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Oxidative Synthesis, Optical Resolution, and Characterization of Mixed Sulfenato and Sulfinato Cobalt(III) Complexes

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Twelve new mixed sulfenato and sulfinato cobalt(III) complexes were prepared via successive H_2O_2 oxidation of $[Co(SCH_2CH_2NH_2)_3]$, $[Co\{SCH_2CH(COOCH_3)NH_2\}_3]$, and related complexes. These oxidation products, [Co(sulfenato-*N,S*)$_n$(sulfinato-*N,S*)$_{3-n}$] (n=3, 2, 1, and 0), were optically resolved by means of column chromatography or preferential crystallization of a diastereomeric molecular compound with *d*-tartaric acid. The mixed sulfenato and sulfinato complexes show characteristic variation of absorption spectra with the change of "n" in [Co(sulfenato-*N,S*)$_n$(sulfinato-*N,S*)$_{3-n}$] (n=3, 2, 1, and 0). It is concluded that the (*R*) configuration of the sulfenato group is more stable than the (*S*) one in the *fac*(*S*)-Λ-[Co(sulfenato-*N,S*)$_n$(sulfinato-*N,S*)$_{3-n}$].

Owing to the high nucleophilicity of the thiolato sulfur atom coordinated to cobalt(III) ion, the reaction of the thiolato complex with other metal ion, Co^{3+}, Zn^{2+}, Ag^+, *etc.*,[1] or with carbonium ion, CH_3^+, $C_2H_5^+$, $C_6H_5CH_2^+$, *etc.*,[2] yielded easily μ-thiolato or thioether complex, respectively. Furthermore, it has been reported that the successive oxidation of the thiolato cobalt(III) complex generates several sulfur-bonded sulfenato and sulfinato complexes.[3] These complexes are of interest in connection with their kinetic and spectrochemical behaviors. However, no optically active sulfenato or sulfinato complex except $[Co\{S(O)CH_2CH(COOH)NH_2\}(en)_2]^{2+}$ has been reported so far and consequently their stereochemical aspects have not been investigated systematically.

Present study is concerned with the preparation and optical resolution of mixed sulfenato and sulfinato complexes, [Co(sulfenato-*N,S*)$_n$(sulfinato-*N,S*)$_{3-n}$] (n= 3, 2, 1, and 0), and related complexes. These optically active complexes were obtained by means of three methods, preferential crystallization of a diastereomeric molecular compound, column chromatography, and stereospecific substitution reaction. The complexes were identified from their visible and ultraviolet absorption, circular dichroism (CD), and ^{13}C NMR spectra, and their spectrochemical and stereochemical features were discussed. A preliminary report has been presented.[4]

Abbreviations used for ligands are as follows: Haet, 2-aminoethanethiol $HSCH_2CH_2NH_2$; Haese, 2-aminoethanesulfenic acid $HS(O)CH_2CH_2NH_2$; Haesi, 2-aminoethanesulfinic acid $HS(O)_2CH_2CH_2NH_2$; L-Hcym, L-cysteine methyl ester $HSCH_2CH(COOCH_3)NH_2$; L-cyme, (*R*)-2-amino-2-(methoxycarbonyl)ethanesulfenic acid $HS(O)CH_2CH(COOCH_3)NH_2$; L-Hcymi, (*R*)-2-amino-2-(methoxycarbonyl)ethanesulfinic acid $HS(O)_2CH_2CH(COOCH_3)NH_2$; L-$H_2$cys, L-cysteine $HSCH_2CH(COOH)NH_2$; L-H_2cyse, (*R*)-2-amino-3-sulfenopropanoic acid $HS(O)CH_2CH(COOH)NH_2$; L-H_2cysi, (*R*)-2-amino-3-sulfinopropanoic acid $HS(O)_2CH_2CH(COOH)NH_2$; L-H_2pene, (*R*)-2-amino-3-methyl-3-sulfenobutanoic acid $HS(O)C(CH_3)_2CH(COOH)NH_2$; en, ethylenediamine $NH_2CH_2CH_2NH_2$; *d*-H_2tart, *d*-tartaric acid *d*-$C_4H_6O_6$.

Experimental

Preparation, Separation, and Optical Resolution of Complexes. *(1) [Co(aese)$_n$(aesi)$_{3-n}$] (n=3, 2, 1, and 0)*: To a solution of 3.5 g (30 mmol) of 2-aminoethanethiol hydrochloride in 30 cm^3 of water was gradually added 3.6 g (10 mmol) of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ and the mixture was stirred at 95 °C for 1 h. The blue-green curdy precipitate of $[Co(aet)_3]$ was filtered and washed with water. A stoichiometric amount (21 mmol) of 2.86% aqueous H_2O_2 was added dropwise to suspension of 2.0 g (7 mmol) of $[Co(aet)_3]$ in 25 cm^3 of water with stirring below 5 °C, leading to an orange-red solution instantly. This solution was filtered in order to remove a little amount of unreacted $[Co(aet)_3]$. On addition of acetone (200 cm^3) and ether (200 cm^3) to the filtrate, an orange precipitate was obtained. This was dissolved in a small amount of water, adsorbed on a column (2 cm × 100 cm) of anion-exchange resin (QAE-Sephadex A-25, *d*-tartrate form) and eluted with water. Five colored bands, orange(I), orange(II), orange(III), yellow orange(IV), and orange yellow(V), were eluted in this order. Bands, II, III, and IV, were major products, and I and V minor ones. At this stage each of the bands was partially resolved: the earlier eluted fractions of band II, III, IV, or V showed negative CD at the longest wavelength region of the first d-d absorption band.

The oxidation of eluate II or III by diluted H_2O_2 (*ca.* 2%) produced bands IV and V which were separated by column chromatography. Similarly, eluate IV generated band V and a new yellow band VI, and eluate V did single band VI. The sparingly soluble yellow complex VI could also be obtained *via* oxidation of eluate II, III, IV, or V by an excess 30% H_2O_2. These results indicate that the oxidation process is stepwise in a series of II (or III)→IV→V→VI.

Each eluate was concentrated in a vacuum rotatory evaporator at *ca.* 8 °C to yield the precipitate. The precipitate was collected by filtration and washed with acetone and ether. But the precipitate could not be isolated from eluate I because of the low yield and very hygroscopic property. Complex II partially isomerized into complex III during the crystallization, which was identified by column chromatographic treatment and ^{13}C NMR spectra. It was confirmed from the absorption measurement and the following elemental analyses that complexes II (and III), IV, V, and VI correspond to n=3, 2, 1, and 0 of [Co(aese)$_n$(aesi)$_{3-n}$], respectively.

Found for II: C, 21.08; H, 5.56; N, 12.25%. Calcd for $[Co(aese)_3]\cdot 0.5H_2O = C_6H_{19}N_3O_{3.5}S_3Co$: C, 20.93; H, 5.56; N, 12.20%. Found for III: C, 19.08; H, 6.12; N, 11.22%. Calcd for $[Co(aese)_3]\cdot 2.5H_2O = C_6H_{23}N_3O_{5.5}S_3Co$: C, 18.94; H, 6.09; N, 11.22%. Found for IV: C, 18.39; H, 5.62; N, 10.79%. Calcd for $[Co(aese)_2(aesi)]\cdot 2H_2O = C_6H_{22}N_3O_6S_3Co$: C, 18.61; H, 5.72; N, 10.48%. Found for V: C, 18.50; H, 5.17; N, 10.84%. Calcd for $[Co(aese)(aesi)_2]\cdot H_2O = C_6H_{20}N_3O_6S_3Co$: C, 18.70; H, 5.23; N, 10.90%. Found for VI: C, 18.80; H, 4.80; N, 10.90%. Calcd for $[Co(aesi)_3] = C_6H_{18}N_3O_6S_3Co$: C, 18.80; H, 4.73; N, 10.96%.

(2) Molecular Compound of III with d-*Tartaric Acid,* $d\text{-}C_4H_6O_6\cdot(+)^{CD}_{500}\text{-}[Co(aese)_3]\cdot H_2O$ *and Its Derivatives*: The optical resolution of III was achieved using *d*-tartaric acid as a resolving agent. Racemate III, $[Co(aese)_3]\cdot 2.5H_2O$ (1.0 g, 2.76 mmol), was dissolved in an ethanol–water (2:1) mixture and then $d\text{-}H_2tart$ (0.42 g, 2.76 mmol) was added to the solution. After a few minutes, an orange-red diastereomeric molecular compound, $d\text{-}H_2tart\cdot(+)^{CD}_{500}\text{-}[Co(aese)_3]\cdot H_2O$ began to deposit as needle-like crystals. The crystals were filtered and washed with ethanol. Found: C, 23.72; H, 5.22; N, 8.35%. Calcd for $d\text{-}H_2tart\cdot(+)^{CD}_{500}\text{-}[Co(aese)_3]\cdot H_2O = C_{10}H_{26}N_3O_{10}S_3Co$: C, 23.86; H, 5.21; N, 8.35%.

The diastereomeric molecular compound was converted into $(+)^{CD}_{500}\text{-}[Co(aese)_3]$ by treating with an equimolar amount of $Ca(OH)_2$.

Optically pure complexes corresponding to IV, V, and VI were prepared by the oxidation of $(+)^{CD}_{500}\text{-}[Co(aese)_3]$. The CD spectra were measured with the eluates and their concentrations were calculated from the optical densities referring to those of the corresponding racemates. The oxidation products of $(+)^{CD}_{500}$-II were same as those of $(+)^{CD}_{500}$-III.

(3) Partial Resolution of $[Co(aet)_3]$: A solution of 1.0 g (2.0 mmol) of $\Lambda\text{-}[Co(en)_3]Br_3\cdot H_2O$ in 20 cm^3 of water was added to a solution of 0.5 g (6.5 mmol) of 2-aminoethanethiol and of 0.5 g (12 mmol) of sodium hydroxide in 20 cm^3 of water. The mixture was stirred at 70 °C. After a few minutes, the precipitate of $[Co(aet)_3]$ which shows optical activity began to deposit. This was filtered and washed with water. Its oxidative derivatives, II, III, IV, V and VI, were obtained according to the same procedure mentioned above and separated by the column chromatography using anion-exchange resin (QAE-Sephadex A-25, Cl^- form). These oxidation products showed positive CD at the longest wavelength region of the first d-d transition band. Their $\Delta\varepsilon$ values were 13.0% compared with those of optically pure complexes $(+)^{CD}_{500}$-III, $(+)^{CD}_{485}$-IV, $(+)^{CD}_{468}$-V, and $(+)^{CD}_{440}$-VI, respectively, which were obtained from the previous two methods. This enantiomer ratio $(+)/(-)=1.30$ was used to the calculation of the optical purity of $(+)^{CD}_{500}$-II resolved by column chromatography, which was approximately optically pure.

(4) $[Co(\text{L-}cym)_3]$: The procedure employed for this preparation was analogous to that of $[Co(aet)_3]$. To a solution of 8.0 g (47 mmol) of L-cysteine methyl ester hydrochloride in 70 cm^3 of water was gradually added 5.6 g (15.6 mmol) of $Na_3[Co(CO_3)_3]\cdot 3H_2O$, and the mixture was stirred at 95 °C for an hour. The blue-green curdy precipitate of $[Co(\text{L-cym})_3]$ was filtered and washed with water. Found: C, 29.89; H, 5.32; N, 8.76%. Calcd for $[Co(\text{L-cym})_3]\cdot H_2O = C_{12}H_{26}N_3O_7S_3Co$: C, 30.06; H, 5.47; N, 8.76%.

(5) $[Co(\text{L-}cyme)_n(\text{L-}cymi)_{3-n}]$ *(n=3, 2, 1, and 0)*: These complexes were prepared *via* H_2O_2 oxidation of $[Co(\text{L-cym})_3]$ and isolated by the analogous column chromatographic technique used for $[Co(aese)_n(aesi)_{3-n}]$ (n=3, 2, 1, and 0).

To a suspension of 2.0 g (4.2 mmol) of $[Co(\text{L-cym})_3]\cdot H_2O$ in 30 cm^3 of water was added 20 cm^3 (12.6 mmol) of 6.43% aqueous H_2O_2 with stirring below 5 °C, leading to an orange-red solution. On addition of acetone and ether, an orange precipitate appeared. This was dissolved in a small amount of water, adsorbed on a column (QAE-Sephadex A-25, *d*-tartrate form) and eluted with water. Four colored bands, orange (II′, major), orange (III′, minor), yellow-orange (IV′, major), and orange-yellow (V′, minor), were eluted in this order. Each band was composed of single optical isomer. Therefore, this system showed the high stereoselectivity as well as that of tris(L-cysteinato-*N,S*)cobaltate(III) (3−).[6] Some yellow-orange bands remained on the column, which seem to be partially hydrolyzed products because of their negative charges. The absorption and CD spectra of bands II′, III′, IV′, and V′ correspond to n=3, 3, 2, and 1 of $[Co(\text{L-cyme})_n(\text{L-cymi})_{3-n}]$, respectively. The insoluble yellow complex $[Co(\text{L-cymi})_3]$ (VI′) was prepared by oxidation of $[Co(\text{L-cym})_3]$ with excess 30% H_2O_2. After concentrating each eluate, a small amount of acetone and ether was added to the solution, and the precipitate was filtered off. Complex II′ as well as II partially changed into complex III′ during the crystallization, though the other eluates showed no isomerization. Found for II′: C, 26.48; H, 4.98; N, 7.37%. Calcd for $[Co(\text{L-cyme})_3]\cdot 2H_2O = C_{12}H_{28}N_3O_{11}S_3Co$: C, 26.42; H, 5.17; N, 7.70%. Found for III′: C, 26.98; H, 4.88; N, 7.89%. Calcd for $[Co(\text{L-cyme})_3]\cdot 1.5H_2O = C_{12}H_{27}N_3O_{9.5}S_3Co$: C, 26.87; H, 5.07; N, 7.83%. Found for IV′: C, 26.01; H, 4.78; N, 7.56%. Calcd for $[Co(\text{L-cyme})_2(\text{L-cymi})]\cdot 1.5H_2O = C_{12}H_{27}N_3O_{11.5}S_3Co$: C, 26.09; H, 4.93; N, 7.61%. Found for V′: C, 26.00; H, 4.61; N, 7.56%. Calcd for $[Co(\text{L-cyme})(\text{L-cymi})_2]\cdot 0.5H_2O = C_{12}H_{25}N_3O_{11.5}S_3Co$: C, 26.18; H, 4.58; N, 7.63%. Found for VI′: C, 25.78; H, 4.72; N, 7.52%. Calcd for $[Co(\text{L-cymi})_3] = C_{12}H_{24}N_3O_{12}S_3Co$: C, 25.86; H, 4.34; N, 7.54%.

The complex $[Co(\text{L-cymi})_3]$ (VI′) was easily hydrolyzed in diluted sodium hydroxide solution (0.1 mol dm^{-3}) and the resulting complex had high solubility. The CD and absorption spectra of this hydrolyzed complex were quite similar to those of $[Co(\text{L-cysi})_3]^{3-}$.

(5) Λ*-(*R*)- and* Λ*-(*S*)-*$[Co(aese)(en)_2]^{2+}$: $\Lambda\text{-}[Co(aet)(en)_2](ClO_4)_2$ was obtained according to the procedure previously reported.[5] The stoichiometric oxidation of the Λ-complex gave an orange solution. After addition of 2-propanol to the solution, an orange precipitate appeared, which showed almost the same CD spectrum as that of Λ-(*R*) isomer in $[Co(\text{L-cyse})(en)_2]^+$. The filtrate contained Λ-(*S*) isomer predominantly. The concentrations of solutions used for CD spectral measurement were determined from the optical densities referring to that of the racemate.

(6) $Na_3[Co(\text{L-}cysi)_3]$: This compound was prepared *via* oxidation of green $Na_3[Co(\text{L-cys})_3]$ with excess 30% H_2O_2. The procedure forms the only one isomer stereoselectively.[6] Found: C, 13.63; H, 4.56; N, 5.31%. Calcd for $Na_3[Co(\text{L-cysi})_3]\cdot 11H_2O = C_9H_{37}N_3O_{23}S_3CoNa_3$: C, 13.87; H, 4.78; N, 5.31%.

(7) $K[Co(aesi)_2(\text{L-}cysi)]$: The solution of 2-aminoethanethiol, L-cysteine, and KOH (2:1:4) was added to the solution of $[Co(NH_3)_6]Cl_3$ (a stoichiometric amount). The mixture was heated until no further evolution of ammonia could be detected. Then an excess of 30% H_2O_2 was added to the reaction mixture. After the column chromatography, the desired complex was obtained. Found: C, 16.07; H, 4.29; N, 7.93%. Calcd for $K[Co(aesi)_2(\text{L-cysi})] = C_7H_{23}N_3O_{11}S_3CoK$: C, 16.18; H, 4.46; N, 8.07%.

Measurements. The visible and ultraviolet absorption spectra were measured on a Shimadzu UV-200 and a Hitachi 330 spectrophotometers. The CD spectra were recorded on a JASCO MOE-1 spectropolarimeter. The absorption and CD measurements of the complexes were made in aqueous solutions at ambient temperature. The ^{13}C NMR spectra were measured with a Varian XL-100-15 NMR spectrometer in D_2O containing dioxane as an internal standard.

Results and Discussion

Optical Resolution. So far only a limited number of neutral complexes have been optically resolved, where the available methods were stereoselective decomposition by bacteria,[7] circular dichromatic excitation,[8] and column chromatography,[9] no preferential crystallization of a diastereomer having been applied. In the present study, three techniques were applied effectively to the optical resolution of neutral complexes $[\mathrm{Co(aese)}_n(\mathrm{aesi})_{3-n}]$ (n=3, 2, 1, and 0). The first method is a modification of column chromatography; the anion-exchange resin (QAE-Sephadex A-25) was used as *d*-tartrate form and the eluting solvent was water. In the course of separation, all eluates contain no salt advantageously. The second method is the preferential crystallization of a diastereomeric molecular compound *d*-$\mathrm{H_2tart}\cdot(+)^{\mathrm{CD}}_{600}$-$[\mathrm{Co(aese)_3}]\cdot\mathrm{H_2O}$ (molecular compound of III). This is the first case of optical resolution of a neutral complex *via* diastereomer formation. The composition and structure of this diastereomeric molecular compound has been confirmed by the single crystal X-ray structure analysis.[10] The third method is the substitution reaction with partial retention of configuration (see Experimental).

Geometrical Isomerism. The unsymmetrical nature of bidentate ligands such as 2-aminoethanethiol, L-cysteine methyl ester, and L-cysteine leads to the possibility of two geometrical isomers, *fac*(*S*) and *mer*(*S*), for the tris(bidentate)cobalt(III) complexes of $[\mathrm{Co(N)_3(S)_3}]$ type. It has been shown by the investigations of trinuclear derivatives of $[\mathrm{Co(aet)_3}]$[1a] that the complex exists only in the *fac*(*S*) form. The visible and ultraviolet absorption spectra of the present starting thiolato complexes $[\mathrm{Co(aet)_3}]$, $[\mathrm{Co(L\text{-}cym)_3}]$, and $[\mathrm{Co(L\text{-}cys)_3}]^{3-}$ are quite similar as shown in Fig. 1. Furthermore, the ^{13}C NMR spectra of their oxidation products, which have a C_3 symmetry, suggest that the starting complexes have *fac*(*S*) geometry. The energy difference between the two isomers, *fac* and *mer*, has been discussed by Burdett, who concluded that the most stable geometry will be *fac* for a low spin d^6 configuration such as $[\mathrm{Co(CN)_3(H_2O)_3}]$, $[\mathrm{Cr(CO)_3(PH_3)_3}]$, and $[\mathrm{M(CO)_3(P_4S_3)_3}]$ (M=Cr and Mo).[11] A similar trend is also found in the tris(bidentate-*N*,*S*)cobalt(III) complexes.

Characterization of $[\mathrm{Co(aese)}_n(\mathrm{aesi})_{3-n}]$ *(n=3, 2, 1, and 0).* Table 1 shows the absorption spectral data of the complexes. The absorption spectra of the complexes containing thiolato groups exhibit a characteristic weak band at *ca.* 17000 cm^{-1}.[12] All the oxidation products did not show this band and therefore contain no thiolato group. The intense absorption bands appeared in the near-ultraviolet region (*ca.* 32000—37000 cm^{-1}) indicate that the coordination of sulfur-containing ligands occurs through the sulfur atoms.[3] Complexes II and III, both of which are the precursors of complexes IV, V, and VI in the oxidation reaction, gave the same absorption spectra (Fig. 2). Since the most intense band at *ca.* 27000 cm^{-1} is due to the sulfenato groups,[3] the two complexes can be identified to the diastereomers of $[\mathrm{Co(aese)_3}]$. The gradual decrease in molar extinction coefficients at 27000 cm^{-1} along a series of II (or III)→IV→V just corresponds to the decrease in the number of sulfenato groups. Complex VI does not exhibit the 27000 cm^{-1} band and therefore no sulfenato group exists in this complex. The assignments are well supported by the oxidation reaction scheme (Scheme 1). Thus, complexes II (and III), IV, V, and VI correspond to n=3, 2, 1, and 0 of $[\mathrm{Co(aese)}_n(\mathrm{aesi})_{3-n}]$, respectively.

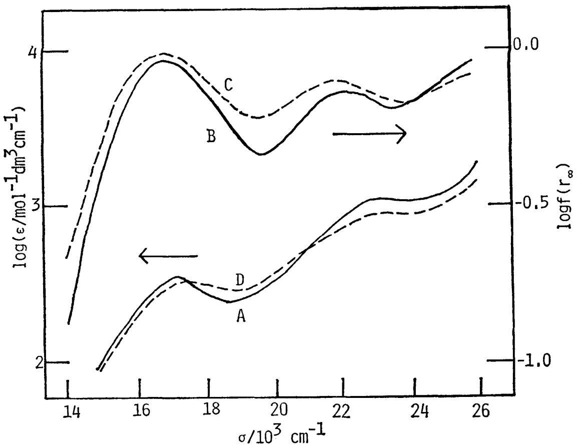


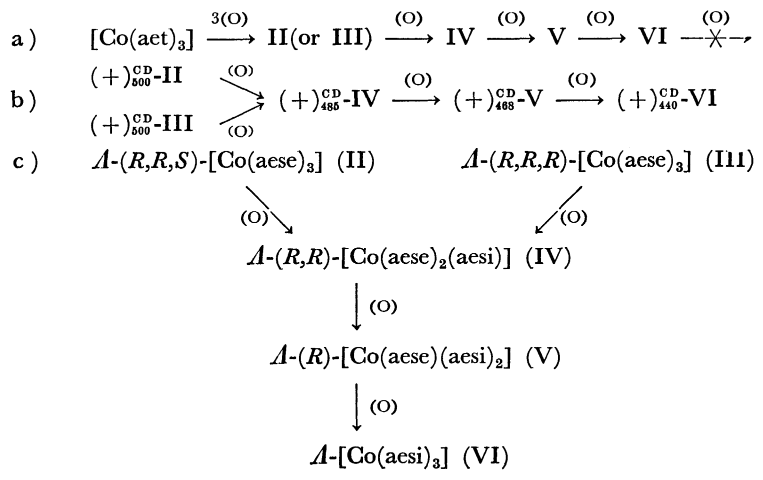
Fig. 1. Absorption spectra of A: $[\mathrm{Co(aet)_3}]$ (in aqueous solution), B: $[\mathrm{Co(aet)_3}]$ and C: $[\mathrm{Co(L\text{-}cym)_3}]$ (in solid diluted by MgO), and D: $[\mathrm{Co(L\text{-}cym)_3}]$ (in 0.1 mol dm^{-3} NaOH solution).

Table 1. Absorption data of the complexes

Complex	$\sigma_{\max}(\log\varepsilon)$[a]
$[\mathrm{Co(aet)_3}]$[b]	17.2, 22.7, 30.8$^{\mathrm{sh}}$, 36.4
$[\mathrm{Co(aet)_3}]$[c]	16.9, 22.4
$[\mathrm{Co(L\text{-}cym)_3}]$[c]	17.3, 22.2
$[\mathrm{Co(L\text{-}cym)_3}]$[d]	17.4(2.59), 22.9(2.98), 28.7(3.51)$^{\mathrm{sh}}$, 36.2(4.27)
$[\mathrm{Co(L\text{-}cys)_3}]^{3-}$	17.5(2.48), 22.5(2.96), 36.4(4.27)
$[\mathrm{Co(aese)_3}]$ (II or III)	21.5(2.92), 27.9(4.21), 37.0(3.76), 42.9(3.80)
$[\mathrm{Co(aese)_2(aesi)}]$	22.0(2.96)$^{\mathrm{sh}}$, 27.3(4.07), 35.6(4.09)
$[\mathrm{Co(aese)(aesi)_2}]$	22.0(2.86)$^{\mathrm{sh}}$, 27.0(3.91), 34.0(4.24)
$[\mathrm{Co(aesi)_3}]$	24.4(2.71), 32.8(4.23), 35.7(4.00)$^{\mathrm{sh}}$
$[\mathrm{Co(L\text{-}cyme)_3}]$ (II′ or III′)	20.9(3.07), 27.3(4.19), 36.1(3.76),
$[\mathrm{Co(L\text{-}cyme)_2(L\text{-}cymi)}]$	21.0(2.97)$^{\mathrm{sh}}$, 26.6(4.06), 35.0(4.07)
$[\mathrm{Co(L\text{-}cyme)(L\text{-}cymi)_2}]$[d]	21.6(2.94)$^{\mathrm{sh}}$, 26.7(4.01), 34.0(4.26)
$[\mathrm{Co(L\text{-}cymi)_3}]$[d]	24.5(3.15)$^{\mathrm{sh}}$, 32.7(4.43), 35.3(4.25)$^{\mathrm{sh}}$
$[\mathrm{Co(L\text{-}cysi)(aesi)_2}]^{-}$	24.4(2.89), 32.7(4.50), 35.5(4.32)$^{\mathrm{sh}}$
$[\mathrm{Co(L\text{-}cysi)_3}]^{3-}$	26.4(2.90), 32.5(4.43), 35.3(4.25)$^{\mathrm{sh}}$

a) Wave numbers are given in 10^3 cm^{-1} unit, log ε (in parentheses) in mol^{-1} dm^3 cm^{-1}, and sh means a shoulder. b) The absorption confficient of the complex could not be determined. c) Obtained by diffuse reflection method in 15000—25000 cm^{-1}. d) 0.1 mol dm^{-3} NaOH solution.

The CD spectra of complexes II, III, IV, V, and VI are shown in Figs. 3 and 4 and Table 2. The



Scheme 1.

a): Oxidation scheme of racemate complex, b): oxidation scheme of optically active complex, c): assignments.

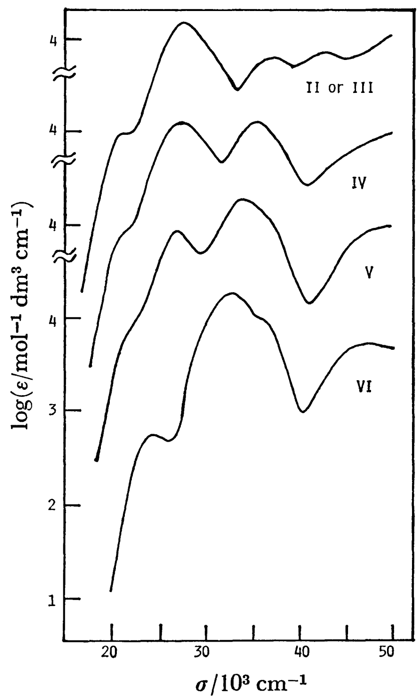


Fig. 2. Absorption spectra of the complexes $[\mathrm{Co(aese)}_n(\mathrm{aesi})_{3-n}]$: II or III ($n$=3), IV ($n$=2), V ($n$=1), and VI ($n$=0).

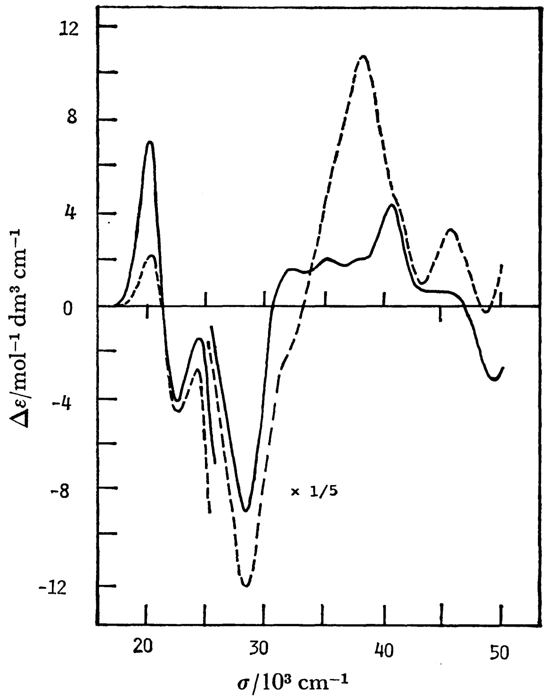


Fig. 3. CD spectra of the complexes $(+)^{\mathrm{CD}}_{500}$-II (——) and $(+)^{\mathrm{CD}}_{500}$-III (- - -).

complexes containing sulfenato groups should have two CD contributions, one from the configurational chirality based on the skew pair of chelate rings (Δ or Λ) and the other from the chirality based on the asymmetric sulfur donor atoms of sulfenato groups (*S* or *R*). The oxidation of Λ-$[\mathrm{Co(aet)(en)_2}]^{2+}$ produced two sulfenato diastereomers Λ-(*R*) and Λ-(*S*), whose absorption and CD spectra are shown in Fig. 5. Both complexes showed a positive CD band at the longest wavelength region of the first d-d absorption band, whereas the almost enantiomeric CD patterns appeared in the remaining regions. Similar results have been reported for the oxidation products of Λ-$[\mathrm{Co(L\text{-}cyse)(en)_2}]^+$;[3c] the configurational chirality dominates the CD band at the longest wavelength region of the first d-d absorption band but the CD bands at remaining regions depend on the chirality of sulfenato group. The complexes of $(+)^{\mathrm{CD}}_{500}$-II, $(+)^{\mathrm{CD}}_{500}$-III, $(+)^{\mathrm{CD}}_{485}$-IV, $(+)^{\mathrm{CD}}_{468}$-V, and $(+)^{\mathrm{CD}}_{440}$-VI are tentatively assigned to the Λ-configuration on the basis of the sign of the longest wavelength CD band (Figs. 3 and 4). The absolute configuration of sulfur center can be characterized on the basis of the CD sign in the sulfenato absorption band region at *ca.* 27000 cm^{-1}; the (*R*) and (*S*) configurations correspond to a negative and a positive band, respectively. The ^{13}C NMR spectrum of complex III showed only two resonances and that complex II six resonances (Fig. 6 and Table 3). Therefore, the *fac*(*S*)-Λ-(*R*,*R*,*R*) configuration can be assigned for Λ-III and the *fac*(*S*)-Λ-(*R*,*R*,*S*) one for Λ-II. The fact that the oxidation of the com-

TABLE 2. CD DATA OF THE COMPLEXES

Complex	$\sigma_{\mathrm{ext}}(\Delta\varepsilon)$[a)]
Λ-(R)-$[\mathrm{Co(aese)(en)_2}]^{2+}$	19.1(+1.39), 22.7(−2.84), 27.7(−16.90), 35.4(+11.48)
Λ-(S)-$[\mathrm{Co(aese)(en)_2}]^{2+}$	19.8(+2.60), 26.6(+11.71), 35.4(−11.59)
$(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(aese)_3}]$ (II)	20.0(+6.96), 22.4(−4.12), 28.1(−44.16), 31.8(+7.58), 35.0(+9.84), 38.0(+10.03), 40.4(+21.78)
$(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(aese)_3}]$ (III)	20.0(+2.20), 22.6(−4.56), 28.2(−60.31), 31.4(−4.56)$^{\mathrm{sh}}$, 38.2(+53.33), 41.0(+20.86)$^{\mathrm{sh}}$, 45.6(+16.46), 48.5(−0.85)
$(+)^{\mathrm{CD}}_{485}$-$[\mathrm{Co(aese)_2(aesi)}]$ (IV)	20.6(+1.46), 28.0(−14.04), 35.4(+12.64), 39.0(+11.84), 45.6(+4.90)
$(+)^{\mathrm{CD}}_{468}$-$[\mathrm{Co(aese)(aesi)_2}]$ (V)	21.4(+3.91), 26.4(−19.43), 31.0(−4.98)$^{\mathrm{sh}}$, 35.0(+18.45), 44.6(+7.15)
$(+)^{\mathrm{CD}}_{440}$-$[\mathrm{Co(aesi)_3}]$ (VI)	22.7(+2.04), 25.6(−2.39), 31.7(−10.86), 36.4(+7.86), 46.2(+5.13)
$[\mathrm{Co(L\text{-}cyme)_3}]$ (II′)	19.8(−6.26), 22.1(+4.60), 27.8(+45.10), 30.3(−8.12), 40.4(−13.08), 42.8(−5.32)$^{\mathrm{sh}}$
$[\mathrm{Co(L\text{-}cyme)_3}]$ (III′)	19.6(−0.71), 22.2(+3.90), 27.8(+49.30), 31.3(+7.01)$^{\mathrm{sh}}$, 34.5(−18.80)$^{\mathrm{sh}}$, 38.0(−28.60), 45.0(−19.70)
$[\mathrm{Co(L\text{-}cyme)_2(L\text{-}cymi)}]$ (IV′)	20.5(−2.43), 26.6(+24.24), 34.4(−21.74), 39.0(−11.25), 45.6(−7.39)
$[\mathrm{Co(L\text{-}cyme)(L\text{-}cymi)_2}]$[b)] (V′)	21.1(−3.04), 26.2(+21.17), 30.5(+6.76)$^{\mathrm{sh}}$, 34.4(−16.94), 38.3(−3.90)$^{\mathrm{sh}}$, 41.7(+6.43)
$[\mathrm{Co(L\text{-}cymi)_3}]$[b)] (VI′)	22.5(−2.91), 25.8(+5.74), 31.7(+15.11), 35.6(−14.81), 41.2(+6.04), 45.5(+2.42)
$[\mathrm{Co(aesi)_2(L\text{-}cysi)}]^-$	22.7(−2.87), 25.6(+3.21), 31.7(+15.51), 35.7(−13.31), 41.3(+7.59)
$[\mathrm{Co(L\text{-}cysi)_3}]^{3-}$	22.7(−3.16), 25.6(+3.48), 31.8(+17.98), 35.7(−17.20), 41.3(+7.59)

a) Wave numbers are given in $10^3\ \mathrm{cm^{-1}}$ unit, $\Delta\varepsilon$ (in parentheses) in $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$, and sh means a shoulder.
b) $0.1\ \mathrm{mol\,dm^{-3}}$ NaOH solution.

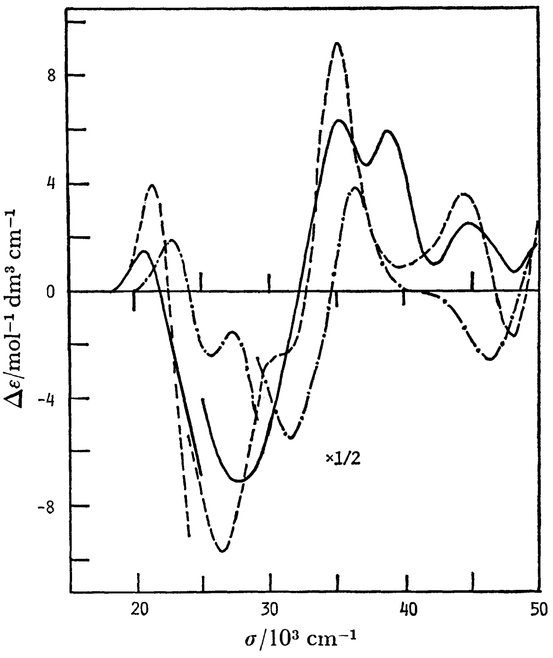


Fig. 4. CD spectra of the complexes $(+)^{\mathrm{CD}}_{485}$-IV (——), $(+)^{\mathrm{CD}}_{468}$-V (- - -), and $(+)^{\mathrm{CD}}_{440}$-VI (—·—).

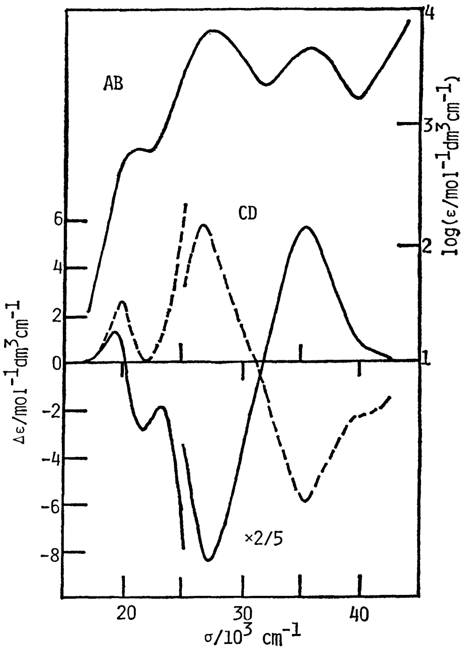


Fig. 5. Absorption and CD spectra of Λ-(R)-$[\mathrm{Co(aese)(en)_2}]^{2+}$ (——) and Λ-(S)-$[\mathrm{Co(aese)(en)_2}]^{2+}$ (- - -).

plexes Λ-(R,R,S)-II and Λ-(R,R,R)-III generated the same products leads to an unequivocal assignment of complexes IV and V; $(+)^{\mathrm{CD}}_{485}$-IV and $(+)^{\mathrm{CD}}_{468}$-V have Λ-(R,R) and Λ-(R) configurations, respectively. This assignment is consistent with the result of the X-ray single crystal structure analysis of d-$\mathrm{H_2tart}\cdot(+)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(aese)_3}]\cdot\mathrm{H_2O}$ in which the cobalt(III) complex III has the *fac*(S)-Λ-(R,R,R) structure.[10)]

$[\mathrm{Co(L\text{-}cyme)_n(L\text{-}cymi)_{3-n}}]$ (n=3, 2, 1, and 0). The absorption and CD spectra of complexes II′, III′, IV′, V′, and VI′ (Figs. 7 and 8, and Tables 1 and 2) are similar to those of $(-)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(aese)_3}]$ (II), $(-)^{\mathrm{CD}}_{500}$-$[\mathrm{Co(aese)_3}]$ (III), $(-)^{\mathrm{CD}}_{485}$-$[\mathrm{Co(aese)_2(aesi)}]$ (IV), $(-)^{\mathrm{CD}}_{468}$-$[\mathrm{Co(aese)(aesi)_2}]$ (V), and $(-)^{\mathrm{CD}}_{440}$-$[\mathrm{Co(aesi)_3}]$ (VI), respectively. Furthermore, complex III′ exhibited only four $^{13}\mathrm{C}$ NMR resonances (Table 3), which indicate that complex III′ has the *fac*(S)-Δ-(S,S,S) structure with $\mathrm{C_3}$ symmetry. The stepwise oxidation scheme of this system is entirely similar to Scheme 1. The assignment of structure is as follows; Δ-(R,S,S)-$[\mathrm{Co(L\text{-}cyme)_3}]$ for II′, Δ-(S,S,S)-$[\mathrm{Co(L\text{-}cyme)_3}]$ for III′, Δ-(S,S)-$[\mathrm{Co(L\text{-}cyme)_2(L\text{-}cymi)}]$ for IV′, Δ-(S)-[Co(L-

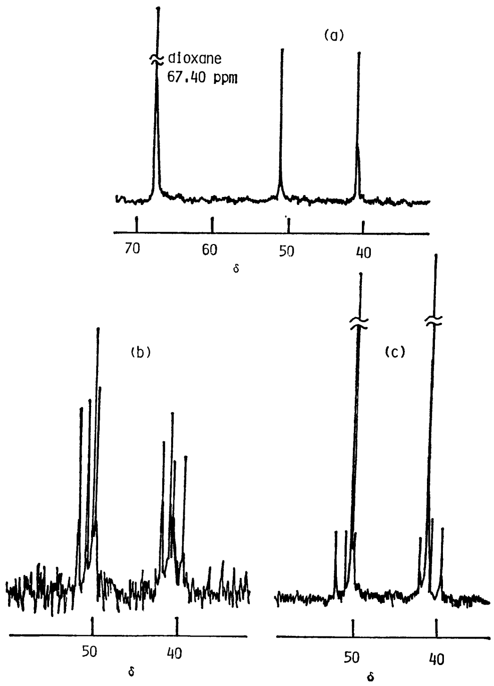


Fig. 6. ^{13}C NMR spectra of the tris(sulfenato) complexes.
(a): III, (b): II (partially isomerized), (c): II+III (1:1).

Table 3. Chemical shifts of ^{13}C NMR spectra[a)]

Complex	δ
[Co(aese)$_3$] (II)	40.35, 41.65, (42.17), 43.10, 51.69, (52.07), 52.76, 53.97
[Co(aese)$_3$] (III)	42.17, 52.07
[Co(L-cyme)$_3$] (III′)	53.58, 54.34, 55.47, 173.55

a) In D_2O containing *ca.* 80 mg of dioxane (δ=67.40) as an internal standard.

cyme)(L-cymi)$_2$] for V′, and Δ-[Co(L-cymi)$_3$] for VI′. Assuming that the ester group $-COOCH_3$ in L-cym$^-$, L-cyme$^-$, or L-cymi$^-$ ligand takes an equatorial orientation, the chelate ring conformations of Δ- and Λ-complexes become (*lel*)$_3$ and (*ob*)$_3$, respectively. Because no Λ-isomer was detected in this [Co(L-cyme)$_n$-(L-cymi)$_{3-n}$] system, the experimental result means that the Δ-(*lel*)$_3$ conformation is of primary importance to the stability of these complexes.

[Co(L-cysi)$_3$]$^{3-}$ and [Co(aesi)$_2$(L-cysi)]$^-$ Complexes. The absorption and CD spectra of the complexes, $(-)^{CD}_{440}$-[Co(aesi)$_3$], $(-)^{CD}_{440}$-[Co(L-cysi)$_3$]$^{3-}$, and $(-)^{CD}_{440}$-[Co(aesi)$_2$(L-cysi)]$^-$, are shown in Fig. 9, and Tables 1 and 2. These three complexes and $(-)^{CD}_{440}$-[Co(L-cymi)$_3$] show quite similar absorption and CD spectra to one another. Since $(-)^{CD}_{440}$-[Co(aesi)$_3$] and $(-)^{CD}_{440}$-[Co(L-cymi)$_3$] complexes were assigned to the *fac*(*S*)-Δ structure as described above, two remaining complexes can be assigned reasonably to the same *fac*(*S*)-Δ configuration. The geometry of [Co(L-cysi)$_3$]$^{3-}$ assigned from ^{13}C NMR spectrum[13)] is identical with the present results. Thus, it is concluded that the *ac*(*S*) geometry is preferentially formed for the [Co(N)$_3$(S)$_3$] type complexes and Δ-configuration is significantly stable for the complexes containing L-cysteine or its derivatives.

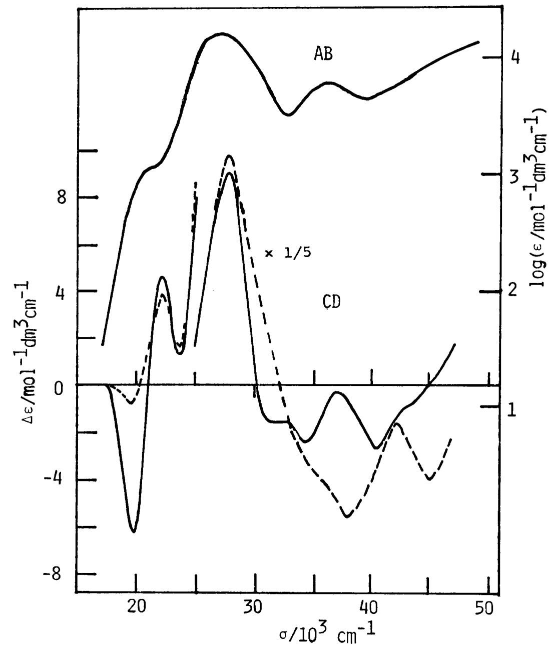


Fig. 7. Absorption and CD spectra of the complexes II′ (——) and III′ (- - -).

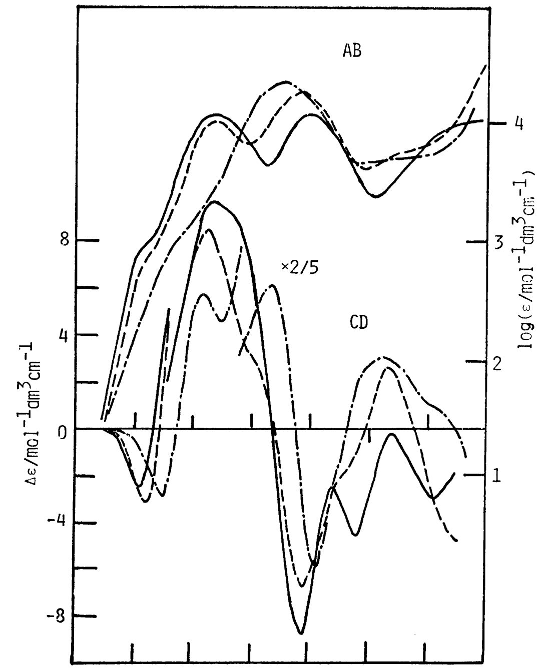


Fig. 8. Absorption and CD spectra of the complexes IV′ (——) in water; V′ (—) and VI′ (—·—) in 0.1 mol dm^{-3} NaOH solution.

Stereoselectivity of Chiral Sulfenato Sulfur Atoms. The $R \rightleftarrows S$ interconversion of sulfenato group was reported in diluted solution of Λ-(*R*)- or Λ-(*S*)-[Co(L-cyse-*N*,*S*)(en)$_2$]$^+$ complex and the equilibrium ratio *S*/*R* became 3.[3c)] The result was explained as fol-

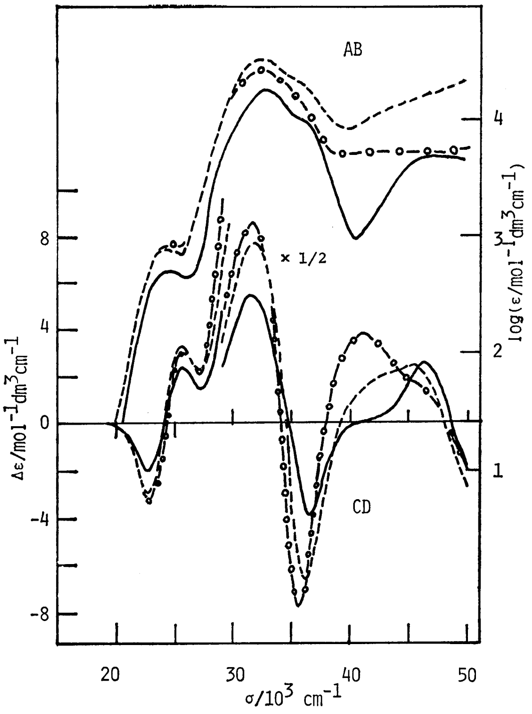


Fig. 9. Absorption and CD spectra of the tris(sulfinato) complexes (−)$^{CD}_{440}$-VI (——), [Co(aesi)$_2$(L-cysi)]$^-$ (- - -), and [Co(L-cysi)$_3$]$^{3-}$ (—○—).

lows; the cobalt–sulfur bond breaking and re-forming occurred to produce the (*S*) configuration, which has lesser steric hindrance toward the ethylenediamine chelate ring because of an equatorial orientation of carboxylate than the (*R*) one. Present systems also showed such interconversions. Complexes II and II′ partially isomerized into complexes III and III′, respectively, during the crystallization in a vacuum rotary evaporator at *ca.* 8 °C. This fact was confirmed by ^{13}C NMR spectra. The spectrum of crystallized complex II was identical to that of a mixture of complexes II and III (Fig. 6 and Table 3). This result was supported by the chromatographic separation. The isomerization of Λ-(*R*,*R*,*S*) configuration into Λ-(*R*,*R*,*R*) one occurs easily but the reverse does not. Similarily, the crystallized complex II′ was a mixture of complexes II′ and III′, this fact being detected by the ^{13}C NMR spectra (Table 3) and chromatographic separation. The isomerization of Δ-(*R*,*S*,*S*) configuration into Δ-(*S*,*S*,*S*) one takes place but its reverse change does not occur. Other complexes, Λ-(*R*,*R*)-[Co(aese)$_2$(aesi)], Λ-(*R*)-[Co(aese)$_2$(aesi)], Δ-(*S*,*S*)-[Co(L-cyme)$_2$(L-cymi)], and Δ-(*S*)-[Co(L-cyme)(L-cymi)$_2$], showed no change even after crystallization.

Figure 10 shows the view of *fac*(*S*)-Δ-[Co(L-cym)$_3$] projected down the threefold axis. There are six lone pairs on the three sulfur donor atoms, they being divided into two groups, three axial and three equatorial. In the first oxidation process from *fac*(*S*)-[Co(L-cym)$_3$] to *fac*(*S*)-[Co(L-cyme)(L-cym)$_2$], the (*R*) and (*S*) configurations will be formed. In the second and third oxidation steps of the remaining sulfur atoms for (*R*)-[Co(L-cyme)(L-cym)$_2$], however, oxygen atom will take preferentially the equatorial position rather than the axial one to avoid the steric interaction with the first sulfenato oxygen. Consequently the (*R*,*S*,*S*) and (*S*,*S*,*S*) configurations will be formed. The consideration agrees with the fact that no Δ-(*R*,*R*,*S*) and Δ-(*R*,*R*,*R*) isomers occurred in Δ-[Co(L-cyme)$_3$]. The isomerization from Δ-(*R*,*S*,*S*) (II′) to Δ-(*S*,*S*,*S*) (III′) can be also explained; in the Δ-(*S*,*S*,*S*) isomer, all sulfenato oxygens occupy the equatorial positions and the mutual repulsion among them will be weak as compared with Δ-(*R*,*S*,*S*) isomer. This argument apparently conflicts with the experimental result that the yield of II′ is significantly higher than that of III′. However, the formation ratio does not reflect the relative stability because the equilibrium state was not realized in our experiment owing to very short reaction time. A similar argument can be also applied to *fac*(*S*)-Λ-[Co(aese)$_3$], in which the Λ-(*R*,*R*,*R*) configuration becomes the most stable species.

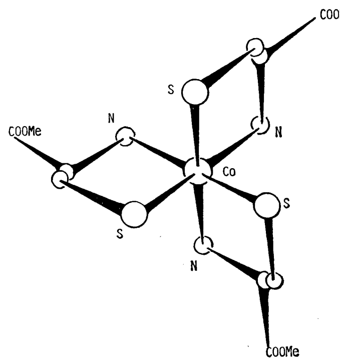


Fig. 10. A perspective view of the *fac*(*S*)-Δ-(*lel*)$_3$-[Co(L-cym)$_3$] projected down the threefold axis of the complex, the axial or equatorial group on sulfur lone pairs denotes parallel or perpendicular one to the C_3 axis, respectively.

It has been shown that the oxidation of [Co(L-cyse)(en)$_2$]$^+$ or [Co(L-pene)(en)$_2$]$^+$ complex proceeds approximately 10^3 times slower than that of the corresponding thiolato complex.[3c)] In the present systems of [Co(L-cym)$_3$] and [Co(aet)$_3$], significant amounts of [Co(L-cyme)$_2$(L-cymi)] (*ca.* 50%) and [Co(aese)$_2$(aesi)] (*ca.* 30%) were nevertheless derived by the very short reaction time, further oxidation products, V′ and VI′ or V and VI, being in small yields. Product IV or IV′ is regarded as the superimposed one of II and III or II′ and III′, respectively. Four oxygen atoms occupy three equatorial and one axial positions and two axial positions remain unoccupied in both complexes. Therefore, the steric hindrance in IV (or IV′) is not largely different from that in II and III (or II′ and III′). On the other hand, complexes V and VI (or V′ and VI′) require the further oxygen attack to the remaining axial positions. Such a process seems to have a large energy barrier.

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