting pattern of the first d-d absorption band. A remarkable feature is observed in the CD curves of two isomers (Fig. 2); namely they are almost enantiomeric to each other in the d-d transition band region. This is probably related to the fact that the two geometrical isomers are mutually quasi-enantiomeric as is seen in Fig. 3. The CD curves in Fig. 2 are explained by the contributions from two kinds of chiralities, one being the ($S$) asymmetric carbon atom of the L-alaninate ligand and the other the quasi-enantiomeric orientation of substituent $-CH_3$ on the chelate ring.

On assumption that the CD contributions of both chiralities are additive, the following equations are obtained.

$$\mathrm{CD}[\text{red-violet}] = \mathrm{CD}[S] + \mathrm{CD}[\textit{trans}],$$

$$\mathrm{CD}[\text{blue-violet}] = \mathrm{CD}[S] + \mathrm{CD}[\textit{cis}],$$

and

$$\mathrm{CD}[\textit{trans}] = -\mathrm{CD}[\textit{cis}],$$

where CD[$S$] represents the contributions of ($S$) asymmetric carbon, and CD[*trans*] and CD[*cis*] those of the quasi-enantiomeric geometrical configuration. Two contributions, CD[$S$] and CD[*trans*] were calculated rom the equations,

$$\mathrm{CD}[S] = 1/2\{\mathrm{CD}[\text{red-violet}] + \mathrm{CD}[\text{blue-violet}]\},$$

$$\mathrm{CD}[\textit{trans}] = -\mathrm{CD}[\textit{cis}]$$

$$= 1/2\{\mathrm{CD}[\text{red-violet}] - \mathrm{CD}[\text{blue-violet}]\}.$$

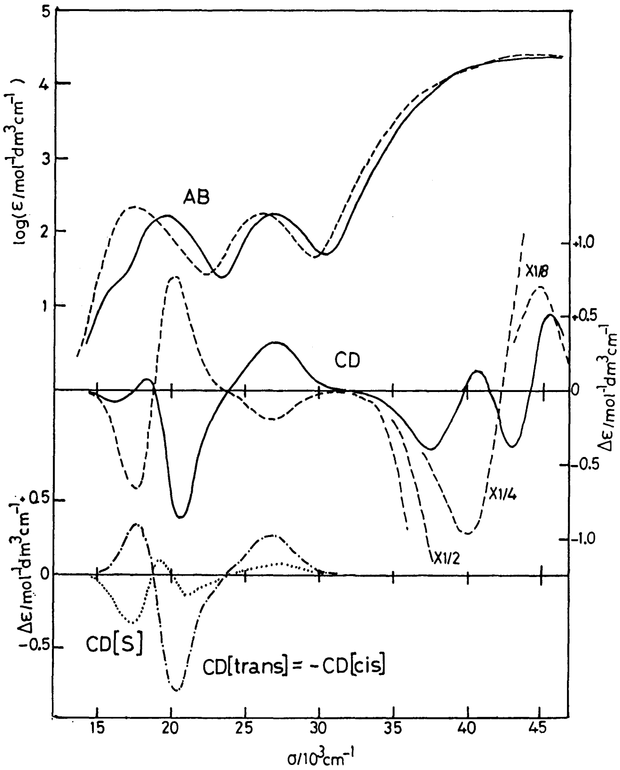
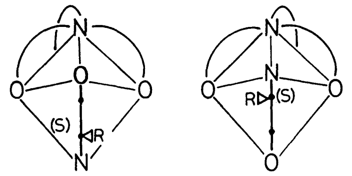


Fig. 2. Absorption (AB) and CD curves of *trans*(*N*) (——) and *cis*(*N*) (------) isomers of [Co(L-ala)(ata)]$^-$. Caclulated CD curves for asymmetric carbon (····) and quasi-enantiomeric (-·-·-) effects are also shown.



trans(N) cis(N)

Fig. 3. Two quasi-enantiomeric geometrical isomers of [Co(am)(ata)]$^-$. ($S$) denotes absolute configuration of the asymmetric carbon.

The obtained curves are also illustrated in Fig. 2. The CD[$S$] curve consists of three extrema (−, +, and −) from the longer wavelength side in the first d-d transition band region and the pattern and intensity are similar to the vicinal effect curve of the L-alaninate ligand in *trans*(*N*)-[Co(ox)(L-ala)$_2$]$^-$.[6] The CD[*trans*] curve shows two (+ and −) and one (+) component in the first and second d-d transition band region, respectively, and the contribution of CD[*trans*] or CD[*cis*] to the observed CD is larger than that of CD[$S$], the pattern of the observed CD being mainly determined by the quasi-enantiomeric effect.

*(2) [Co(am)(tren)]$^{2+}$ Complexes.* Kimura *et al.*[7] prepared tren complexes with amino carboxylate ligands and isolated two isomers, orange and red, of [Co(gly)(tren)]$^{2+}$. Recently it has been found from the X-ray crystal structure analyses that the orange isomer has *trans*(*N,t-N*) structure and the red one *cis*(*N,t-N*).[8] Two isomers, orange and red, of the L-alaninato complex show absorption spectra analogous to those

TABLE 1. ABSORPTION DATA OF [Co(tripod)(bidentate)]-TYPE COMPLEXES
(Wave numbers and log $\varepsilon$ values (in parentheses) are given in $10^3$ cm$^{-1}$ and mol$^{-1}$ dm$^3$ cm$^{-1}$, respectively.)

| Complex | d-d Tansition band | | Ultraviolet band | |
|---|---|---|---|---|
| | 1st | 2nd | | |
| *trans*(*N*)-[Co(L-ala)(ata)]$^-$ | 16 sh(1.3)<br>19.6(2.22) | 26.8(2.24) | 46.7(4.35) | |
| *cis*(*N*)-[Co(L-ala)(ata)]$^-$ | 17.5(2.34) | 26.1(2.24) | 46.3(4.37) | |
| *trans*(*N*,*t*-*N*)-[Co(gly)(tren)]$^{2+}$ b) | 21.2(2.01) | 29.2(2.00) | | |
| *cis*(*N*,*t*-*N*)-[Co(gly)(tren)]$^{2+}$ b) | 20.0(1.96) | 28.8(1.88) | | |
| *trans*(*N*,*t*-*N*)-[Co(L-ala)(tren)]$^{2+}$ | 21.2(2.08) | 28.9(2.03) | 44.4(4.29) | |
| *cis*(*N*,*t*-*N*)-[Co(L-ala)(tren)]$^{2+}$ | 19.9(2.06) | 28.6(2.01) | 44.1(4.27) | |
| *trans*(*N*,*t*-*N*)-[Co(L-val)(tren)]$^{2+}$ | 21.1(2.09) | 28.9(2.04) | 44.4(4.28) | |
| *trans*(*N*,*t*-*N*)-[Co(L-ser)(tren)]$^{2+}$ | 21.1(2.07) | 28.9(2 03) | 44.6(4.27) | |
| *trans*(*N*,*t*-*N*)-[Co(L-phe)(tren)]$^{2+}$ | 21.2(2.09) | 29.2(2 05) | 46.8(4.35) | |
| *trans*(*N*,*t*-*N*)-[Co(D-pgly)(tren)]$^{2+}$ | 21.1(2.16) | 29 sh(2.1) | 47.6(4.34) | |
| *trans*(*N*,*t*-*N*)-[Co(L-cys)(tren)]$^{2+}$ | 16.5 sh(1.3)<br>20.7(2.15) | 26.5 sh(2.4) | 34.7(4.28) | 47(4.09) |
| [Co(en)(tren)]$^{3+}$ | 21.4(2.04) | 29.6(1.98) | 45.5(4.27) | |
| [Co(*R*-pn)(tren)]$^{3+}$ | 21.3(2.06) | 29.6(2.00) | 45 sh(4.3) | 49.5(4.47) |
| [Co(ata)(en)] | 17 sh<br>19.1(2.19) | 27.3(2.25) | 44.5(4.33) | |
| [Co(ata)(*R*-pn)] | 16.5 sh<br>19.2(2.21) | 27.4(2.27) | 44.7(4.34) | |

a) sh=Shoulder. b) Ref. 7.

TABLE 2. CD DATA OF [Co(tripod)(bidentate)]-TYPE COMPLEXES
(Wave numbers and $\Delta\varepsilon$ values (in parentheses) are given in $10^3$ cm$^{-1}$ and mol$^{-1}$ dm$^3$ cm$^{-1}$, respectively.)

| Complex | d-d Transition band | | Ultraviolet band |
|---|---|---|---|
| | 1st | 2nd | |
| *trans*(*N*)-[Co(L-ala)(ata)]$^-$ | 16.1(−0.083)<br>18.4(+0.080)<br>20.6(−0.863) | 27.0(+0.325) | 37.6(−0.40)<br>40.7(+0.12)<br>42.9(−0.40)<br>45.5(+0.52) |
| *cis*(*N*)-[Co(L-ala)(ata)]$^-$ | 17.5(−0.669)<br>20.3(+0.763) | 26.7(−0.202) | 40.0(−3.76)<br>44.8(+5.6) |
| *trans*(*N*,*t*-*N*)-[Co(L-ala)(tren)]$^{2+}$ | 19.5(+0.194)<br>21.8(−0.657) | 29.0(+0.118) | 39.4(−1.17)<br>46.3(+0.57)<br>49.3(−0.55) |
| *cis*(*N*,*t*-*N*)-[Co(L-ala)(tren)]$^{2+}$ | 18.8(−0.160)<br>20.9(+0.267) | 26(−0.05)<br>29.0(−0.122) | 39.4(−0.66)<br>43.9(+0.8)<br>48.2(−1.11) |
| *trans*(*N*,*t*-*N*)-[Co(L-val)(tren)]$^{2+}$ | 19.4(+0.215)<br>21.7(−0.820) | 29.0(+0.149) | 39.5(−2.15) |
| *trans*(*N*,*t*-*N*)-[Co(L-ser)(tren)]$^{2+}$ | 18.7(+0.020)<br>21.5(−0.603) | 29.0(+0.077) | 40.0(−1.36) |
| *trans*(*N*,*t*-*N*)-[Co(L-phe)(tren)]$^{2+}$ | 19.5(+0.062)<br>21.9(−0.367) | 29.3(+0.055) | 37.5(−0.70) |
| *trans*(*N*,*t*-*N*)-[Co(D-pgly)(tren)]$^{2+}$ | 19.0(−0.125)<br>21.7(+1.685) | 29.0(−0.180) | 39.1(+3.44)<br>44.2(−4.75) |
| *trans*(*N*,*t*-*N*)-[Co(L-cys)(tren)]$^{+}$ | 17.0(+0.116)<br>18.7(−0.016)<br>21.3(+0.744) | 25.6(−0.787) | 34.8(−5.6)<br>39.5(+1.5)<br>45 (+4.2)<br>48.5(+6.3) |
| [Co(*R*-pn)(tren)]$^{3+}$ | 19.7(−0.225)<br>22.1(+0.397) | 28.7(−0.138) | 44.8(+4.1) |
| [Co(ata)(*R*-pn)] | 17.4(+0.059)<br>19.2(−0.043)<br>21.4(+0.228) | 27.6(−0.134) | 46.1(+4.2) |

of the corresponding orange and red isomers of the glycinato complex, respectively (Table 1). Therefore, the orange isomer is *trans*(*N*,*t*-*N*) and the red *cis*(*N*,*t*-*N*). Though a pair of isomers, red-violet and blue-violet, were also isolated for each ata complex with the other amino carboxylates,[2] only orange isomer was obtained for each tren complex with L-val, L-ser, L-phe, and D-pgly. A series of hydrolysis studies[9] on [CoCl$_2$(tren)]$^+$ suggested that steric hindrance of hydrogen atoms on the aminoethyl chelate ring makes the chloro ligand *cis* to the tertiary amine more labile, and X-ray crystal structure analyses of the two isomers of [Co(gly)(tren)]$^{2+}$ showed that unfavorable non-bonded interactions between the amino protons of the glycinate ring and the adjacent protons on the carbon and nitrogen atoms of tren make the *cis*(*N*,*t*-*N*) structure (red isomer) unstable[8] In fact, the formation ratio of the red isomer to the orange one was rather low for the tren complex with L-alaninate. Instability of the red isomer seems to increase with an increase in the bulkiness of a substituent on the amino carboxylate chelate ring. All orange isomers obtained have *trans*(*N*,*t*-*N*) structure from the same reason as that described for the L-alaninate complex. All these *trans*(*N*,*t*-*N*) isomers have similar CD patterns (+ and −) from the longer wavelength side in the first d-d transition band region, except for the D-pgly isomer, which shows the opposite sign pattern (− and +) (Table 2).

The two isomers of [Co(L-ala)(tren)]$^{2+}$ show almost enantiomeric CD in the d-d transition band region (Fig. 4). On the basis of the same assumption as that for the ata complex, the CD contributions of (*S*) asymmetric carbon and the quasi-enantiomeric chirality were separated. The calculated CD contribution of the latter chirality is comparable in intensity to that of the former (Fig. 4). The pattern of the CD[*trans*(*N*,*t*-*N*)] is analogous to that of the CD[*trans*] for the ata complex; *i.e.*, two (+ and −) and one (+) components are present in the first and second d-d transition band region, respectively. The asymmetric carbon contribution CD[*S*] well coincides with the observed CD of the [Co(L-ala)(NH$_3$)$_4$]$^{2+}$ in the first band region (Fig. 4).

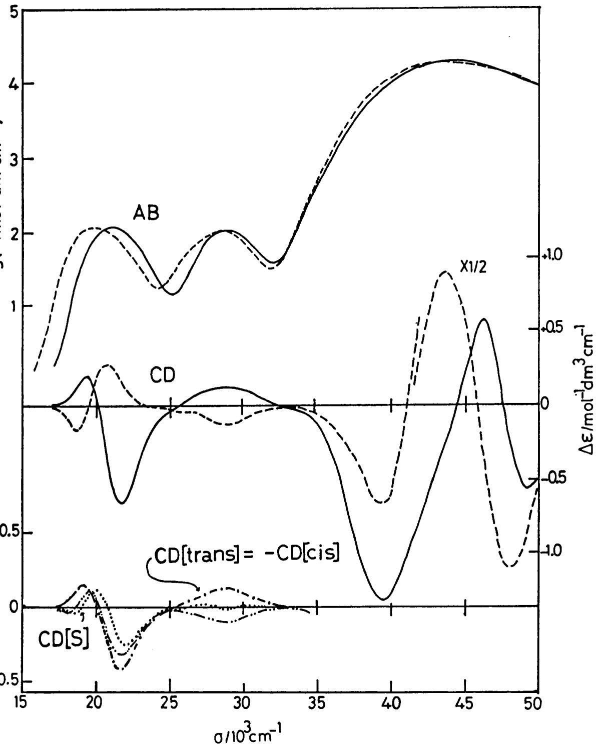


Fig. 4. Absorption (AB) and CD curves of *trans*(*N*,*t*-*N*) (——) and *cis*(*N*, *t*-*N*) (------) isomers of [Co(L-ala)(tren)]$^{2+}$. Calculated CD curves for asymmetric carbon (····) and quasi-enantiomeric (-·-·-) effects are also shown. Another asymmetric carbon effect curve (-······-) is the observed one for [Co(L-ala)(NH$_3$)$_4$]$^{2+}$ complex.

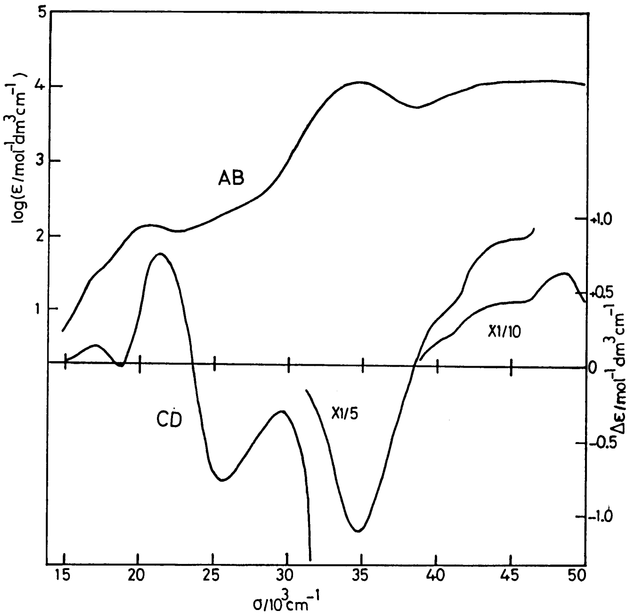


Fig. 5. Absorption (AB) and CD curves of *trans*(*N*, *t*-*N*)-[Co(L-cys)(tren)]$^+$ complex.

The L-cysteinate complex is in a complicated situation. When L-cysteinate coordinates through the N and O donors, the α-substituent $-CH_2S^-$ is directed at the same side as in the other L-amino carboxylate complexes (Fig. 3), but when it does through N and S donors, the substituent $-CO_2^-$ is at the opposite side. Jackson *et al.*[10] first prepared two isomers, brown and ink-blue, of [Co(L-cys)(tren)]$^+$ with N and S donors and assigned those to *trans*(*N*,*t*-*N*) and *cis*(*N*,*t*-*N*) structures, respectively, from their absorption, $^1$H- and $^{13}$C-nuclear magnetic resonance spectra. In the present work only the brown isomer, *trans*(*N*,*t*-*N*), was isolated, which showed a CD pattern enantiomeric to the L-alaninate complex of *trans*(*N*,*t*-*N*) structure in accordance with the *N*,*S*-coordination of L-cys ligand (Fig. 5).

*(3) [Co(da)(ata)] Complexes.* For en and *R*-pn, each only one complex of this type was prepared. The absorption spectrum of the *R*-pn complex was very similar to that of the en complex, having a broad first d-d band in agreement with the *mer*-CoN$_3$O$_3$ chromophore (Fig. 6 and Table 1). As the donor atoms at each end of *R*-pn have almost the same ligand-field strength, the discrimination of the two isomers, *trans*(*N**,*t*-*N*) and *cis*(*N**,*t*-*N*) in Fig. 1, is impossible only from the absorption spectra, in contrast to the case of amino carboxylate complex. In order to examine whether the isolated crystals contain only one isomer or both, the $^1$H-NMR spectrum was measured.

It was found that the *R*-pn complex revealed two methyl doublets with about the same intensity (Fig. 7-a). Thus the complex is a 1 : 1 mixture of two isomers, *trans*(*N**,*t*-*N*) and *cis*(*N**,*t*-*N*), which are quasi-enantiomeric geometrical isomers (Fig. 8). If the same argument as that described for the L-ala complex is

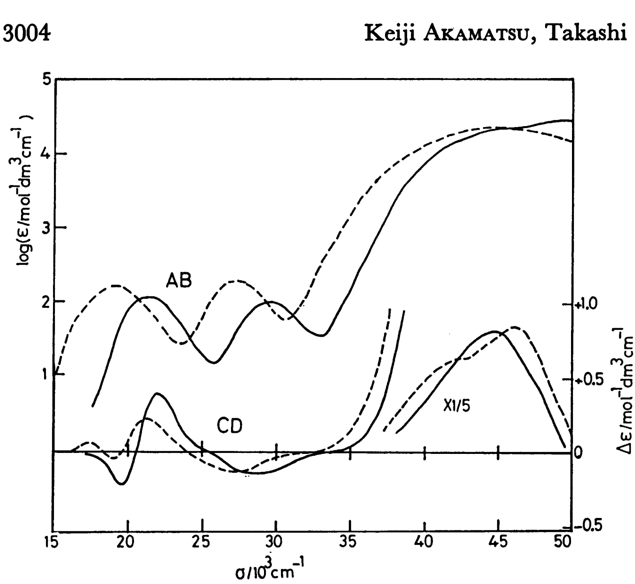


Fig. 6. Absorption (AB) and CD curves of [Co(ata)(*R*-pn)] (------) and [Co(*R*-pn)(tren)]$^{3+}$ (——).

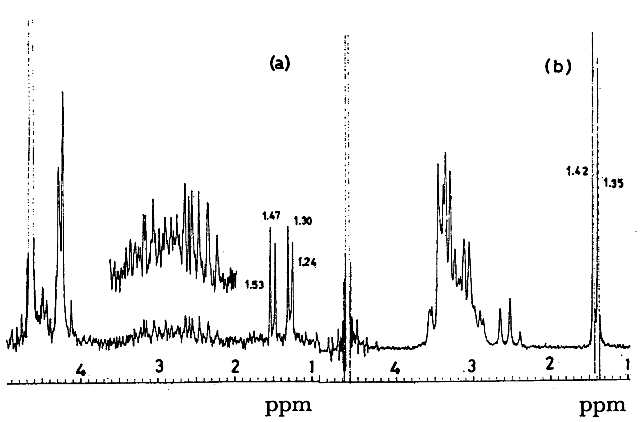


Fig. 7. $^1$H-NMR spectra of (a) [Co(ata)(*R*-pn)] and (b) [Co(*R*-pn)(tren)]$^{3+}$.

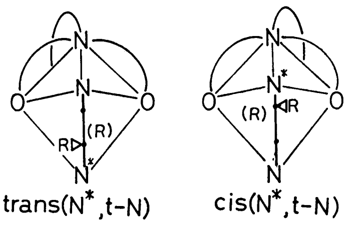


Fig. 8. Two quasi-enantiomeric geometrical isomers of [Co(ata)(*R*-pn)]. (*R*) denotes absolute configuration of the asymmetric carbon.

applicable to the *R*-pn complex, the observed CD curve (Fig. 6) should approximately correspond to a CD contribution CD[*R*], which contains two contributions, from (*R*) asymmetric carbon and λ-gauche conformation of the chelate ring.[11] In spite of a difference in the type of chromophore, the CD[*R*] contribution curve in Fig. 6 is roughly enantiomeric to the CD[*S*] curve of [Co(L-ala)(ata)]$^-$ (Fig. 2) or [Co(L-ala)(tren)]$^{2+}$ (Fig. 4) in the first and second d-d transition band region.

*(4) [Co(da)(tren)]$^{3+}$ Complexes.* Also in this case, only one complex was prepared for every 1,2-diamine (en or *R*-pn).

These complexes have a $CoN_6$ chromophore and their absorption spectra (Table 1) closely resembled that of [Co(en)$_3$]$^{3+}$ in regard to the position, intensity and half-width of the first d-d transition band. This indicates that the tripodlike ligand, tren, has about the same ligand-field strength as that of two en ligands. The $^1$H-NMR spectrum of the [Co(*R*-pn)(tren)]$^{3+}$ complex showed only one methyl doublet (Fig. 7-b). Thus the complex consists of only one isomer, *trans*(*N**,*t*-*N*) or *cis*(*N**,*t*-*N*) in Fig. 1. Both isomers have unfavorable non-bonded interactions among the protons on the *R*-pn nitrogen atoms and on the carbon and nitrogen atoms of the tren. However, concerning the orientation of the substituent $-CH_3$, steric crowding in the *trans*(*N**,*t*-*N*) structure is less unfavorable than that in *cis*(*N**,*t*-*N*); thus the only one isomer obtained is assigned to *trans*-(*N**,*t*-*N*). Therefore, its CD curve (Fig. 6) consists of two contributions, one from CD[*R*] and the other CD[*trans*(*N**,*t*-*N*)]. Though the pattern of the observed CD for [Co(*R*-pn)(tren)]$^{3+}$ complex is similar to that for [Co(*R*-pn)(NH$_3$)$_4$]$^{3+}$, which has no quasi-enantiomeric effect and shows two (− and +) and one (−) component in the first and second d-d transition band region, respectively,[11] the intensity of the tren complex is much larger than that of the tetraammine complex. The subtraction of the CD curve for the tetraammine complex from that for the tren complex is expected to give an approximate CD[*trans*(*N**,*t*-*N*)] contribution. The pattern of this CD contribution in the first and second d-d transition band region is analogous to that of CD[*R*] and the intensity for the CD[*trans*(*N**,*t*-*N*)] is smaller than that for CD[*R*].

*(5) Conclusion.* The CD spectral data described above lead one to the following conclusion: 1. CD patterns of the [Co(L-am)(ata)]$^-$ or [Co(L-am)(tren)]$^{2+}$ complexes in the d-d band region are governed by the "vicinal effect" of amino carboxylate ligands, which consists of two contributions, the asymmetric carbon effect and the quasi-enantiomeric effect, the latter being dominant. 2. The *trans*(*N*) or *trans*(*N*,*t*-*N*) isomer shows two (+ and −) or three (−, + and −) CD components in the first d-d band region, and one (+) component in the second, while the *cis*(*N*) or *cis*(*N*,*t*-*N*) isomer shows two (− and +) and one (−) component in the first and second band region, respectively. 3. The CD patterns of this type of complex are not affected from the varieties of the first coordination spheres or chromophore (for example, the two isomers of the ata complex belong to *trans*- and *cis*-$CoN_2O_4$ chromophore and those of the tren complex $CoN_5O$). 4. For the corresponding *R*-pn complexes, the quasi-enantiomeric effect has a sign opposite to that for the L-ala complexes because the substituent $-CH_3$ is at the opposite side.

## References

1) Abbreviations of ligands: L-ala = L-alaninate, am = amino carboxylate, ata = nitrilotriacetate, L-cys = L-cysteinate(2-), da = 1,2-diamine, en = ethylenediamine, gly = glycinate, L-phe = L-phenylalaninate, D-pgly = D-phenylglycinate, L-ser = L-serinate, *R*-pn = (*R*)-propylenediamine, tren = tris(2-aminoethyl)amine, and tripod = tripodlike quadridentate.

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