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# Stereochemistry of Cobalt(III) Complexes with Thioethers. II.[1] Geometrical Isomers, Absorption, and Circular Dichroism Spectra of Bis(terdentate-*N,S,O*) Complexes

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Two cobalt(III) complexes containing terdentate thioethers, bis[(2-aminoethylthio)acetato]cobalt(III)(1+), and bis[3-(2-aminoethylthio)propionato]cobalt(III)(1+) were prepared and separated into five and six geometrical isomers, respectively, by ion-exchange column chromatography. The isomers were identified on the basis of their electronic absorption and NMR spectra. The circular dichroism spectra of optically resolved isomers were measured and discussed in relation to the absolute configurations.

Some cobalt(III) complexes with multidentate thioether ligands have so far been reported.[2–15] It appears that the presence of thioether donor atoms induces an extreme specificity concerning the formation of geometrical isomers.[6–9] As an example, of the bis(terdentate) type cobalt(III) complexes with linear terdentate ligands having the donor atom sequence N–S–N[11,14] or O–S–O,[15] only one or two geometrical isomers of three possible ones have been isolated. Recently, a bis(L-methioninato)cobalt(III) complex[11] of the $[Co(N)_2(O)_2(S)_2]$ type has been prepared and its three geometrical isomers obtained. The complex is the first example for the isolation of all the possible isomers of a complex with multidentate thioethers.

In the present work, two linear terdentate ligands having the donor atom sequence N–S–O, (2-aminoethylthio)acetic acid (Haeta$=NH_2CH_2CH_2SCH_2CO_2H$) and 3-(2-aminoethylthio)propionic acid (Haetp$=NH_2CH_2CH_2SCH_2CH_2CO_2H$), were used, and the absorption and circular dichroism (CD) spectra of their cobalt(III) complexes studied. For the bis(terdentate-*N,S,O*) type cobalt(III) complexes, six geometrical isomers are possible. So far no report seems to have appeared with respect to the isolation of six geometrical isomers of such [Co(A–B–C)$_2$] type complex, though two isomers of $[Co(aeta)_2]^+$ have recently been reported.[16]

## Experimental

*Preparation, Separation, and Optical Resolution of the Complexes. (1) Bis[(2-aminoethylthio)acetato]cobalt(III) Chloride, [Co(aeta)$_2$]Cl:* To a hot solution (*ca.* 70 °C) of 9 g cobalt(II) chloride hexahydrate in 80 cm$^3$ of water was added a solution of 9.35 g of (2-aminoethylthio)acetic acid hemihydrochloride[1] and 1.51 g of sodium hydroxide dissolved in 80 cm$^3$ of water. Fifteen grams of $PbO_2$ was gradually added to the mixed solution on a water bath, whereupon the solution turned violet. The mixture was stirred at 70 °C for *ca.* 40 min. The reaction mixture was filtered in order to remove excess lead dioxide after being cooled to room temperature. A considerable amount of brownish violet precipitate appeared which was filtered off.

The filtrate was poured into an ion exchange column containing Dowex 50 W×8 resin (200—400 mesh, Na$^+$ form, 4.5×40 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.15 M aqueous solution of NaCl at the rate of 1 cm$^3$ per min. Five colored bands, brownish violet (A-1), purple (A-2), red (A-3), another red (A-4), and reddish purple (A-5), were eluted in this order. The eluates of these bands were separately concentrated in a vacuum evaporator and then the deposit, NaCl, was filtered off. To each of the filtrates was added a large amount of ethanol. The complexes thus obtained were crystallized from a minimum quantity of water by adding ethanol and then acetone, and dried in a vacuum desiccator over $CaCl_2$. The isomers were obtained in comparable yields, except for A-2 which showed a somewhat higher yield. Found for A-1: C, 25.76; H, 4.44; N, 7.71%. Calcd for $[Co(aeta)_2]Cl=C_8H_{16}N_2S_2O_4ClCo$: C, 26.49; H, 4.45; N, 7.72%. Found for A-2: C, 26.28; H, 4.62; N, 7.82%. Calcd for $[Co(aeta)_2]Cl=C_8H_{16}N_2S_2O_4ClCo$: C, 26.49; H, 4.45; N, 7.72%. Found for A-3: C, 25.04; H, 4.83; N, 7.81%. Calcd for $[Co(aeta)_2]Cl\cdot H_2O=C_8H_{18}N_2S_2O_5ClCo$: C, 25.24; H, 4.77; N, 7.36%. Found for A-4: C, 24.46; H, 5.10; N, 7.56%. Calcd for $[Co(aeta)_2]Cl\cdot 1.5H_2O=C_8H_{19}N_2S_2O_{5.5}ClCo$: C, 24.65; H, 4.91; N, 7.15%. Found for A-5: C, 24.80; H, 4.85; N, 7.75%. Calcd for $[Co(aeta)_2]Cl\cdot H_2O=C_8H_{18}N_2S_2O_5ClCo$: C, 25.24; H, 4.77; N, 7.36%.

Of the five isomers, four except A-1 were optically resolved.

*A-2, $(-)_{589}$-[Co(aeta)$_2$]Cl,* (trans(O)): This isomer was resolved by using $(-)_{589}$-K[Co(edta)]·2H$_2$O as a resolving agent. The racemic chloride (0.36 g) and the resolving agent (0.21 g) were dissolved in 2 cm$^3$ of water at 40 °C. After being cooled to room temperature, the mixed solution was allowed to stand overnight in a refrigerator. A small amount of less soluble diastereomer was deposited as violet needles and recrystallized from a minimum quantity of water. The yield was 0.25 grams. Found: C, 27.91; H, 4.87; N, 7.33%. Calcd for $(-)_{589}$-$[Co(aeta)_2][Co(edta)]\cdot 5H_2O=C_{18}H_{38}N_4S_2O_{17}Co_2$: C, 28.28; H, 5.01; N, 7.33%.

Optically active chloride was obtained from the diastereomer by using an anion exchange resin (Dowex 1×8, Cl$^-$ form). Found: C, 26.23; H, 4.49; N, 7.71%. Calcd for $(-)_{589}$-$[Co(aeta)_2]Cl=C_8H_{16}N_2S_2O_4ClCo$: C, 26.49; H, 4.45; N, 7.72%.

*A-3, $(-)_{589}$-[Co(aeta)$_2$]Cl·H$_2$O,* (trans(S)): Attempts to resolve this isomer by means of the resolving agents $(-)_{589}$-K[Co(edta)]·2H$_2$O, $(+)_{589}$-Na[Co(ox)$_2$(en)]·H$_2$O, Na$_2$[Sb$_2$(*d*-tart)$_2$]·2H$_2$O, and Ag$_2$(*d*-H$_2$tart); (*d*-H$_4$tart$=C_4O_6H_6$), were unsuccessful. However, spontaneous resolution[17] was observed for the crystals prepared as follows: 0.5 g of the racemic chloride monohydrate was dissolved in 5 cm$^3$ of water at 40 °C and the solution was kept standing in a refrigerator for several days for crystallization. Crystals arbitrarily chosen then showed optical activity. No hemihedral facets, however, were found for the crystals. Found: C, 24.93; H, 4.83; N, 7.45%. Calcd for $(-)_{589}$-[Co(aeta)$_2$]-

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Cl·$H_2O=C_8H_{18}N_2S_2O_5ClCo$: C, 25.24; H, 4.77; N, 7.36%.

*A-4, (+)*$_{589}$-*[Co(aeta)*$_2$*]*$^+$, (cisciscis): The racemic chloride (0.39 g), dibenzoyl-*d*-tartaric acid (*d*-$H_2$tart-bz$_2$) (0.38 g), and sodium hydroxide (0.08 g) were dissolved in 10 cm$^3$ of water at 40 °C. The mixed solution was then evaporated to 2 cm$^3$ and cooled in a refrigerator overnight. The red diastereomer deposited was recrystallized from 2 cm$^3$ of hot water by adding acetone. Found: C, 36.47; H, 4.75; N, 4.92%. Calcd for $(+)_{589}$-[Co(aeta)$_2$]$_2$(*d*-tart-bz$_2$)·5.5$H_2O$= $C_{34}H_{55}N_4S_4O_{21.5}Co_2$: C, 36.79; H, 4.99; N, 5.05%.

Optically active chloride was obtained from the diastereomer by using an anion exchange resin (Dowex 1×8, Cl$^-$ form). The CD spectrum of this complex was measured with the eluate, and the concentration was calculated from the CD intensity referring to that of the diastereomer.

*A-5, (−)*$_{589}$-*[Co(aeta)*$_2$*]Cl·2.25H*$_2$*O*, (trans(N)): The racemic chloride (0.39 g) and the resolving agent $Na_2$[$Sb_2$(*d*-tart)$_2$]·2$H_2O$ (0.16 g) were dissolved in 3 cm$^3$ of water at 40 °C. The mixed solution was allowed to stand for a few days in a refrigerator to crystallize. The less soluble diastereomer (reddish purple) precipitated was filtered off and recrystallized from 2 cm$^3$ of hot water by adding ethanol. This was converted into the optically active chloride by using an anion exchange resin (Dowex 1×8, Cl$^-$ form). Found: C, 23.46; H, 4.94; N, 6.90%. Calcd for $(-)_{589}$-[Co(aeta)$_2$]Cl·2.25$H_2O=C_8H_{20.5}N_2S_2O_{6.25}ClCo$: C, 23.83; H, 5.12; N, 6.95%.

*(2) Bis[3-(2-aminoethylthio)propionato]cobalt(III) Chloride, [Co(aetp)*$_2$*]Cl*: This complex was prepared and separated according to the same method as that for [Co(aeta)$_2$]Cl with use of 3-(2-aminoethylthio)propionic acid[1] instead of (2-aminoethylthio)acetic acid.

Five colored bands, brownish violet (B-1), purple (B-2), another purple (B-3+B-4), reddish purple (B-5), and violet (B-6), were eluted in this order. The yields for B-1 and B-2 isomers were very low. It was confirmed by the absorption spectral behavior in the thioether charge transfer band region that the third eluate consists of two isomers B-3 and B-4, and that the B-1, B-2, and B-4 have a configuration in which the two sulfur atoms occupy *trans* positions. The eluates were separately concentrated in a vacuum evaporator and the deposit, NaCl, was filtered off. To each of the concentrated solution was added a large amount of ethanol. The desired complex was collected by filtration and recrystallized from a small amount of water by adding ethanol and acetone, and then dried in a vacuum desiccator over $CaCl_2$. However, complete separation of B-3 and B-4 isomers by means of an ion exchange resin (Dowex 50 W×8 or SP-Sephadex C-25) was unsuccessful. The pure products of these two isomers were obtained as follows. After removal of excess laed dioxide, the reaction mixture was evaporated to 50 cm$^3$ and cooled in an ice bath, and B-3 isomer was then crystallized as the bromide salt. On the other hand, the pure product of B-4 isomer could be fractionally crystallized from the mixed eluate of B-3 and B-4 isomers because of its low solubility. Found for B-1: C, 27.52; H, 5.70; N, 6.44%. Calcd for [Co(aetp)$_2$]Cl·2.5$H_2O=C_{10}H_{25}N_2S_2O_{6.5}ClCo$: C, 27.56; H, 5.78; N, 6.43%. Found for B-2: C, 26.76; H, 6.14; N, 5.90%. Calcd for [Co(aetp)$_2$]Cl·4$H_2O=C_{10}H_{28}N_2S_2O_8ClCo$: C, 25.95; H, 6.10; N, 6.05%. Found for B-3: C, 21.74; H, 5.06; N, 5.23%. Calcd for [Co(aetp)$_2$]Br·3.5$H_2O$·1/2NaBr$=C_{10}H_{27}N_2S_2O_{7.5}BrCo$·1/2NaBr: C, 21.85; H, 4.95; N, 5.10%. Found for B-4: C, 27.96; H, 5.43; N, 6.58%. Calcd for [Co(aetp)$_2$]Cl·2$H_2O=C_{10}H_{24}N_2S_2O_6ClCo$: C, 28.14; H, 5.67; N, 6.56%. Found for B-5: C, 29.18; H, 5.50; N, 6.90%. Calcd for [Co(aetp)$_2$]Cl·$H_2O=C_{10}H_{22}N_2S_2O_5ClCo$: C, 29.38; H, 5.42; N, 6.85%. Found for B-6: C, 27.60; H, 5.73; N, 6.47%. Calcd for [Co(aetp)$_2$]Cl·2.5$H_2O=C_{10}H_{25}N_2S_2O_{6.5}ClCo$: C, 27.56; H, 5.78; N, 6.43%.

*B-3, (−)*$_{589}$-*[Co(aetp)*$_2$*]Cl·2H*$_2$*O*, (trans(O)): The racemic bromide (0.55 g) and the resolving agent $K_2$[$Sb_2$(*d*-tart)$_2$]·3$H_2O$ (0.32 g) were dissolved in 5 cm$^3$ of water at 50 °C. After cooling to room temperature, the mixed solution was allowed to stand for a week in a refrigerator. The less soluble diastereomer deposited was recrystallized from a small amount of water, and converted into the chloride salt by using an anion exchange resin (Dowex 1×8, Cl$^-$ form). Found: C,23.47; H,4.68; N,5.40%. Calcd for $(-)_{589}$-[Co(aetp)$_2$]Cl·2$H_2O$·1.2KCl$=C_{10}H_{24}N_2S_2O_6ClCo$·1.2KCl: C,23.26; H,4.69; N,5.43%.

*B-2, (+)*$_{589}$-*[Co(aetp)*$_2$*]*$^+$, (mer-trans(S)); *B-4, (+)*$_{589}$-*[Co(aetp)*$_2$*]*$^+$, (trans(S)); *B-5, (+)*$_{589}$-*[Co(aetp)*$_2$*]*$^+$, (cisciscis); *and B-6, (+)*$_{589}$-*[Co(aetp)*$_2$*]*$^+$, (trans(N)): These four isomers were partially or completely resolved into their optical antipodes by chromatographic technique.

An aqueous solution containing 0.1 g of the complex was poured into a column of SP-Sephadex C-25 (Na$^+$ form, 3×120 cm). The adsorbed band was eluted with a 0.1 M aqueous solution of $K_2$[$Sb_2$(*d*-tart)$_2$]·3$H_2O$ at the rate of 0.3 cm$^3$/min. Under these conditions, 7—10 days were necessary for the complete elution of the complex, which produced a broad band. The eluate was separated into fractions of 5 cm$^3$ each. A few fractions eluted first, which showed CD spectra completely enantiomeric to those of the last fractions, were collected and after removal of the excess elution agents converted into the chloride salt by using an anion exchange resin (Dowex 1×8, Cl$^-$ form). This eluate of the chloride salt was used to measure the CD spectrum, and its concentration was calculated from the optical density referring to that of the racemate.

In all of the four isomers, the first eluates showed positive optical rotations for the Na-D line. A complete band separation into the antipodes was only observed for B-4 isomer.

*Measurements.* The electronic absorption spectra were measured on a Shimadzu UV-200 spectrophotometer in aqueous solutions. The CD spectra were obtained with a Jasco MOE-1 spectropolarimeter, by use of a cell with 1 cm pathlength. A Jasco DIP-4 digital polarimeter was used to check the optical rotations. The $^1$H NMR spectra were recorded in deuterium oxide on a Varian XL-100-15 spectrometer with DSS as the internal reference. All the measurements were carried out at room temperature.

## Results and Discussion

*Separation of Isomers.* For the present [Co(terdentate-*N,S,O*)$_2$]$^+$ type complexes, six geometrical isomers are possible. They are denoted by *tr.tr.tr.*, *trans(S)*, *trans(O)*, *trans(N)*, *cisciscis*, and *mer-trans(S)*, respectively, as shown in Fig. 1.

In the [Co(aeta)$_2$]$^+$ complex, five geometrical isomers were obtained. A-1 and A-2 seem to correspond to the two isomers reported by Hori[16] from a comparison of absorption spectra. For the [Co(aetp)$_2$]$^+$ complex, six geometrical isomers were separated chromatographically, which is the first example for the isolation of all the possible isomers of the [Co(A–B–C)$_2$] type complex. A molecular model examination reveals that the aeta ligand, which forms two five-membered chelate rings by coordination, strongly prefers the facial coordina-

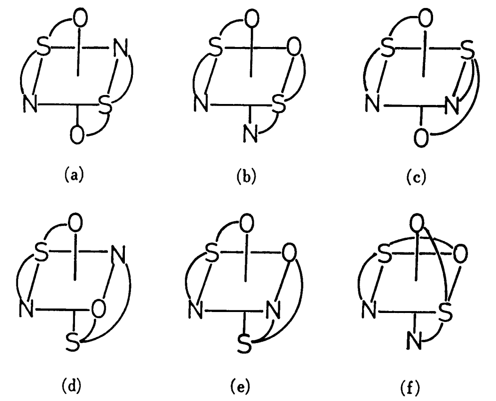


Fig. 1. Six possible geometrical isomers for the [Co(terdentate-*N,S,O*)$_2$]$^+$ type complex: (a) *tr.tr.tr.*, (b) *trans(S)*, (c) *trans(O)*, (d) *trans(N)*, (e) *cisciscis*, and (f) *mer-trans(S)*.

tion, whereas the aetp ligand which forms a five- and a six-membered chelate ring will take the meridionally coordinated form readily. It is therefore reasonable to expect that the *mer-trans*(*S*) isomer does not exist in the aeta complex. These circumstances seem to be common with the bis(terdentate) type cobalt(III) complexes containing linear *O,S,O*-[15] or *O,N,O*-terdentate[18—21] ligands.

An optical antipode exists for each five isomers of the six geometrical ones, except for *tr.tr.tr.* which has an inversion center. Accordingly, A-1 and B-1 isomers which could not be optically resolved are expected to have the *tr.tr.tr.* geometry.

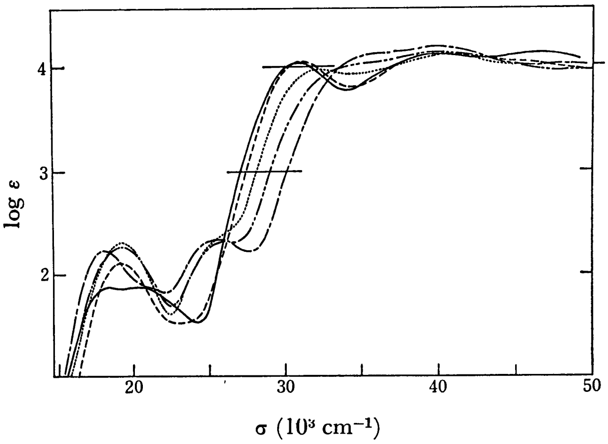


Fig. 2. Absorption spectra of the isomers of [Co(aeta)$_2$]Cl: A-1 *tr.tr.tr.* (——), A-2 *trans(O)* (·—·—·), A-3 *trans(S)* (-----), A-4 *cisciscis* (—··—··—), and A-5 *trans(N)* (······).

*Absorption Spectra and Configuration Assignments.* The absorption spectra of [Co(aeta)$_2$]$^+$ are shown in Fig. 2 and summarized in Table 1. In the near-ultraviolet region, the complexes show intense sulfur-to-metal charge transfer bands. The bands for A-1 and A-3 are located at lower energy side than those for the other three isomers. The charge transfer band of this type has been recognized to occur at a lower energy side for the cobalt(III) complexes with two ligating S atoms in *trans* positions than for the corresponding *cis* complexes.[12,13,15] Additional support was recently given to this absorption spectral criterion by the X-ray crystal structure analysis of *trans*(*S*)-[Co(*S*-methyl-L-cysteinato)$_2$]ClO$_4$·H$_2$O.[22] Thus, A-1 and A-3 isomers can be assigned to the *trans*(*S*) or *tr.tr.tr.* configuration and others to the *trans*(*O*), *trans*(*N*), or *cisciscis* one.

Table 1. Absorption data of isomers of [Co(aeta)$_2$]Cl and [Co(aetp)$_2$]Cl

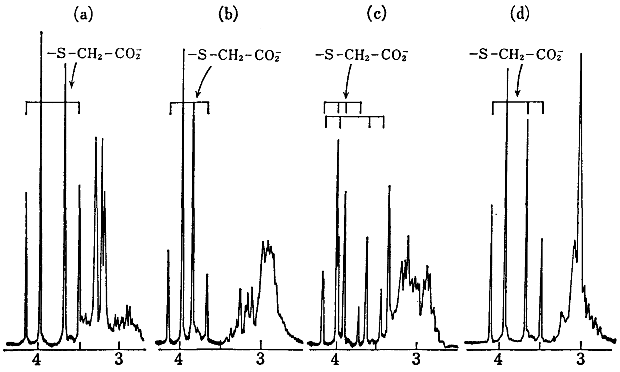
| [Co(aeta)$_2$]Cl[a] | | $\sigma_{max}$[b] (log ε) | | |
|---|---|---|---|---|
| Isomer | Configuration | First d-d band | Second d-d band | Charge transfer band region |
| A-1 | *tr.tr.tr.* | 18.4(1.87)<br>20.4(1.87) | | 30.9(4.04)<br>40.1(4.11)<br>46.3(4.11) |
| A-2 | *trans*(*O*) | 18.1(2.24)<br>20.8(1.88)[c] | 25.3(2.34) | 35.1(4.09)[c]<br>40.0(4.17)<br>48.3(4.04) |
| A-3 | *trans*(*S*) | 19.2(2.10) | | 31.2(4.04)<br>40.2(4.12) |
| A-4 | *cisciscis* | 19.2(2.27) | 26.1(2.32) | 33.7(3.98)[c]<br>40.0(4.12) |
| A-5 | *trans*(*N*) | 19.2(2.31) | 25.5(2.36)[c] | 32.4(3.97)<br>40.7(4.11)<br>47.8(4.01) |
| [Co(aetp)$_2$]Cl[a] | | | | |
| B-1 | *tr.tr.tr.* | 17.5(1.92)<br>20.7(2.02) | | 29.2(4.13)<br>39.1(4.02)<br>47.2(4.13) |
| B-2 | *mer-trans*(*S*) | 18.9(2.59) | 25.3(2.55)[c] | 31.2(4.26)<br>39.7(4.04) |
| B-3[d] | *trans*(*O*) | 17.8(2.32)<br>21.1(2.05) | 26.4(2.40)[c] | 34.2(4.19)<br>40.5(4.00) |
| B-4 | *trans*(*S*) | 18.8(2.60) | | 29.7(4.15)<br>39.3(4.03)<br>47.4(4.08) |
| B-5 | *cisciscis* | 19.0(2.42) | 25.6(2.46)[c] | 33.0(4.15)<br>42.1(4.06) |
| B-6 | *trans*(*N*) | sh[e]<br>18.8(2.60) | 25.3(2.62)[c] | 31.8(4.10)<br>40.9(4.08) |

a) The racemates. b) Wave numbers are given in $10^3$ cm$^{-1}$ unit. c) A shoulder. d) Bromide salt. e) The wave number could not be determined.

In the first d-d absorption band region, the expected splittings can be calculated semiempirically;[23] the *tr.tr.tr.* and *trans*(*N*) isomers should have the component of lowest energy, since the sulfur atom in the present terdentate ligands is between the oxygen of the carboxyl group and the nitrogen of the amino group in the spectrochemical series.[1] The *tr.tr.tr.* and *trans*(*O*) isomers should have one component in close proximity to the transition of [Co(N)$_6$], and the splitting for *tr.tr.tr.* isomer should be greater than those for *trans*(*N*) and *trans*(*O*) forms. The *trans*(*S*) and *cisciscis* isomers should have two and three components, respectively, in about the same region.

Of the two isomers assigned to the *trans*(*S*) or *tr.tr.tr*, A-1 exhibits two splitting components with the same molar extinction coefficients in the first absorption band region, while A-3 shows apparently a sharp band. This indicates that A-1 is *tr.tr.tr.* and A-3 *trans*(*S*).

On the other hand, of the three isomers assigned to the *trans*(*O*), *trans*(*N*), or *cisciscis*, A-2 exhibits an explicit shoulder at the high energy side of the major peak in the first absorption band region, while both A-4 and A-5 show a sharp peak. In the [Co(L-methioninato)$_2$]-Br[12] complex, both *trans*(*N*) and *trans*(*O*) isomers showed a marked splitting in the first absorption band region, their splitting patterns differing from each other; the *trans*(*O*) isomer showed a broad band with a shoulder at high energy side of the major peak, the *trans*(*N*) one at low energy side. This confirms that A-2 isomer is *trans*(*O*).



ppm from DSS

Fig. 3. The NMR spectra of the isomers of [Co(aeta)$_2$]-Cl in $D_2O$: (a) A-2 *trans(O)*, (b) A-3 *trans(S)*, (c) A-4 *cisciscis*, and (d) A-5 *trans(N)*.

The absorption spectra of A-4 and A-5 isomers are similar to each other, though there is a difference with respect to the position of thioether charge transfer band. $^1H$ NMR spectra of these isomers are shown in Fig. 3. A-2, A-3, and A-5 isomers exhibit a quartet due to methylene protons between carboxyl group and sulfur atom,[15] whereas A-4 shows two sets of quartet. The *trans*(*S*), *trans*(*O*), and *trans*(*N*) structures have $C_2$ symmetry, the *cisciscis* structure $C_1$. The latter isomer should show the most complicated pattern. Accordingly, A-4 can be assigned to *cisciscis*, and A-5 to *trans*(*N*). Further support is given by the signals in the region of amine protons. The amine signals appear at 6.17 and 6.58 ppm from DSS for A-2, at 4.62 and 4.98 ppm for A-3, at 4.49, 4.90, and 6.36 ppm for A-4, and at 5.26 and 6.67 ppm for A-5. This is explained qualitatively in terms of the magnetic anisotropy associated with the C–O single bond.[24–27] In each of the present isomers there are two amine groups; two groups of *trans*(*S*) and *trans*(*N*) isomers and one group of *cisciscis* isomer are in the shield position from the C–O bond of the other ligand, whereas one group of *cisciscis* isomer and two groups of *trans*(*O*) isomer are deshielded by the C–O bond of the other ligand. It is possible to expect that *cisciscis* isomer with $C_1$ symmetry shows the most complicated signals over the wider region than the other three isomers with $C_2$ symmetry.

The absorption spectra of six isomers of [Co(aetp)$_2$]$^+$ are shown in Fig. 4 and summarized in Table 1. According to the same discussion as described above, B-1 isomer can be assigned to *tr.tr.tr.* and B-3 to *trans*(*O*). Of the remaining four isomers, B-5 and B-6 have the thioether charge transfer bands at the higher energy side than B-2 and B-4. Therefore, the former two and the latter two isomers can be assigned to the configurations with two ligating S atoms in *cis* and *trans* positions, respectively. In the first absorption band region, B-5 shows a sharp band, while B-6 exhibits a vague shoulder at the low energy side of the major peak. The spectral behavior corresponds to the expectation from semiempirical theory, and B-5 can be assigned to *cisciscis* and B-6 to *trans*(*N*). The B-2 and B-4 isomers were assigned to *mer-trans*(*S*) and *fac-trans*(*S*) configurations, respectively, on the basis of the low yield of B-2 (see Experimental), and of absorption spectral behavior in which the low energy thioether charge transfer band of B-2 occurs at an exceptional position. These assignments have good correlation with the column chromatographic behavior. Namely, the complexes [Co(aeta)$_2$]$^+$ and [Co(aetp)$_2$]$^+$ have the same elution order of isomers except for B-2-*mer-trans*(*S*) isomer; the order is *tr.tr.tr.*, *trans*(*O*), *trans*(*S*), *cisciscis*, and *trans*(*N*) for both series.

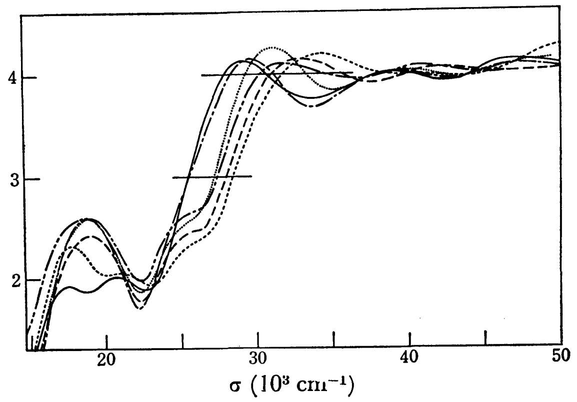


Fig. 4. Absorption spectra of the isomers of [Co(aetp)$_2$]-Cl: B-1 *tr.tr.tr.* (——), B-2 *mer-trans(S)* (······), B-3 *trans(O)* (------), B-4 *trans(S)* (·—·—·), B-5 *cisciscis* (——), and B-6 *trans(N)* (—··—··—); B-3 isomer is a bromide salt.

Thus, the electronic absorption spectra of the corresponding isomers between [Co(aeta)$_2$]$^+$ and [Co(aetp)$_2$]$^+$ complexes are similar to each other but differ in detail. Firstly, the first d-d band intensities of the isomers of [Co(aetp)$_2$]$^+$ are two or three times larger than those of the corresponding isomers of [Co(aeta)$_2$]$^+$. Such kind of intensity difference has been observed between *trans*(*N*)-*RR*-[Co(L-promp)$_2$]$^-$ and *trans*(*N*)-*RR*-[Co(L-proma)$_2$]$^-$ complexes,[28] where L-promp and L-proma are L-prolinate-*N*-monopropionate and L-prolinate-*N*-monoacetate, respectively. Secondly, in the aetp complexes, the thioether charge transfer band is shifted to a lower energy side than that of the corresponding aeta isomer, and the shift direction is the same as that of the first d-d absorption band.

*CD Spectra.* The CD spectra are shown in Figs. 5—8 and Table 2. The complexes have two CD contributions, one from the configurational chirality due to the skew pair of chelate rings and the other from the chirality due to the sulfur donor atoms, though both contributions can not be separated. The observed CD

Table 2. CD Data of isomers of [Co(aeta)$_2$]Cl and [Co(aetp)$_2$]Cl

| [Co(aeta)$_2$]Cl | | $\sigma_{ext}$$^{a)}$ ($\Delta\varepsilon$) | | |
|---|---|---|---|---|
| Isomer | Rotation for Na-D line | First d-d band region | Second d-d band region | Charge transfer band region |
| *trans*(*O*) | (−) | 17.8(−4.04)<br>21.5(+2.64) | 25.4(−1.23) | 36.4(+10.7)<br>42.1(−17.2)<br>47.6(+22.2) |
| *trans*(*S*) | (−) | 17.9(−0.52)<br>20.3(−0.13) | 23.7(−0.15) | 30.9(+23.5)<br>35.7(−10.4)<br>39.6(−14.9)<br>44.9(+23.3) |
| *cisciscis* | (+) | 18.0(+2.51)<br>20.4(−1.19) | 24.6(+0.82) | 32.5(−5.72)<br>38.7(−15.5)<br>43.2(+14.5) |
| *trans*(*N*)$^{b)}$ | (−) | 18.7(−1.63)<br>20.0(−1.48)$^{c)}$ | 26.0(+2.24) | 31.7(+13.6)<br>35.5(−2.09)<br>40.3(+16.5)<br>44.8(−19.5) |
| [Co(aept)$_2$]Cl | | | | |
| *mer-trans*(*S*)$^{b)}$ | (+) | 17.3(+0.37)<br>19.6(−0.44) | 25.1(+0.21) | 31.5(−3.88)<br>36.1(+1.17)<br>38.6(−0.43)<br>44.4(+4.22) |
| *trans*(*O*) | (−) | 18.0(−4.51)<br>21.1(+4.56) | 25.8(−1.25) | 31.7(−8.09)<br>34.8(+4.22)<br>37.7(−6.59)<br>44.2(+14.0)$^{c)}$<br>48.3(+21.6) |
| *trans*(*S*)$^{b)}$ | (+) | 17.2(−1.59)<br>19.6(+5.87) | 26.2(−2.47) | 30.1(−4.36)<br>36.6(−13.6)<br>43.5(+8.12) |
| *cisciscis*$^{b)}$ | (+) | 17.7(+1.52)<br>20.7(−0.17) | 24.2(+0.19)<br>26.5(+0.25) | 31.9(−14.7)<br>37.2(+3.97)<br>43.3(+2.59)<br>46.8(−3.16) |
| *trans*(*N*)$^{b)}$ | (+) | 17.2(−0.27)<br>19.8(+1.25) | 25.6(−0.75) | 31.1(−6.85)<br>36.1(−4.28)<br>42.9(+10.6) |

a) Wave numbers are given in $10^3$ cm$^{-1}$ unit. b) CD spectra were measured with eluates. c) A shoulder.

spectra differ significantly among the different geometrical isomers, but resemble the corresponding geometrical isomers of [Co(aeta)$_2$]$^+$ and [Co(aetp)$_2$]$^+$. Accordingly, it is convenient to discuss each pair of geometrical isomers individually.

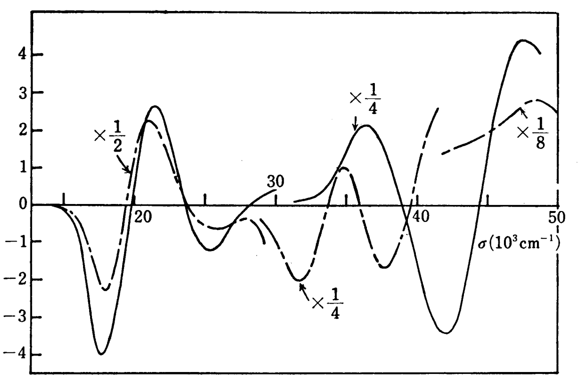


Fig. 5. CD spectra of *trans(O)* complexes: (−)$_{589}$-[Co(aeta)$_2$]$^+$ (——) and (−)$_{589}$-[Co(aetp)$_2$]$^+$ (•—•—•).

In the first absorption band region, both (−)$_{589}$-*trans*(*O*) aeta and (−)$_{589}$-*trans*(*O*) aetp complexes have two CD components, (−) and (+) from low energy side (Fig. 5), though three bands, (+), (−), and (+), have been observed for *trans*(*O*)-[Co(L-methioninato)$_2$]$^+$ [12] and *trans*(*O*)-[Co(*S*-methyl-L-cysteinato)$_2$]$^+$[13] in the corresponding region. In the present *trans*(*O*) isomers with C$_2$ symmetry, there is a weaker field along the unique axis (O–Co–O) than along the other axes perpendicular to it. Thus it is predicted that the $^1$A+$^1$B$_b$(C$_2$) level would be lower in energy than the $^1$B$_a$(C$_2$) level. Consequently, the negative CD components at low energy are assigned to be $^1$A+$^1$B$_b$(C$_2$), and the positive CD components at high energy $^1$B$_a$(C$_2$). The absolute configurations of (−)$_{589}$-*trans*(*O*)-[Co(aeta)$_2$]$^+$ and (−)$_{589}$-*trans*(*O*)-[Co(aetp)$_2$]$^+$ are assigned to *ΔΔΛ*-(*RR*) and *ΔΔΛ*-(*SS*),[29] respectively, according to the CD sign of the $^1$A+$^1$B$_b$(C$_2$) transition, where (*RR*) and (*SS*) represent the chiralities of the chiral sulfur atoms. The absolute configuration of (−)$_{589}$-*trans*(*O*)-[Co(NH$_2$CH$_2$CH$_2$NHCH$_2$CO$_2$)$_2$]$^+$,[30] which exhibits two CD

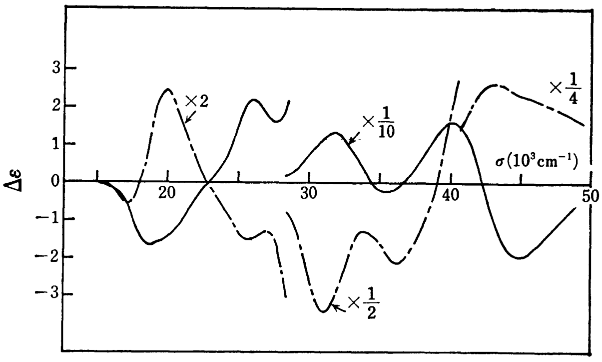


Fig. 6. CD spectra of *trans(N)* complexes: $(-)_{589}$-[Co(aeta)$_2$]$^+$ (——) and $(+)_{589}$-[Co(aetp)$_2$]$^+$ (·—·—·).

peaks of opposite sign, (−) and (+) from low energy side, in the first absorption band region, has been assigned to $\Delta\Delta\Lambda$.

For the *trans*(*N*) isomers (Fig. 6), the aeta $(-)_{589}$-complex exhibits two negative CD bands at 18700 cm$^{-1}$ ($\Delta\varepsilon=-1.63$) and *ca.* 20000 cm$^{-1}$ ($\Delta\varepsilon=-1.48$), but the aetp $(+)_{589}$-complex shows two bands of opposite sign at 17200 cm$^{-1}$ ($\Delta\varepsilon=-0.27$) and 19800 cm$^{-1}$ ($\Delta\varepsilon=+1.25$). On the basis of a consideration similar to that mentioned above, the low energy band is assigned in each case to the $^1A\rightarrow^1B_a(C_2)$ transition and the high energy component to $^1A\rightarrow^1A+^1B_b(C_2)$. Worrell and Busch[7] studied some complexes containing a flexible quadridentate ligand, 1,8-diamino-3,6-dithiaoctane (dadt). Of these complexes, $(+)_{546}$-*sym-cis*-[Co(dadt)Cl$_2$]$^+$, $(+)_{546}$-*sym-cis*-[Co(dadt)ClH$_2$O]$^{2+}$ and $(+)_{546}$-*sym-cis*-[Co(dadt)(H$_2$O)$_2$]$^{3+}$, which have the two ligating NH$_2$ groups in *trans* positions and show a negative and a positive CD component from low energy side of the first absorption band region, were assigned to $\Lambda$ absolute configurations, because in all three cases, the sign pattern is in agreement with that exhibited by the corresponding ethylenediamine and triethylenediamine complexes of $\Lambda$ absolute configuration. The same argument is applied to the present system. The absolute configurations of $(-)_{589}$-*trans*(*N*)-[Co(aeta)$_2$]$^+$ and $(+)_{589}$-*trans*(*N*)-[Co(aetp)$_2$]$^+$ are assigned to $\Delta\Delta\Lambda$-(*SS*) and $\Delta\Lambda\Lambda$-(*SS*) configurations, respectively, according to the sign of the $^1A+^1B_b(C_2)$ transition.

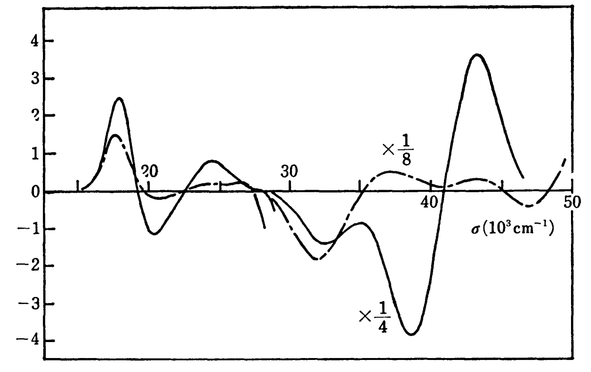


Fig. 7. CD spectra of *cisciscis* complexes: $(+)_{589}$-[Co(aeta)$_2$]$^+$ (——) and $(+)_{589}$-[Co(aetp)$_2$]$^+$ (·—·—·).

In the *cisciscis* isomers (Fig. 7), the parential arguments as above seem to have limited applicability because of the lowering of symmetry and the difficulty in the assignment of three components. However, the CD contribution of this geometrical isomer is mainly due to the configurational chirality, since the two chiral sulfur atoms form a meso combination ((*R*) and (*S*)). Therefore, the major CD component in the first absorption band region is related to the molecular framework; *cisciscis* isomers of both aeta and aetp $(+)_{589}$-complexes exhibit a strong positive and a negative band and can be assigned to $\Delta\Lambda\Lambda$ configuration.

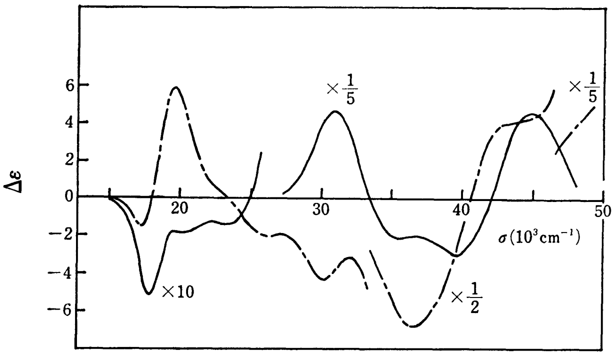


Fig. 8. CD spectra of *trans(S)* complexes: $(-)_{589}$-[Co(aeta)$_2$]$^+$ (——) and $(+)_{589}$-[Co(aetp)$_2$]$^+$ (·—·—·).

For the *trans*(*S*) isomers (Fig. 8), the aeta $(-)_{589}$-complex exhibits two weak CD components in the first absorption band region and a strong CD band in the thioether charge transfer band region, whereas the aetp $(+)_{589}$-complex shows a strong major CD band in the first absorption band region and a relatively weak band in the thioether charge transfer band region. These CD patterns cannot be related directly to their absolute configurations, because the *trans*(*S*) forms do not have CD contribution due to the skew pair of chelate rings according to the ring pairing method[31] but only the contribution due to the two chiral sulfur donor atoms.

In the low energy thioether charge transfer band region, medium or strong CD bands are generally observed for all isomers. The correlation of the charge transfer CD spectra of the *trans*(*N*) isomers between the aeta and aetp complexes is good as regards position and sign; the aeta $\Delta\Delta\Lambda$-(*SS*)-complex has a (+) band, the aetp $\Delta\Lambda\Lambda$-(*SS*)-complex a (−) band.

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