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Synthesis and Optical Resolution of $[Rh^{III}(S)_3(N)_3]$ Type Complexes Containing a Thiolato, Sulfenato, or Sulfinato Donor Group

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Rhodium(III) complexes, $[Rh(SCH_2CH_2NH_2)_3]$ and $[Rh\{S(O)CH_2CH_2NH_2\}_n\{S(O)_2CH_2CH_2NH_2\}_{3-n}]$ (n=3, 2, 1, and 0), were prepared and optically resolved by means of column chromatography or preferential crystallization of diastereomeric molecular compound with (R,R)-tartaric acid, d-$C_4H_6O_6\cdot(-)^{\rm CD}_{300}$-$[Rh\{S(O)CH_2CH_2NH_2\}_3]\cdot H_2O$ or d-$C_4H_6O_6\cdot(+)^{\rm CD}_{300}$-$[Rh\{S(O)CH_2CH_2NH_2\}_2\{S(O)_2CH_2CH_2NH_2\}]$. All the present complexes have only the *fac*(S) geometry. The (R) configuration of sulfenato group is more stable than the (S) one in the Λ-isomer.

In a previous paper[1)] we have reported the synthesis, optical resolution, and stereoselectivity of neutral cobalt(III) complexes, $[Co(aet)_3]$ and $[Co(aese)_n(aesi)_{3-n}]$ (n=3, 2, 1, and 0).[2)] These S-bonded sulfenato and sulfinato cobalt(III) complexes showed several unique chemical and spectrochemical behaviors. In particular, one of the isomers of $[Co(aese)_3]$ was resolved *via* diastereomeric molecular compound with (R,R)-tartaric acid. It is interesting to compare the properties of cobalt(III) complexes with those of the corresponding rhodium(III) complexes, because there is a general tendency for the metals of the second transition series to exhibit a greater affinity toward sulfur donors than do the metals of the first transition series.[3)] No optically active sulfenato or sulfinato complexes has so far been reported for rhodium(III). This paper is concerned with the preparation, optical resolution, and stereochemistry of $[Rh(aet)_3]$ and $[Rh(aese)_n(aesi)_{3-n}]$ (n=3, 2, 1, and 0).

Experimental

Preparation, Separation, and Optical Resolution of Complexes. (1) $[Rh(aet)_3]$: To a solution of 3.0 g (39 mmol) of 2-aminoethanethiol and 1.5 g (38 mmol) of sodium hydroxide in 20 cm³ of water was added 2.0 g (9.6 mmol) of $RhCl_3$ and the mixture was stirred at 95 °C for 4 h. The white curdy precipitate with a yellow tint (1.5 g, 47%) was filtered and washed with water. Found: C, 21.52; H, 5.41; N, 12.59%. Calcd for $[Rh(aet)_3]=C_6H_{18}N_3S_3Rh$: C, 21.75; H, 5.48; N, 12.68%.

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

To a suspension of 1.0 g (3.0 mmol) of $[Rh(aet)_3]$ in 20 cm³ of water was added 20 cm³ (9.0 mmol) of 1.5% aqueous H_2O_2 with stirring below 5 °C, leading to a faint yellow solution. On addition of acetone (100 cm³) and diethyl ether (200 cm³), a faint yellow precipitate (1.2 g) appeared. This was dissolved in a small amount of water, adsorbed on a column of anion-exchange resin {QAE Sephadex A-25, (R,R)-tartrate form} and eluted with water. The eluates were collected with five cm³ portions. Four complexes, I, II, III, and IV, were eluted in this order. At this stage all complexes were partially resolved: The earlier eluted fractions of each complex showed positive CD at the longest wavelength regon of the first d-d absorption band.

Combined eluate of each the complex was concentrated in a vacuum rotary evaporator at *ca.* 8 °C to give the precipitate. The precipitate was collected by filtration and washed with ethanol–ether (1:1). The complex I partially isomerized into the complex II during the crystallization. The isomerization was confirmed by column chromatography and the ¹³C NMR spectra. The sparingly soluble white complex V was obtained *via* oxidation of $[Rh(aet)_3]$ by an excess of 30% H_2O_2. Further oxidation of each complex I, II, III, or IV by dilute H_2O_2 showed that the oxidation process is stepwise in a series of I (or II)→III→IV→V and the complex V was the final oxidation product. On the basis of the absorption measurements and elemental analyses, the complexes I (and II), III, IV, and V were assigned to n=3, 2, 1, and 0 in $[Rh(aese)_n(aesi)_{3-n}]$ series, respectively. Found for I: C, 15.76; H, 5.60; N, 9.20%. Calcd for $[Rh(aese)_3]\cdot 4H_2O=C_6H_{26}N_3O_7S_3Rh$: C, 15.97; H, 5.80; N, 9.31%. Found for II: C, 16.75; H, 5.45; N, 9.76%. Calcd for $[Rh(aese)_3]\cdot 3H_2O=C_6H_{24}N_3O_6S_3Rh$: C, 16.63; H, 5.58; N, 9.70%. Found for III: C, 16.77; H, 5.14; N, 9.85%. Calcd for $[Rh(aese)_2(aesi)]\cdot 2H_2O=C_6H_{22}N_3O_6S_3Rh$: C, 16.71; H, 5.14; N, 9.74%. Found for IV: C, 16.52; H, 4.66; N, 9.52%. Calcd for $[Rh(aese)(aesi)_2]\cdot 1.5H_2O=C_6H_{21}N_3O_{6.5}S_3Rh$: C, 16.44; H, 4.83; N, 9.59%. Found for V: C, 16.77; H, 4.32; N, 9.58%. Calcd for $[Rh(aesi)_3]\cdot 0.5H_2O=C_6H_{19}N_3O_{6.5}S_3Rh$: C, 16.51; H, 4.39; N, 9.63%.

(3) Optical Resolution: The racemate II, $[Rh(aese)_3]\cdot 3H_2O$ (1.0 g, 2.3 mmol), or the racemate III, $[Rh(aese)_2(aesi)]\cdot 2H_2O$ (1.0 g, 2.3 mmol), was dissolved in an ethanol-water (2:1) mixture and then (R,R)-tartaric acid (0.35 g, 2.3 mmol) was added to the solution, and after a few minutes, a slightly yellow diastereomeric molecular compound, d-$C_4H_6O_6\cdot(-)^{\rm CD}_{300}$-$[Rh(aese)_3]\cdot H_2O$ (II*) or a white diastereomeric molecular compound, d-$C_4H_6O_6\cdot(+)^{\rm CD}_{300}$-$[Rh(aese)_2(aesi)]$ (III*) began to deposit, respectively. The crystals were filtered and washed with ethanol. Found for II*: C, 21.64; H, 4.71; N, 7.55%. Calcd for d-$C_4H_6O_6\cdot(-)^{\rm CD}_{300}$-$[Rh(aese)_3]\cdot H_2O=C_{10}H_{26}N_3O_{10}S_3Rh$: C, 21.95; H, 4.79; N, 7.67%. Found for III*: C, 21.79; H, 4.44; N, 7.72%. Calcd for d-$C_4H_6O_6\cdot(+)^{\rm CD}_{300}$-$[Rh(aese)_2(aesi)]=C_{10}H_{24}N_3O_{10}S_3Rh$: C, 22.02; H, 4.44; N, 7.70%.

The diastereomeric molecular compound, II* or III*, was converted into $(-)^{\rm CD}_{300}$-II or $(+)^{\rm CD}_{300}$-III by treating with an equimolar amount of $Ca(OH)_2$. The CD spectrum was measured for the filtrate whose concentration was calculated from the measured absorbance using the extinction coefficient of the corresponding racemate.

Optically pure complexes IV and V could be prepared by the oxidation of the optically active complex II or III, $(-)^{\rm CD}_{300}$-$[Rh(aese)_3]$ or $(+)^{\rm CD}_{300}$-$[Rh(aese)_2(aesi)]$. The oxidation product of $(-)^{\rm CD}_{300}$-I, which was obtained by the column chromatography described above, was the same as that of $(-)^{\rm CD}_{300}$-II.

(4) $[Co(aese)_3]$: The *rac*{Δ-(S,S,S)/Λ-(R,R,R)}-$[Co(aese)_3]$ was obtained by the previously reported procedure.[1)]

Measurements. The visible and ultraviolet absorption spectra were measured on a Hitachi 330 spectrophotometer. The CD spectra were recorded on a JASCO MOE-1 spectropolarimeter and the MCD spectra were measured on the same instrument in 1.5 T magnetic field. The absorption, CD and MCD measurements of the complexes were made in aqueous solutions at room temperature. The ^{13}C NMR spectra were obtained with a Varian XL-100-15 NMR spectrometer in D_2O containing dioxane as an internal standard.

Results and Discussion

Geometry of [Rh(aet)$_3$]. The absorption spectra and data of [Rh(aet)$_3$] are shown in Fig. 1 and Table 1, respectively. The corresponding cobalt(III) complex [Co(aet)$_3$] takes the *fac(S)* geometry and its absorption peaks appear at 17200, 22700, and 36400 cm^{-1}, which were assigned to the first and second spin-allowed d-d transitions[1,4] ($^1T_1 \leftarrow {}^1A_1$), ($^1T_2 \leftarrow {}^1A_1$), and Co(σ^*)←S(σ) LMCT transition, respectively.[1,5] Analogously the absorption bands of [Rh(aet)$_3$] at 25000, 29500, and 44200 cm^{-1} are assigned to $^1T_1 \leftarrow {}^1A_1$, $^1T_2 \leftarrow {}^1A_1$, and Rh(σ^*)←S(σ) LMCT transitions, respectively.[4,5] The complex II, which was the oxidation product of [Rh(aet)$_3$], showed two ^{13}C NMR resonances, and therefore has C_3 symmetry (Table 2). As will be shown later both the complexes I and II have the *fac(S)* geometry. Therefore, it is concluded that the starting thiolato complex [Rh(aet)$_3$] exists in the *fac(S)* form.

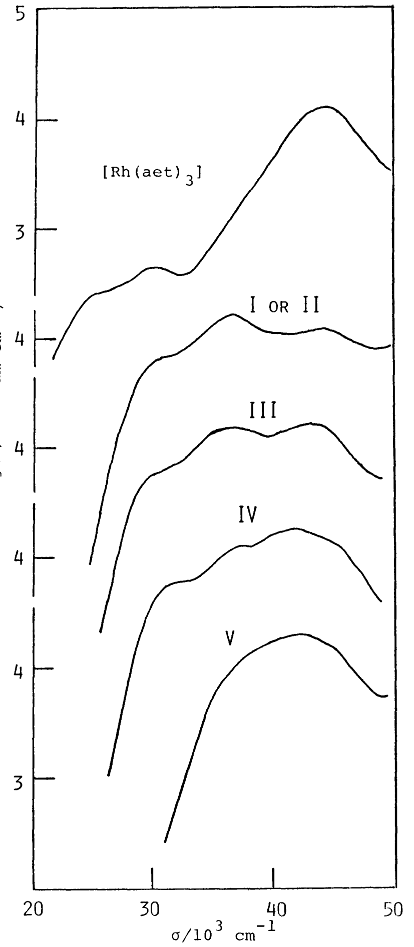

Fig. 1. Absorption spectra of [Rh(aet)$_3$] and [Rh(aese)$_n$(aesi)$_{3-n}$]: I or II (n=3), III (n=2), IV (n=1), and V (n=0).

Characterization of [Rh(aese)$_n$(aesi)$_{3-n}$] (n=3, 2, 1, and 0). The absorption spectra of the complexes for the series are shown in Fig. 1. All complexes showed an intense band in 42000—44000 cm^{-1} region, which is assigned to the Rh(σ^*)←S(σ) LMCT transition. The complexes I—IV show another intense band at *ca.* 36000 cm^{-1} whose molar absorption coefficient decreases successively with the decrease of the number of sulfenato groups. Therefore, the bands at *ca.* 36000 cm^{-1} can be assigned to LMCT Rh(σ^*)←sulfenato group. The d-d absorption bands of these oxidation products are somewhat obscured by the intense LMCT

TABLE 1. ABSORPTION AND CD SPECTRAL DATA

Complex	$\sigma_{max}(\log\varepsilon)^{a)}$	$\sigma_{ext}(\Delta\varepsilon)^{b)}$
[Rh(aet)$_3$]	25.0(2.5)^{sh}	
	29.5(2.7)	
	44.2(4.2)	
$(-)^{CD}_{300}$-[Rh(aese)$_3$] (I)	30.9(3.86)^{sh}	30.3(−7.69)^{sh}
	36.1(4.21)	35.3(−30.6)
		38.5(−16.1)
	43.6(4.06)	42.2(+15.5)
$(-)^{CD}_{300}$-[Rh(aese)$_3$] (II)	30.9(3.86)^{sh}	30.3(−15.5)^{sh}
	36.1(4.21)	35.5(−57.6)
	43.6(4.06)	43.9(+61.8)
$(-)^{CD}_{300}$-[Rh(aese)$_2$(aesi)]	31.3(3.83)^{sh}	30.7(−15.5)^{sh}
(III)	36.1(4.11)	35.1(−40.0)
		37.3(−27.7)
	43.1(4.23)	43.1(+38.5)
		49.5(+35.0)
$(-)^{CD}_{300}$-[Rh(aese)(aesi)$_2$]	32.0(3.75)^{sh}	32.3(−16.7)^{sh}
(IV)	37.0(4.07)	35.1(−25.2)
		38.5(−9.23)^{sh}
	42.4(4.25)	41.0(+5.65)^{sh}
		44.4(+11.1)
$(-)^{CD}_{300}$-[Rh(aesi)$_3$] (V)		35.7(−11.4)^{sh}
		39.1(−18.6)
	41.7(4.29)	44.1(+15.5)
[Co(aese)$_3$]	13.2(0.6)$^{sh,c)}$	
	21.5(2.92)	
	27.9(4.21)	
	37.0(3.76)	

a, b) Wave numbers are given in 10^3 cm^{-1} unit, log ε or Δε (in parentheses) in mol^{-1} dm^3 cm^{-1}, and sh means a shoulder. c) This is assigned to the spin-forbidden ligand field transition, $^3T_1 \leftarrow {}^1A_1$.[4]

TABLE 2. CHEMICAL SHIFTS OF ^{13}C NMR SPECTRA$^{a)}$

Complex	δ
[Rh(aese)$_3$] (I)	40.53, 40.69, (41.07),$^{b)}$ 41.88, 50.93, (51.31),$^{b)}$ 51.91, 52.98
[Rh(aese)$_3$] (II)	41.07, 51.31

a) In D_2O containing dioxane (δ=67.40) as an internal standard. b) The signals are resulted from the partial isomerization of the complex I into II.

TABLE 3. MCD SPECTRAL DATA

Complex	*rac*{*Δ-(S,S,S)/Λ-(R,R,R)*}-[Co(aese)$_3$]	*rac*-[Rh(aese)$_3$] (II)
$\sigma_{\rm ext}(\Delta\varepsilon_{\rm M})$[a]	12.7(+0.00052)	
	14.4(−0.00022)	
	17.7(−0.0013)	
	21.1(+0.123)	29.9(+0.180)
	25.3(−0.689)	34.3(−1.08)
	27.4(+0.434)	37.7(+0.507)
	30.0(−0.244)	42.6(−0.360)
	35.1(−0.488)	
	40.0(−0.651)	

a) Wave numbers are given in 10^3 cm^{-1} unit, $\Delta\varepsilon_{\rm M}$ (in parentheses) in mol^{-1} dm^3 cm^{-1} T^{-1}.

bands. The MCD pattern of the racemic complex II is similar to that of *rac*{*Δ-(S,S,S)/Λ-(R,R,R)*}-[Co(aese)$_3$] in the spin-allowed d-d and LMCT region (Table 3 and Fig. 2). The *Λ-(R,R,R)*-[Co(aese)$_3$] showed the CD extrema at 20000 cm^{-1} ($\Delta\varepsilon=+6.96$) and 22400 cm^{-1} ($\Delta\varepsilon=-4.12$) in the ligand field transition region[1] and the corresponding MCD extremum at 21100 cm^{-1} ($\Delta\varepsilon_{\rm M}=+0.12$). The MCD extremum of the rhodium(III) complex *rac*-II at 29900 cm^{-1} ($\Delta\varepsilon_{\rm M}=+0.18$) is assigned to the ligand field transition on the analogy of the MCD pattern. The shoulder at *ca.* 30000 cm^{-1} of the complex III or IV in Fig. 3 is assigned to the ligand field transition band. A similar band of [Rh(aesi)$_3$] (V) was quite obscured in the absorption spectrum but the CD shoulder exists at 35700 cm^{-1}.

The complexes containing the 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 atom of sulfenato group (*S* or *R*). Since the complex $(-)^{\rm CD}_{300}$-II has C$_3$ symmetry as determined from the ^{13}C NMR spectrum, the structure is one of the following four with *fac(S)* geometry, *Δ-(R,R,R)*, *Δ-(S,S,S)*, *Λ-(R,R,R)*, or *Λ-(S,*-

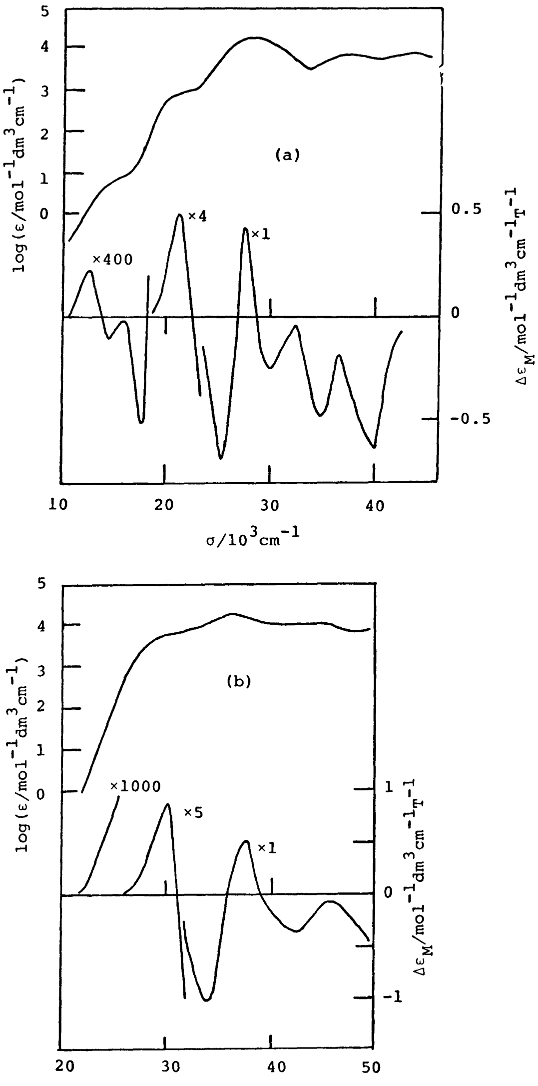

Fig. 2. Absorption and MCD spectra of (a): *rac*{*Δ-(S,S,S)/Λ-(R,R,R)*}-[Co(aese)$_3$] and (b): the complex II.

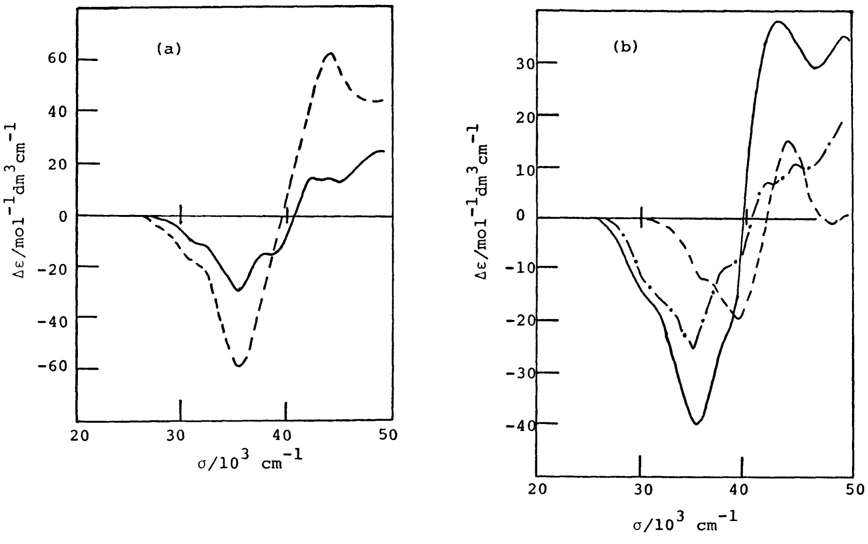

Fig. 3. CD spectra of the complexes (a): $(-)^{\rm CD}_{300}$-I (——), and $(-)^{\rm CD}_{300}$-II (---), and (b): $(-)^{\rm CD}_{300}$-III (——), $(-)^{\rm CD}_{300}$-IV (—·—), and $(-)^{\rm CD}_{300}$-V (---).

S,S). The absolute configurations of sulfenato groups can be deduced from the cobalt(III) complexes by the CD sign and intensity ($\Delta\varepsilon$) in the sulfenato LMCT region.[1,6] For example, a positive CD band ($\Delta\varepsilon = +11.71$) was observed in the sulfenato LMCT reigon (*ca.* 27000 cm^{-1}) for *Λ-(S)*-$[\mathrm{Co(aese)(en)_2}]^{2+}$, and a negative one for the *Λ-(R)* complex.[1] Assuming the same criterion for the sulfenato rhodium(III) complexes, it can be concluded that all the complexes $(-)^{\rm CD}_{300}$-I, $(-)^{\rm CD}_{300}$-II, $(-)^{\rm CD}_{300}$-III, and $(-)^{\rm CD}_{300}$-IV have mainly (*R*) sulfenato groups, because the $\Delta\varepsilon_{\rm ext}$ values were -30.6, -57.6, -40.0, and -21.2 for $(-)^{\rm CD}_{300}$-I, $(-)^{\rm CD}_{300}$-II, $(-)^{\rm CD}_{300}$-III, and $(-)^{\rm CD}_{300}$-IV, respectively. The oxidation of the complexes $(-)^{\rm CD}_{300}$-I and $(-)^{\rm CD}_{300}$-II gave the same product $(-)^{\rm CD}_{300}$-III, which in succession gave the $(-)^{\rm CD}_{300}$-IV. These observations lead to the assignments *(R,R,S)*, *(R,R,R)*, *(R,R)*, and *(R)* for $(-)^{\rm CD}_{300}$-I, $(-)^{\rm CD}_{300}$-II, $(-)^{\rm CD}_{300}$-III, and $(-)^{\rm CD}_{300}$-IV, respectively. As in the case of *fac(S)*-$[\mathrm{Co(aese)_3}]$,[1] three sulfenato oxygen atoms of the *Δ-(R,R,R)* isomer should take the crowded axial positions on the *fac(S)* plane, whereas the oxygen atoms of the *Λ-(R,R,R)* isomer occupy the less-crowded equatorial ones. Therefore, the *Λ-(R,R,R)* configuration is desirable as the structure of the complex $(-)^{\rm CD}_{300}$-II rather than the *Δ-(R,R,R)* one. The latter isomer was apparently undetectable in the preparation of *fac-(S)*-$[\mathrm{Rh(aese)_3}]$. In conclusion the complex $(-)^{\rm CD}_{300}$-I, $(-)^{\rm CD}_{300}$-II, $(-)^{\rm CD}_{300}$-III, $(-)^{\rm CD}_{300}$-IV, or $(-)^{\rm CD}_{300}$-V has *Λ-(R,R,S)*, *Λ-(R,R,R)*, *Λ-(R,R)*, *Λ-(R)*, or *Λ* configuration, respectively. These assignments rationalize the isomerization of $(-)^{\rm CD}_{300}$-I into $(-)^{\rm CD}_{300}$-II in the aqueous solutions, because the latter having less-crowded configuration than the former. The configurational chirality of $[\mathrm{Co(aese)}_n\mathrm{(aesi)}_{3-n}]$ ($n=3$, 2, 1, or 0) was assigned on the basis of the sign of the longest wavelength CD band: the *Λ*-configuration show a positive CD.[1] It is noteworthy that this relation is reversed in the present complexes $[\mathrm{Rh(aese)}_n\mathrm{(aesi)}_{3-n}]$ ($n=3$, 2, 1, and 0). This is probably due to the close overlapping of the d-d and LMCT bands (both in absorption and CD spectra) in the rhodium(III) complexes.

The column chromatographic behaviors also support the above chirality assignment. It the separation using QAE-Sephadex A-25 {(*R*,*R*)-tratrate form} with water as eluent, the *Λ* isomers were eluted more rapidly than the corresponding *Δ* ones in both the cobalt(III) and rhodium(III) complexes.

The optical resolution *via* diastereomeric molecular compound with *d*-tartaric acid was successful for the two kinds of rhodium(III) complexes, *fac(S)*-$[\mathrm{Rh(aese)_3}]$ and *fac(S)*-$[\mathrm{Rh(aese)_2(aesi)}]$. The less soluble diastereomeric molecular compound *d*-$\mathrm{C_4H_6O_6}\cdot(-)^{\rm CD}_{300}$-$[\mathrm{Rh(aese)_3}]\cdot\mathrm{H_2O}$ has the same composition as the corresponding cobalt(III) compound *d*-$\mathrm{C_4H_6O_6}\cdot(+)^{\rm CD}_{500}$-$[\mathrm{Co(aese)_3}]\cdot\mathrm{H_2O}$. Since the X-ray diffraction study of the latter compound showed that the contains the *fac(S)-Λ-(R,R,R)* isomer,[7] it seems that the configuration of $(-)^{\rm CD}_{300}$-$[\mathrm{Rh(aese)_3}]$ (III) is *fac(S)-Λ-(R,R,R)*. This is in accord with the above assignment from CD. The another molecular compound containing *fac(S)*-$[\mathrm{M(aese)_2(aesi)}]$ was found only in the rhodium(III) series and not in the cobalt(III) series. It remains puzzling that the isomer which forms the less soluble diastereomeric molecular compound with *d*-tartaric acid has the *Δ-(S,S)* configuration for the $[\mathrm{Rh(aese)_2(aesi)}]$ complex in contrast to the case of $[\mathrm{Rh(aese)_3}]$, for which the less soluble molecular compound contains the *Λ-(R,R,R)* isomer.

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2) Abbreviations used for ligands are as follows: Haet, 2-aminoethanethiol $\mathrm{HSCH_2CH_2NH_2}$; Haese, 2-aminoethanesulfenic acid $\mathrm{HS(O)CH_2CH_2NH_2}$; Haesi, 2-aminoethanesulfinic acid $\mathrm{HS(O)_2CH_2CH_2NH_2}$.

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4) The assignments of d-d bands are in an approximation of $\mathrm{O_h}$ symmetry.

5) LMCT means ligand-to-metal charge transfer.

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