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# Preparation and Some Properties of $[Co^{II or III}\{Rh^{III}$ (aet or L-cys-*N*,*S*)$_3\}_2]$-Type S-Bridged Trinuclear Complexes

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(Received August 25, 1989)

The reactions of *fac*-[Rh(aet)$_3$] (aet=2-aminoethanethiolate) or ΔLLL-*fac*-[Rh(L-cys-*N*,*S*)$_3]^{3-}$ (L-cys=L-cysteinate) with $[CoCl(NH_3)_5]^{2+}$ produced $[Co^{III}\{Rh^{III}$ (aet or L-cys-*N*,*S*)$_3\}_2]^{3+or3-}$, while the reactions with $Co^{2+}$ formed $[Co^{II}\{Rh^{III}$(aet or L-cys-*N*,*S*)$_3\}_2]^{2+or4-}$ which were oxidized to give $[Co^{III}\{Rh^{III}$ (aet or L-cys-*N*,*S*)$_3\}_2]^{3+or3-}$. These complexes were optically resolved or separated by fractional crystallization or column chromatography, and characterized from their absorption, CD and $^{13}$C NMR spectra. The reactions of *fac*-ΔLLL-[Rh(L-cys-*N*,*S*)$_3]^{3-}$ with $[CoCl(NH_3)_5]^{2+}$ or $Co^{2+}$ at room temperature proceeded with retention of the starting ΔLLL configuration to give the ΔLLLΔLLL isomer, while the reaction with $Co^{2+}$ at high temperature (ca. 95 °C) was accompanied by inversion to form the ΔLLLΛLLL, ΛLLLΛLLL, and ΔLLLΔLLL isomers. Cyclic voltammetric measurements of $[Co^{III}\{Rh^{III}$(aet or L-cys-*N*,*S*)$_3\}_2]^{3+or3-}$ in water showed a quasi-reversible redox couple corresponding to the central Co(III)/(II) at ca. −0.3 V vs. Ag/AgCl. Their absorption and CD spectra and cyclic voltammograms are discussed in comparison with those of the corresponding $[Co^{III}\{Co^{III}$ (aet or L-cys-*N*,*S*)$_3\}_2]^{3+or3-}$.

The facially arranged thiolato atoms in *fac*-[Co(aet)$_3$] (aet=2-aminoethanethiolate, $NH_2CH_2CH_2S^-$) or *fac*-[Co(L-cys-*N*,*S*)$_3]^{3-}$ (L-cys=L-cysteinate, $NH_2CH(COO^-)$-$CH_2S^-$) function as a terdentate ligand to a variety of transition metal ions forming the S-bridged trinuclear complexes, $[M\{Co^{III}$(aet or L-cys-*N*,*S*)$_3\}_2]^{n+ or n-}$ (M= Fe(III), Co(III), Ni(II), Cu(I), Cu(II), Zn(II), Ru(III), Pb(II)).[1–12] These complexes exhibited characteristic absorption and CD spectra of the trinuclear structure. In the reaction of ΔLLL-*fac*-[Co(L-cys-*N*,*S*)$_3]^{3-}$ with $[CoCl(NH_3)_5]^{2+}$, ΔLLLΔLLL-$[Co^{III}\{Co^{III}$(L-cys-*N*,*S*)$_3\}_2]^{3-}$ was selectively formed while retaining starting ΔLLL configuration, though the reaction with $Co^{2+}$ was accompanied by inversion to form the ΔLLLΛLLL and ΛLLLΛLLL isomers.[9–10,12] A similar chemical behavior is also expected for the use of *fac*-[Rh(aet)$_3$] or *fac*-[Rh(L-cys-*N*,*S*)$_3]^{3-}$ as a starting complex. Hence, in order to investigate the source of these spectrochemical and stereochemical properties, we have undertaken the preparation of S-bridged trinuclear complexes with two *fac*-$[Rh^{III}$ (aet or L-cys-*N*,*S*)$_3$] terminals.

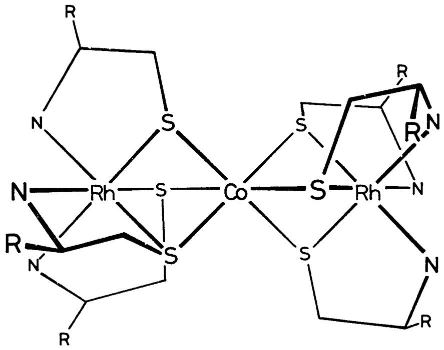

Fig. 1. Structure of ΔΛ- or ΔLLLΛLLL-$[Co^{III}\{Rh^{III}$(aet or L-cys-*N*,*S*)$_3\}_2]^{3+ or 3-}$; R=H for aet and R=$COO^-$ for L-cys.

In this paper we report on the reactions of *fac*-[Rh(aet)$_3$] or newly prepared *fac*-ΔLLL-[Rh(L-cys-*N*,*S*)$_3]^{3-}$ with $Co^{2+}$ or $Co^{3+}$ ($[CoCl(NH_3)_5]^{2+}$). The resultant S-bridged trinuclear complexes with the *fac*-$[Rh^{III}$ (aet or L-cys-*N*,*S*)$_3$] terminals (Fig. 1) were optically resolved or separated, and the isomers were characterized from their absorption, CD, and $^{13}$C NMR spectra in comparison with those of the corresponding $[Co^{III}\{Co^{III}$ (aet or L-cys-*N*,*S*)$_3\}_2]^{3+or3-}$.[8–11] The absorption and CD spectra and cyclic voltammograms of $[Co^{III}\{Rh^{III}$ (aet or L-cys-*N*,*S*)$_3\}_2]^{3+or3-}$ were discussed in terms of the terminal $RhN_3S_3$ and central $CoS_6$ chromophores in the trinuclear complexes.

## Experimental

**1) Preparation of Complexes.** **a)** ***fac*-[Rh(aet)$_3$]** was prepared by the method of Kita et al.[13] Found: C, 21.29; H, 5.53; N, 12.43%. Calcd for [Rh(aet)$_3$]·0.5$H_2O$=$C_6H_{18}N_3S_3$-Rh·0.5$H_2O$: C, 21.75; H, 5.48; N, 12.68%.

**b) ΔLLL-*fac*-$H_3$[Rh(L-cys-*N*,*S*)$_3$].** To a solution containing 3.32 g (83.0 mmol) of NaOH and 5.06 g (41.8 mmol) of L-cysteine in 20 cm$^3$ of water was added 2.18 g (10.4 mmol) of $RhCl_3$. The mixture was stirred at 95 °C for 8 h and to this was added 300 cm$^3$ of water. When the pH of the reaction solution was adjusted to ca. 2 with 1 mol dm$^{-3}$ HCl, a bright yellow precipitate appeared and was collected by filtration. This complex was recrystallized from water by adding 1 mol dm$^{-3}$ HCl and washed with 1 mol dm$^{-3}$ HCl, ethanol, and then ether. It was found from the absorption, CD and $^{13}$C NMR spectral measurements that this complex contained only the ΔLLL-*fac* isomer. Found: C, 22.91; H, 3.91; N, 8.98%. Calcd for $H_3$[Rh(L-cys)$_3$]=$C_9H_{18}N_3O_6S_3Rh$: C, 23.33; H, 3.92; N, 9.07%.

**c) $[Co^{II}\{Rh^{III}(aet)_3\}_2](NO_3)_2$.** To a deoxygenated suspension containing 0.12 g, (0.36 mmol) of *fac*-[Rh(aet)$_3$] in 10 cm$^3$ of water was added a deoxygenated solution containing 0.21 g, (0.72 mmol) of $Co(NO_3)_2\cdot 6H_2O$ in 3 cm$^3$ of water. The mixture was stirred at room temperature for 5 min under a nitrogen atmosphere, whereupon the solution became dark red and a red precipitate appeared. The resulting red complex was collected by filtration and washed with deoxygenated ethanol under a nitrogen atmosphere. Found: C, 16.16; H, 4.65; N, 12.43%. Calcd for $[\mathrm{Co\{Rh(aet)_3\}_2](NO_3)_2\cdot 3H_2O{=}C_{12}H_{36}N_8O_6S_6CoRh_2\cdot 3H_2O}$: C, 16.02; H, 4.71; N, 12.46%.

**d)$(-)^{\mathrm{CD}}_{600}$-$\Delta\Delta$-, $(+)^{\mathrm{CD}}_{600}$-$\Lambda\Lambda$-, and $\Delta\Lambda$-$[\mathrm{Co^{III}\{Rh^{III}(aet)_3\}_2](NO_3)_3}$.** To a suspension containing 1.0 g (3.0 mmol) of *fac*-$[\mathrm{Rh(aet)_3}]$ in 20 cm³ of water was added 0.5 g (1.7 mmol) of $\mathrm{Co(NO_3)_2\cdot 6H_2O}$ in 5 cm³ of water. The mixture was stirred at room temperature for 10 min, whereupon the solution became dark red and the red precipitate of $[\mathrm{Co^{II}\{Rh^{III}(aet)_3\}_2](NO_3)_2}$ appeared. To this was added 5 cm³ of 3% $\mathrm{H_2O_2}$, the solution was stirred at room temperature for 1 h, whereupon the solution became dark brown. To the dark brown solution was added 2 cm³ of saturated $\mathrm{NaNO_3}$, which was kept in a refrigerator overnight. The resulting dark brown crystals (**A-1**) were collected by filtration. After removing the **A-1** isomer by filtration, the filtrate was concentrated to a small volume using a rotary evaporator and then kept in a refrigerator overnight. The resulting needle crystals (**A-2**) were collected by filtration. The **A-1** and **A-2** isomers were recrystallized from water by adding a few drops of saturated $\mathrm{NaNO_3}$. It was found from the optical resolution procedure that the **A-1** and **A-2** isomers contained *meso*- and *rac*-$[\mathrm{Co^{III}\{Rh^{III}(aet)_3\}_2}]^{3+}$ respectively. Found for **A-1**: C, 14.84; H, 4.34; N, 12.95%. Calcd for $[\mathrm{Co\{Rh(aet)_3\}_2](NO_3)_3\cdot 3.5H_2O{=}C_{12}H_{36}N_9O_9S_6CoRh_2\cdot 3.5H_2O}$: C, 14.85; H, 4.47; N, 12.99%. Found for **A-2**: C, 15.47; H, 4.13; N, 13.53%. Calcd for $[\mathrm{Co\{Rh(aet)_3\}_2](NO_3)_3\cdot 1.5H_2O}$: C, 15.42; H, 4.21; N, 13.49%.

A solution containing 0.14 g (0.21 mmol) of $\mathrm{K_2[Sb_2(}d\mathrm{\text{-}tart)_2]\cdot 3H_2O}$ in 3 cm³ of water was added to a solution containing 0.25 g (0.27 mmol) of *rac*-$[\mathrm{Co\{Rh(aet)_3\}_2](NO_3)_3\cdot 1.5H_2O}$ (**A-2**) in 5 cm³ of water and the mixture was stirred at 60 °C for 10 min. When this was allowed to stand at room temperature for 1.5 h, brown crystals of the $(+)^{\mathrm{CD}}_{600}$ diastereomer appeared and were collected by filtration. This was recrystallized from warm water. Found: C, 16.58; H, 3.63; N, 6.80%. Calcd for $[\mathrm{Co\{Rh(aet)_3\}_2][Sb_2(}d\mathrm{\text{-}tart)_2]NO_3\cdot 7H_2O{=}C_{20}H_{40}N_7O_{15}S_6CoRh_2Sb_2\cdot 7H_2O}$: C, 16.62; H, 3.77; N, 6.78%.

Zero point one gram of $(+)^{\mathrm{CD}}_{600}$ -$[\mathrm{Co\{Rh(aet)_3\}_2][Sb_2(}d\mathrm{\text{-}tart)_2]NO_3\cdot 7H_2O}$ was dissolved in a solution containing 4 g of $\mathrm{NaNO_3}$ in 15 cm³ of water and the solution was kept in a refrigerator for a week. The resulting crystals of $(+)^{\mathrm{CD}}_{600}$ -$\Lambda\Lambda$-$[\mathrm{Co\{Rh(aet)_3\}_2](NO_3)_3}$ were collected by filtration. The $\Delta\varepsilon$ values of this complex were evaluated from the absorption spectral datum of the racemic salt. The **A-2** (racemic) isomer was also resolved by SP-Sephadex C-25 column chromatography using 0.075 mol dm⁻³ aqueous $\mathrm{K_2[Sb_2(}d\mathrm{\text{-}tart)_2]\cdot 3H_2O}$ as an eluent. Two bands containing $(-)^{\mathrm{CD}}_{600}$-$\Delta\Delta$ and $(+)^{\mathrm{CD}}_{600}$-$\Lambda\Lambda$ isomers were eluted in this order. The **A-1** isomer was not optically resolved by fractional crystallization of the diastereomer with $[\mathrm{Sb_2(}d\mathrm{\text{-}tart)_2}]^{2-}$ nor by column chromatography.

The meso and racemic isomers of $[\mathrm{Co\{Rh(aet)_3\}_2}]^{3+}$ were also prepared by a method similar to that described above, using $[\mathrm{CoCl(NH_3)_5}]\mathrm{Cl_2}$ instead of $\mathrm{Co(NO_3)_2\cdot 6H_2O}$. The reaction of *fac*-$[\mathrm{Rh(aet)_3}]$ (0.10 g, 0.30 mmol) with $[\mathrm{CoCl(NH_3)_5}]\mathrm{Cl_2}$ (0.05 g, 0.20 mmol) in 10 cm³ of water (60 °C, 1 h) yielded the dark brown solution containing $[\mathrm{Co\{Rh(aet)_3\}_2}]^{3+}$.

**e)$(+)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$-$\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$\mathrm{Na_3[Co^{III}\{Rh^{III}}$(L-cys-$N,S)_3\}_2]$.** Zero point two-nine gram (0.63 mmol) of $\Delta_{\mathrm{LLL}}$-*fac*-$\mathrm{H_3[Rh}$(L-cys-$N,S)_3]$ was dissolved in 15 cm³ of water by adding 0.5 mol dm⁻³ NaOH. To this yellow solution (pH=7—8) was added a solution containing 0.08 g (0.32 mmol) of $[\mathrm{CoCl(NH_3)_5}]\mathrm{Cl_2}$ in 15 cm³ of water; the mixture was stirred at 50 °C for 1 h. To the reaction mixture was added a large amount of ethanol in an ice bath. The resulting brown complex was collected by filtration. This complex was recrystallized from water by adding ethanol in an ice bath. It was found from the QAE-Sephadex A-25 column chromatography and the absorption and CD spectral measurements that this complex contained only $(+)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$-$\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co^{III}\{Rh^{III}}$(L-cys-$N,S)_3\}_2]^{3-}$. Found: C, 16.77; H, 4.50; N, 6.52; Co, 4.05; Rh, 14.55%. Calcd for $\mathrm{Na_3[Co\{Rh(}$L-cys$)_3\}_2]\cdot 14\mathrm{H_2O{=}C_{18}H_{30}N_6O_{12}Na_3S_6CoRh_2\cdot 14H_2O}$: C, 16.62; H, 4.49; N, 6.46; Co, 4.53; Rh, 15.82%.

**f) $(-)^{\mathrm{CD}}_{450}\cdot(-)^{\mathrm{CD}}_{400}$-$\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$- and $(-)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$-$\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$\mathrm{Na_3[Co^{III}\{Rh^{III}}$(L-cys-$N,S)_3\}_2]$.** Zero point six gram (1.29 mmol) of $\Delta_{\mathrm{LLL}}$-*fac*-$\mathrm{H_3[Rh}$(L-cys-$N,S)_3]$ was dissolved in 20 cm³ of water by adding 0.5 mol dm⁻³ NaOH. The yellow solution (pH=7—8) was deoxygenated with nitrogen and to this was added a deoxygenated solution containing 0.2 g (0.84 mmol) of $\mathrm{CoCl_2\cdot 6H_2O}$ in 5 cm³ of water. The yellow solution immediately turned dark red. The dark red solution was stirred at 95 °C for 1 h under a nitrogen atmosphere and then opened to the air. The dark red solution gradually turned brown and this was poured onto a column of QAE-Sephadex A-25 (Cl⁻ form, 3.5 cm×90 cm). After the column had been swept with water, the adsorbed band was eluted with 0.15 mol dm⁻³ aqueous NaCl. A large amount of the dark brown (**B-1**), a small amount of the reddish brown (**B-2**), and the dark brown (**B-3**) bands were eluted in this order. It was found from the absorption and CD spectral measurements that the **B-3** eluate contained $(+)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$-$\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co^{III}\{Rh^{III}}$(L-cys-$N,S)_3\}_2]^{3-}$ and the **B-2** eluate did a by-product. The **B-1** eluate was concentrated to a small volume with a rotary evaporator below 30 °C. The deposited NaCl was filtered off and the filtrate was passed through a column of Sephadex G-10 (3.5 cm×90 cm) by eluting with water. The eluate was again concentrated to a small volume and to this was added a large amount of ethanol in an ice bath. The resulting **B-1** precipitate was collected by filtration. An aqueous solution of the **B-1** precipitate was chromatographed on a QAE-Sephadex A-25 column (Cl⁻ form, 3.5 cm×90 cm), eluting with 0.075 mol dm⁻³ aqueous $\mathrm{K_2[Sb_2(}d\mathrm{\text{-}tart)_2]\cdot 3H_2O}$. After the adsorbed band was separated into two bands, the column was eluted with 0.2 mol dm⁻³ aqueous NaCl. It was found from the absorption and CD spectral measurements that the earlier and later moving bands contained $(-)^{\mathrm{CD}}_{450}\cdot(-)^{\mathrm{CD}}_{400}$-$\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$- and $(-)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$-$\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co^{III}\{Rh^{III}}$(L-cys-$N,S)_3\}_2]^{3-}$ respectively. Each isomer was isolated by the same procedure as that used for the isolation of **B-1**. The formation ratio of the three isomers, $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}:\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}:\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$, was about 6:20:74. Found for $(-)^{\mathrm{CD}}_{450}\cdot(-)^{\mathrm{CD}}_{400}$ isomer: C, 17.28; H, 3.81; N, 6.72%. Calcd for $\mathrm{Na_3[Co\{Rh(}$L-cys$)_3\}_2]\cdot 8.5\mathrm{H_2O\cdot 0.75NaCl}$: C, 17.36; H, 3.80; N, 6.75%. Found for $(-)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$ isomer: C, 16.99; H, 3.90; N, 6.57%. Calcd for $\mathrm{Na_3[Co\{Rh(}$L-cys$)_3\}_2]\cdot 9.5\mathrm{H_2O\cdot NaCl}$: C, 17.48; H, 3.91; N, 6.57%.

When the reaction of $\Delta_{\mathrm{LLL}}$-*fac*-$[\mathrm{Rh}$(L-cys-$N,S)_3]^{3-}$ with $\mathrm{CoCl_2\cdot 6H_2O}$ was carried out at room temperature under a nitrogen atmosphere, the red L-cys isomer was formed. It was found from the absorption and CD spectral measurements that this red isomer contained only $\Delta_{\rm LLL}\Delta_{\rm LLL}$-$[\rm Co^{II}\{Rh^{III}(L\text{-}cys\text{-}\mathit{N,S})_3\}_2]^{4-}$. When this red isomer was oxidized by the air, the brown $\Delta_{\rm LLL}\Delta_{\rm LLL}$-$[\rm Co^{III}\{Rh^{III}(L\text{-}cys\text{-}\mathit{N,S})_3\}_2]^{3-}$ isomer was selectively formed. The absorption an CD spectral changes of the red $\Delta_{\rm LLL}\Delta_{\rm LLL}$-$[\rm Co^{II}\{Rh^{III}(L\text{-}cys\text{-}\mathit{N,S})_3\}_2]^{4-}$ isomer by the air oxidation were monitored and the concentration of this isomer was evaluated from the absorption spectral datum of the resulting $\Delta_{\rm LLL}\Delta_{\rm LLL}$-$[\rm Co^{III}\{Rh^{III}(L\text{-}cys\text{-}\mathit{N,S})_3\}_2]^{3-}$. The isodichroic points were observed at 526, 396, 341, and 276 nm for the CD spectral change.

**g) $\Delta_{\rm LLL}$-*fac*-$\rm K_3[Co(L\text{-}cys\text{-}\mathit{N,S})_3]\cdot 9H_2O$,[8] $\Delta_{\rm LLL}\Delta_{\rm LLL}$-$\rm K_3[Co\{Co(L\text{-}cys\text{-}\mathit{N,S})_3\}_2]\cdot 6.5H_2O$,[8] and *rac*-$\rm [Co\{Co(aet)_3\}_2](NO_3)_3\cdot 1.5H_2O\cdot 0.25NaNO_3$[11]** were prepared by the methods described in previous papers.

**3) Reduction of $[\rm Co^{III}\{Rh(aet)_3\}_2]^{3+}$.** To an anaerobic aqueous solution of $[\rm Co^{III}\{Rh^{III}(aet)_3\}_2](NO_3)_3$ was added a few drops of $\rm NR_4BH_4$ ($\rm R{=}CH_3$ or $\rm C_2H_5$) in a small amount of water under a nitrogen atmosphere. The dark brown solution turned dark red within a few minutes. Contact with the air caused the dark red solution to revert back to the original dark brown.

**4) Measurements.** The electronic absorption spectra were recorded with a JASCO UNIDEC-505 or JASCO UVIDEC-610C spectrophotometer, and the CD spectra with a JASCO J-20 spectropolarimeter. The concentrations of Co and Rh in $(+)^{\rm CD}_{450}\cdot(+)^{\rm CD}_{400}$-$\Delta_{\rm LLL}\Delta_{\rm LLL}$-$[\rm Co^{III}\{Rh^{III}(L\text{-}cys\text{-}\mathit{N,S})_3\}_2]^{3-}$ were determined with a Jarrel-Ash Model-975 ICP spectrophotometer. The $^{13}$C NMR spectra were recorded with a JEOL JNM-FX-100 or FX-90Q NMR spectrometer at the probe temperature in $\rm D_2O$. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. Electrochemical measurements were made with a CV-1B apparatus (Bioanalytical Systems, Inc.) using a platinum-disk working electrode (Bioanalytical Systems, Inc., PTE). An aqueous Ag/AgCl/NaCl (3 mol dm$^{-3}$) electrode (Bioanalytical Systems, Inc., RE-1) and platinum wire were used as reference and auxiliary electrodes, respectively. Electrochemical experiments were conducted at 22 °C in water with 0.1 mol dm$^{-3}$ $\rm NaNO_3$ as the supporting electrolyte and complex concentrations of 1.0 mmol dm$^{-3}$.

## Results and Discussion

**Structural Assignments.** The absorption and CD spectra of the light yellow Rh(III) complex, $[\rm Rh(L\text{-}cys)_3]^{3-}$, are shown in Fig. 2, together with those of *fac*-$[\rm Rh(aet)_3]$ and $\Delta_{\rm LLL}$-*fac*-$[\rm Co(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$, and the data are summarized in Table 1. The light yellow complex shows the two d–d absorption bands at 25.4 and 30.12×10$^3$ cm$^{-1}$ and the sulfur-to-metal charge transfer (SMCT) band at 43.10×10$^3$ cm$^{-1}$. This absorption spectrum coincides well with that of *fac*-$[\rm Rh(aet)_3]$,[13] suggesting that the light yellow complex is *fac*-$[\rm Rh(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$. The d–d absorption and SMCT bands for *fac*-$[\rm Rh(aet\ or\ L\text{-}cys\text{-}\mathit{N,S})_3]^{0\,or\,3-}$ commonly shift to higher energy than those for *fac*-$[\rm Co(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$ (Fig 2). The $^{13}$C NMR spectrum of *fac*-$[\rm Rh(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$ gives three signals ($\delta$=36.7, 69.3, and 181.0) due to the methylene, methine, and carboxylato carbon atoms respectively. This indicates that *fac*-$[\rm Rh(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$ takes either of the $\Delta_{\rm LLL}$ or $\Lambda_{\rm LLL}$ configuration having a $C_3$ symmetry. The CD spectrum of *fac*-$[\rm Rh(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$ exhibits a weak negative band (24.63×10$^3$ cm$^{-1}$) at lower energy of the d–d absorption band region and a positive band (42.74×10$^3$ cm$^{-1}$) in the SMCT band region (Fig. 2). This CD spectral behavior corresponds with that of $\Delta_{\rm LLL}$-*fac*-$[\rm Co(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$, considering that the absorption bands of *fac*-$[\rm Rh(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$ shift to higher energy than those of *fac*-$[\rm Co(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$. Taking these facts into consideration, it is probable that *fac*-$[\rm Rh(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$ selectively takes the $\Delta_{\rm LLL}$ configuration, as does *fac*-$[\rm Co(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$.[14,15]

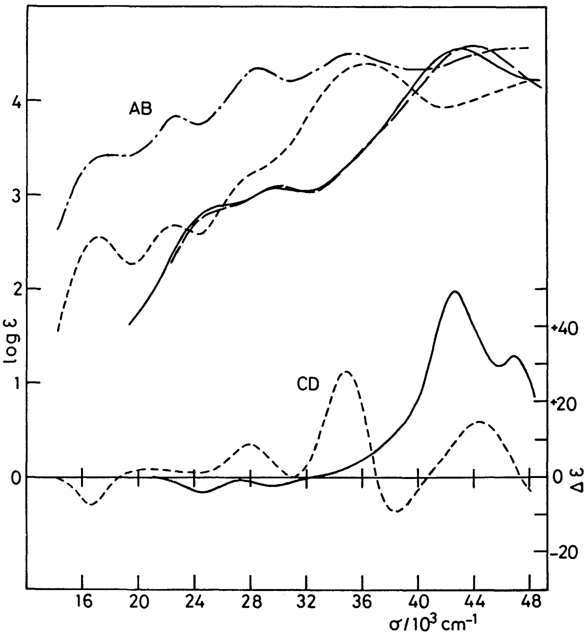

Fig. 2. Absorption and CD spectra of $\Delta_{\rm LLL}$-*fac*-$[\rm Rh(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$ (——), *fac*-$[\rm Rh(aet)_3]$ (— — —), $\Delta_{\rm LLL}$-*fac*-$[\rm Co(L\text{-}cys\text{-}\mathit{N,S})_3]^{3-}$ (------), and $\Delta_{\rm LLL}\Delta_{\rm LLL}$-$[\rm Co^{III}\{Co^{III}(L\text{-}cys\text{-}\mathit{N,S})_3\}_2]^{3-}$ (—·—).

As shown in Figs. 3 and 4 and Table 1, the brown complexes which were formed by the reactions of *fac*-$[\rm Rh(aet\ or\ L\text{-}cys\text{-}\mathit{N,S})_3]^{0\,or\,3-}$ with $[\rm CoCl(NH_3)_5]^{2+}$ show much intense absorption bands in the visible region in comparison with *fac*-$[\rm Rh(aet\ or\ L\text{-}cys\text{-}\mathit{N,S})_3]^{0\,or\,3-}$. Similar intense visible bands have been observed for the S-bridged trinuclear complexes, $[\rm Co^{III}\{Co^{III}(aet\ or\ L\text{-}cys\text{-}\mathit{N,S})_3\}_2]^{3+\,or\,3-}$, which were formed by the reactions of *fac*-$[\rm Co(aet\ or\ L\text{-}cys\text{-}\mathit{N,S})_3\}_2]^{0\,or\,3-}$ with $[\rm CoCl(NH_3)_5]^{2+}$ or $\rm Co^{2+}$ (Fig. 2).[1,2,8–12] The elemental analytical data for all the present brown complexes are in good agreement with the proposed formulas, $[\rm Co\{Rh(aet\ or\ L\text{-}cys\text{-}\mathit{N,S})_3\}_2]^{3+\,or\,3-}$, and the plasma emission spectral analysis for the representative isomer, $(+)^{\rm CD}_{450}\cdot(+)^{\rm CD}_{400}$-$[\rm Co\{Rh(L\text{-}cys\text{-}\mathit{N,S})_3\}_2]^{3-}$, indicates that the molar ratio of Co:Rh in the complex is 1:2. These facts suggest that the brown complexes take the S-bridged trinuclear structure (Fig. 1), $[\rm Co^{III}\{Rh^{III}(aet\ or\ L\text{-}cys\text{-}\mathit{N,S})_3\}_2]^{3+\,or\,3-}$.

Table 1. Absorption and CD Spectral Data of the Complexes

| Complex | Absorption maxima $\sigma/10^3\,\mathrm{cm}^{-1}$ ($\log\varepsilon/\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1}$) | CD extrema $\sigma/10^3\,\mathrm{cm}^{-1}$ ($\Delta\varepsilon/\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1}$) |
|---|---|---|
| $\Delta_{\mathrm{LLL}}$-*fac*-$[\mathrm{Rh}(\text{L-cys-}N,S)_3]^{3-}$ | 25.4 (2.9 sh) | 24.63 (−4.21) |
| | 30.12 (3.08) | 29.59 (−2.26) |
| | 43.10 (4.55) | 42.74 (+49.8) |
| | | 46.73 (+32.6) |
| $(+)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$-$\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co}\{\mathrm{Rh}(\text{L-cys-}N,S)_3\}_2]^{3-}$ | 17.8 (3.4 sh) | 16.86 (−36.3) |
| | 23.42 (4.14) | 20.0 (+7.3 sh) |
| | 28.5 (3.9 sh) | 23.58 (+88.6) |
| | 33.11 (4.35) | 27.93 (−28.9) |
| | 44.25 (4.61) | 30.48 (+10.5) |
| | | 32.15 (−7.5) |
| | | 34.48 (+31.7) |
| | | 37.59 (−12.1) |
| | | 43.10 (+48.3) |
| $(-)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$-$\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co}\{\mathrm{Rh}(\text{L-cys-}N,S)_3\}_2]^{3-}$ | 17.9 (3.3 sh) | 16.66 (+2.0) |
| | 23.47 (4.15) | 19.60 (−0.6) |
| | 28.3 (3.9 sh) | 22.73 (−1.8) |
| | 32.46 (4.16) | 25.32 (+6.3) |
| | 45.04 (4.51) | 32.05 (+9.6) |
| | | 35.97 (−8.8) |
| | | 39.22 (+3.9) |
| | | 42.19 (−5.2) |
| | | 45.87 (−25.9) |
| $(-)^{\mathrm{CD}}_{450}\cdot(-)^{\mathrm{CD}}_{400}$-$\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co}\{\mathrm{Rh}(\text{L-cys-}N,S)_3\}_2]^{3-}$ | 17.3 (3.4 sh) | 16.77 (+35.8) |
| | 23.14 (4.12) | 19.9 (−7.8 sh) |
| | 28.3 (3.8 sh) | 23.25 (−74.5) |
| | 32.86 (4.26) | 27.74 (+27.1) |
| | 44.64 (4.54) | 29.94 (−1.9) |
| | | 32.36 (+41.5) |
| | | 36.10 (−18.5) |
| | | 43.47 (−108.9) |
| | | 48.07 (+14.3) |
| $(-)^{\mathrm{CD}}_{600}$-$\Delta\Delta$-$[\mathrm{Co}\{\mathrm{Rh}(\mathrm{aet})_3\}_2]^{3-}$ | 18.7 (3.4 sh) | 16.86 (−37.3) |
| | 23.56 (4.11) | 20.3 (+5.0 sh) |
| | 28.7 (3.9 sh) | 23.69 (+81.4) |
| | 33.61 (4.26) | 27.93 (−27.0) |
| | 49.38 (4.80) | 30.31 (+10.9) |
| | | 32.68 (−30.0) |
| | | 36.63 (+32.1) |
| | | 43.86 (+117.4) |
| $\Delta\Lambda$-$[\mathrm{Co}\{\mathrm{Rh}(\mathrm{aet})_3\}_2]^{3+}$ | 14.0 (2.2 sh) | |
| | 18.5 (3.4 sh) | |
| | 23.70 (4.20) | |
| | 29.15 (3.93) | |
| | 49.14 (4.82) | |

Sh denotes a shoulder.

This assignment is supported by their $^{13}$C NMR and CD spectral behavior (vide infra).

Three isomers ($\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$, $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$, and $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$) are expected for $[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\text{L-cys-}N,S)_3\}_2]^{3-}$, considering the absolute configuration of the two terminal *fac*-$[\mathrm{Rh}^{\mathrm{III}}(\text{L-cys-}N,S)_3]$ moieties. As shown in Fig. 3, the absorption spectra of the three isomers, $(+)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$, $(-)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$, and $(-)^{\mathrm{CD}}_{450}\cdot(-)^{\mathrm{CD}}_{400}$ are quite similar to one another. Each of the two isomers, $(+)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$ and $(-)^{\mathrm{CD}}_{450}\cdot(-)^{\mathrm{CD}}_{400}$ exhibits three $^{13}$C NMR signals due to the methylene, methine, and carboxylato carbon atoms for the six L-cys ligands ($\delta$=38.25, 66.58, and 178.07 for the $(+)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$ isomer and $\delta$=38.19, 63.11, and 178.45 for the $(-)^{\mathrm{CD}}_{450}\cdot(-)^{\mathrm{CD}}_{400}$ one), while the $(-)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$ isomer does six signals ($\delta$=38.08, 39.19, 62.79, 66.20, 178.13, and 178.50). Furthermore, the $(+)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$ and $(-)^{\mathrm{CD}}_{450}\cdot(-)^{\mathrm{CD}}_{400}$ isomers show intense CD bands which are almost enantiomeric to each other, though the $(-)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$ isomer does weak CD bands over the whole region (Fig. 3). These facts suggest that the former isomers correspond to the $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$, and $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ configurations having a $D_3$ symmetry and the latter isomer does the $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ having a $C_3$ symmetry. The $^{13}$C NMR signal due to the methine carbon atom for the $(+)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$ isomer locates at ca. 3 ppm lower magnetic field than that for the $(-)^{\mathrm{CD}}_{450}\cdot$

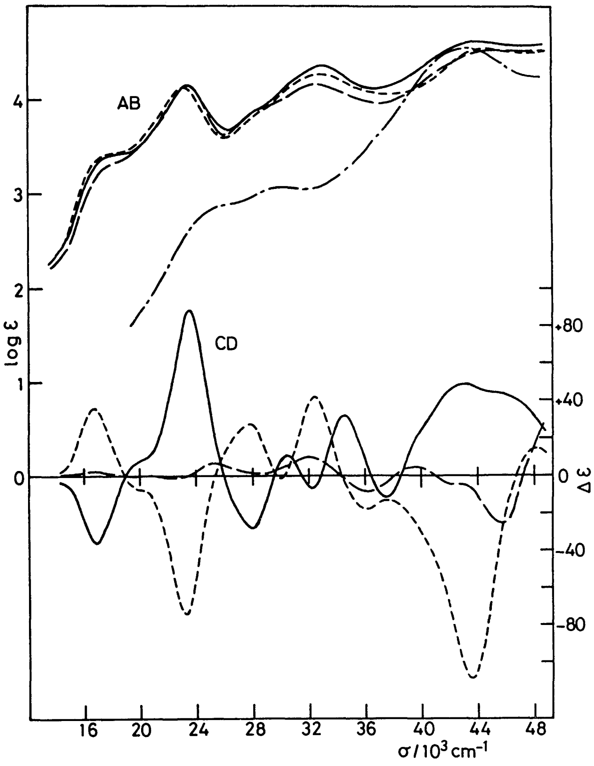

Fig. 3. Absorption and CD spectra of $(+)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$-$\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-(——), $(-)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$-$\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-(– – –), and $(-)^{\mathrm{CD}}_{450}\cdot(-)^{\mathrm{CD}}_{400}$-$\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co^{III}\{Rh^{III}(L\text{-}cys\text{-}}N,S)_3\}_2]^{3-}$ (-----), and $\Delta_{\mathrm{LLL}}$-*fac*-$[\mathrm{Rh(L\text{-}cys\text{-}}N,S)_3]^{3-}$ (–·–·–).

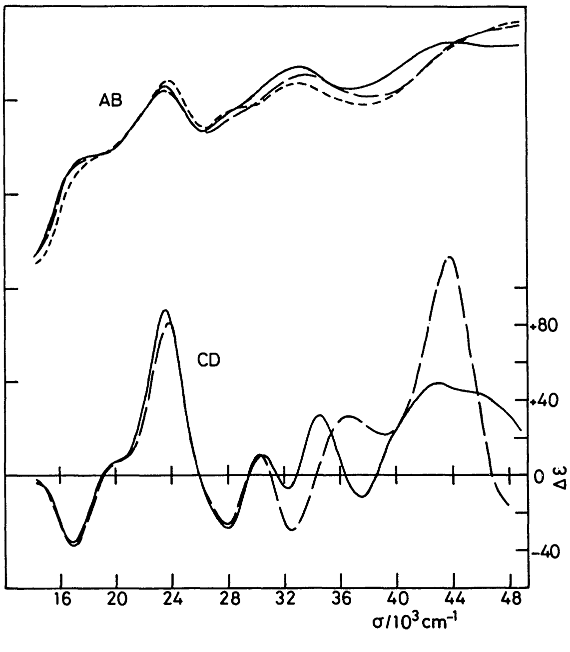

Fig. 4. Absorption and CD spectra of $(-)^{\mathrm{CD}}_{600}$-$\Delta\Delta$-(– – –) and $\Delta\Lambda$-$[\mathrm{Co^{III}\{Rh^{III}(aet)_3\}_2}]^{3+}$ (-----), and $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co^{III}\{Rh^{III}(L\text{-}cys\text{-}}N,S)_3\}_2]^{3-}$ (——).

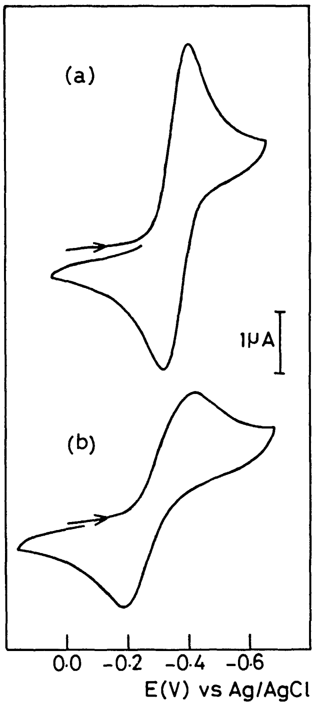

Fig. 5. Cyclic voltammograms of *rac*-$[\mathrm{Co^{III}\{Rh^{III}(aet)_3\}_2}]^{3+}$ (a) and $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co^{III}\{Rh^{III}(L\text{-}cys\text{-}}N,S)_3\}_2]^{3-}$ (b) in water (0.1 mol dm$^{-3}$ NaNO$_3$) at a platinum disk electrode (scan rate 50 mV s$^{-1}$, initial potential 0.0 V).

$(-)^{\mathrm{CD}}_{400}$ isomer, although the signal due to the methylene or carboxylato carbon atom for the former isomer locates at nearly the same position as that for the latter one. This $^{13}$C NMR spectral behavior of the $(+)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$ and $(-)^{\mathrm{CD}}_{450}\cdot(-)^{\mathrm{CD}}_{400}$ isomers are in good agreement with those of the $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$, and $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ isomers of the analogous $[\mathrm{Co^{III}\{Co^{III}(L\text{-}cys\text{-}}N,S)_3\}_2]^{3-}$ respectively.[8,9] Accordingly, it can be assigned that the $(+)^{\mathrm{CD}}_{450}\cdot(+)^{\mathrm{CD}}_{400}$ isomer takes the $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$ configuration and the $(-)^{\mathrm{CD}}_{450}\cdot(-)^{\mathrm{CD}}_{400}$ isomer does the $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ one.

For $[\mathrm{Co^{III}\{Rh^{III}(aet)_3\}_2}]^{3+}$. three isomers ($\Delta\Delta$, $\Delta\Lambda$, and $\Lambda\Lambda$) are also possible. The **A-2** isomer of $[\mathrm{Co^{III}\{Rh^{III}(aet)_3\}_2}]^{3+}$ was optically resolved into the $(+)^{\mathrm{CD}}_{600}$ and $(-)^{\mathrm{CD}}_{600}$ ones, while the **A-1** isomer could not. This result indicates that the **A-1** and **A-2** isomers take the meso ($\Delta\Lambda$) and racemic ($\Delta\Delta$ and $\Lambda\Lambda$) forms, respectively, taking the similarity of their absorption spectra into consideration (Fig. 4 and Table 1). As shown in Fig. 4, the CD spectrum of the $(-)^{\mathrm{CD}}_{600}$ isomer agrees well with that of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co^{III}\{Rh^{III}(L\text{-}cys\text{-}}N,S)_3\}_2]^{3-}$. Accordingly, the $(-)^{\mathrm{CD}}_{600}$ and $(+)^{\mathrm{CD}}_{600}$ isomers can be assigned to $\Delta\Delta$- and $\Lambda\Lambda$-$[\mathrm{Co^{III}\{Rh^{III}(aet)_3\}_2}]^{3+}$ respectively.

**Electrochemistry of the Trinuclear Complexes.** As given in Fig. 5 and Table 2, the cyclic voltammograms for $[\mathrm{Co^{III}\{Rh^{III}(aet)_3\}_2}]^{3+}$ and $[\mathrm{Co^{III}\{Rh^{III}(L\text{-}cys\text{-}}N,S)_3]^{3-}$ at a Pt-disk electrode display one quasi-reversible redox couple at ca. $E°'=-0.3$ V, and no other redox process is observed in the potential region of +0.8—−0.8 V (vs. Ag/AgCl). In analogy to the characterized

Table 2. Electrochemical Data of [Co{M(aet or L-cys-*N*,*S*)$_3$}$_2$]$^{3+\ \mathrm{or}\ 3-}$ (M=Rh(III), Co(III))

| Complex | $E_{\mathrm{pc}}$/V | $E_{\mathrm{pa}}$/V | $E^{\circ\prime}$/V |
|---|---|---|---|
| $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co{Rh(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ | −0.42 | −0.19 | −0.31 |
| *rac*-[Co{Rh(aet)$_3$}$_2$]$^{3+}$ | −0.40 | −0.32 | −0.36 |
| *meso*-[Co{Rh(aet)$_3$}$_2$]$^{3+}$ | −0.39 | −0.31 | −0.35 |
| *rac*-[Co{Co(aet)$_3$}$_2$]$^{3+}$ | −0.70 | −0.62 | −0.66 |

At 22 °C in water (0.1 mol dm$^{-3}$ NaNO$_3$) at a platinum disk electrode with scan rate 50 mV s$^{-1}$. $E^{\circ\prime}=(E_{\mathrm{pc}}+E_{\mathrm{pa}})/2$ in V vs. Ag/AgCl (3 mol dm$^{-3}$ NaCl) from cyclic voltammetry.

electrochemistry of the [Co$^{\mathrm{III}}${Co$^{\mathrm{III}}$(aet or L-cys-*N*,*S*)$_3$}$_2$] system,[10,11] this redox process is assigned as the redox couple corresponding to the reaction: [Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(aet or L-cys-*N*,*S*)$_3$}$_2$]$^{3+\mathrm{or}3-}$+e$^-$ $\rightleftharpoons$ [Co$^{\mathrm{II}}${Rh$^{\mathrm{III}}$(aet or L-cys-*N*,*S*)$_3$}$_2$]$^{2+\mathrm{or}4-}$. The peak current is proportional to the square root of the scan rate and the ratio of anodic to cathodic peak currents is nearly unity for each of the present complexes. At a scan rate of 50 mV s$^{-1}$, the observed peak separation ($E_{\mathrm{pc}}-E_{\mathrm{pa}}$) is 80 mV for [Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(aet)$_3$}$_2$]$^{3+}$ and that for [Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ is much larger (230 mV). The redox potentials due to the central Co(III)/(II) for [Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(aet or L-cys-*N*,*S*)$_3$}$_2$]$^{3+\mathrm{or}3-}$ are ca. 300 mV more positive than those for the analogous [Co$^{\mathrm{III}}${Co$^{\mathrm{III}}$(aet or L-cys-*N*,*S*)$_3$}$_2$]$^{3+\mathrm{or}3-}$ (Table 2),[10,11] indicating that replacement of the *fac*-[Co$^{\mathrm{III}}$(aet or L-cys-*N*,*S*)$_3$] terminal by the *fac*-[Rh$^{\mathrm{III}}$(aet or L-cys-*N*,*S*)$_3$] one dramatically stabilizes the central Co(II) oxidation state. This can be ascribed to the poorer electron-donating ability of the facially arranged thiolato atoms in the *fac*-[Rh$^{\mathrm{III}}$(aet or L-cys-*N*,*S*)$_3$] terminal. The reduction potential difference resulting from the difference in the configuration of the complexes is very slight; the $E^{\circ\prime}$ value for *meso*-[Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(aet)$_3$}$_2$]$^{3+}$ is only 10 mV more positive than that for the corresponding racemic isomer (Table 2). The difference is more profound for changing ligand from aet to L-cys, where $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ is reduced 50 mV more easily than *rac*-[Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(aet)$_3$}$_2$]$^{3+}$ (Table 2).

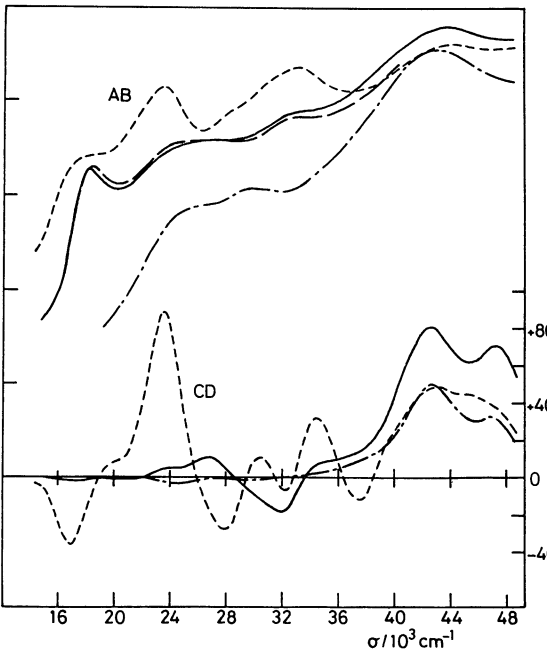

Fig. 6. Absorption and CD spectra of [Co$^{\mathrm{II}}${Rh$^{\mathrm{III}}$(aet)$_3$}$_2$]$^{2+}$ (— — —), $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co$^{\mathrm{II}}${Rh$^{\mathrm{III}}$(L-cys-*N*,*S*)$_3$}$_2$]$^{4-}$ (——), $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ (-----), and $\Delta_{\mathrm{LLL}}$-*fac*-[Rh(L-cys-*N*,*S*)$_3$]$^{3-}$ (—-—-).

**Formation and Properties.** The reactions of *fac*-[Rh(aet)$_3$] or $\Delta_{\mathrm{LLL}}$-*fac*-[Rh(L-cys-*N*,*S*)$_3$]$^{3-}$ with [CoCl(NH$_3$)$_5$]$^{2+}$ readily gave the brown trinuclear complexes, [Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(aet)$_3$}$_2$]$^{3+}$ or $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$, as the reactions of *fac*-[Co(aet)$_3$] or $\Delta_{\mathrm{LLL}}$-*fac*-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ with [CoCl(NH$_3$)$_5$]$^{2+}$.[8,9,12] This indicates that *fac*-[Rh(aet or L-cys-*N*,*S*)$_3$]$^{0\mathrm{or}3-}$ function as a terdentate ligand coordinating to a metal ion through the facially arranged thiolato donor atoms, as in the case of *fac*-[Co(aet or L-cys-*N*,*S*)$_3$]$^{0\mathrm{or}3-}$. The reaction of *fac*-[Rh(aet)$_3$] with Co$^{2+}$ initially formed the red complex which was changed to the brown [Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(aet)$_3$}$_2$]$^{3+}$ complex by the H$_2$O$_2$ or air oxidation, though the red complex was fairly stable under a nitrogen atmosphere. The red aet complex was also formed by the reduction of the brown [Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(aet)$_3$}$_2$]$^{3+}$ complex with use of BH$_4^-$. As shown in Fig 6, the pattern of absorption spectral deviation between the red aet complex and *fac*-[Rh(aet or L-cys-*N*,*S*)$_3$]$^{0\mathrm{or}3-}$ is similar to that between [Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(aet or L-cys-*N*,*S*)$_3$}$_2$]$^{3+\mathrm{or}3-}$ and *fac*-[Rh(aet or L-cys-*N*,*S*)$_3$]$^{0\mathrm{or}3-}$, though the absorption intensity in the visible region of the red aet complex is weaker than those of [Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(aet or L-cys-*N*,*S*)$_3$}$_2$]$^{3+\mathrm{or}3-}$. Taking these facts and the elemental analytical result into consideration, the red aet complex is assigned to take the trinuclear structure with Co(II) center, [Co$^{\mathrm{II}}${Rh$^{\mathrm{III}}$(aet)$_3$}$_2$]$^{2+}$. Similarly, the reaction of $\Delta_{\mathrm{LLL}}$-*fac*-[Rh(L-cys-*N*,*S*)$_3$]$^{3-}$ with Co$^{2+}$ formed the red L-cys complex. The absorption spectrum of the red L-cys complex coincides well with that of the red [Co$^{\mathrm{II}}${Rh$^{\mathrm{III}}$(aet)$_3$}$_2$]$^{2+}$ complex (Fig. 6), though the red L-cys complex could not be isolated because of its quite high solubility and the oxidation to the brown [Co$^{\mathrm{III}}${Rh$^{\mathrm{III}}$(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ complex. Accordingly, it is possible to say that the red L-cys complex also takes the S-bridged trinuclear structure, [Co$^{\mathrm{II}}${Rh$^{\mathrm{III}}$(L-cys-*N*,*S*)$_3$}$_2$]$^{4-}$. The reactions of *fac*-

$[\mathrm{Co}(\text{aet or L-cys-}N,S)_3]^{0\text{or}3-}$ with $\mathrm{Co}^{2+}$ have immediately produced $[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Co}^{\mathrm{III}}(\text{aet or L-cys-}N,S)_3\}_2]^{3+\text{or}3-}$ because of the rapid air oxidation, and the intermediate $[\mathrm{Co}^{\mathrm{II}}\{\mathrm{Co}^{\mathrm{III}}(\text{aet or L-cys-}N,S)_3\}_2]^{2+\text{or}4-}$ complexes could not be observed.[1,2,8–12] The detection of the intermediate Co(II) complexes in this work indicates that the *fac*-$[\mathrm{Rh}^{\mathrm{III}}(\text{aet or L-cys-}N,S)_3]$ terminal stabilizes the central Co(II) oxidation state in comparison with the $[\mathrm{Co}^{\mathrm{III}}(\text{aet or L-cys-}N,S)_3]$ one, and this is in line with the fact that the $E^{\circ\prime}$ values of the central Co(III)/(II) for $[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\text{aet or L-cys-}N,S)_3\}_2]^{3+\text{or}3-}$ are much more positive than those for $[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Co}^{\mathrm{III}}(\text{aet or L-cys-}N,S)_3\}_2]^{3+\text{or}3-}$ (vide supra). The air oxidation of the red $[\mathrm{Co}^{\mathrm{II}}\{\mathrm{Rh}^{\mathrm{III}}(\text{L-cys-}N,S)_3\}_2]^{4-}$ complex which was formed at room temperature caused a CD spectral change simultaneously with the absorption spectral change to $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\text{L-cys-}N,S)_3\}_2]^{3-}$ and the well-defined isodichroic points observed at 526, 396, 341, and 276 nm confirm that the red L-cys complex changed only to $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\text{L-cys-}N,S)_3\}_2]^{3-}$. From this CD spectral behavior, it is suggested that the red L-cys complex is the $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$ isomer of $[\mathrm{Co}^{\mathrm{II}}\{\mathrm{Rh}^{\mathrm{III}}(\text{L-cys-}N,S)_3\}_2]^{4-}$. In contrast to the reaction at room temperature, $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-, $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-, and $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\text{L-cys-}N,S)_3\}_2]^{3-}$ were formed in a ratio of ca. 74:20:6 when the red solution of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co}^{\mathrm{II}}\{\mathrm{Rh}^{\mathrm{III}}(\text{L-cys-}N,S)_3\}_2]^{4-}$ was heated at ca. 95 °C for 1 h followed by the air oxidation. However, no configurational inversion occurred upon heating the solution of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\text{L-cys-}N,S)_3\}_2]^{3-}$ under the same conditions. These facts point out that the configurational inversion occurs in $[\mathrm{Co}^{\mathrm{II}}\{\mathrm{Rh}^{\mathrm{III}}(\text{L-cys-}N,S)_3\}_2]^{4-}$. For the reaction of $\Delta_{\mathrm{LLL}}$-*fac*-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ with $\mathrm{Co}^{2+}$, the configurational inversion has occurred even at room temperature to give the three isomers, $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-, $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-, and $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Co}^{\mathrm{III}}(\text{L-cys-}N,S)_3\}_2]^{3-}$.[8,9] This implies that an electron transfer from the central Co(II) to the terminal M(III) (M=Co or Rh), which makes the $\Delta_{\mathrm{LLL}}$-*fac*-$[\mathrm{M}(\text{L-cys-}N,S)_3]$ terminal labile,[5,9,12] takes place with much energy for Rh(III) than for Co(III).

As shown in Fig. 6, each of the present trinuclear complexes shows an intense absorption band at ca. $42\times10^3\,\mathrm{cm}^{-1}$, which corresponds to the SMCT band for the mononuclear *fac*-$[\mathrm{Rh}(\text{aet or L-cys-}N,S)_3]^{0\text{or}3-}$ complexes. In the corresponding region, each of the $\Delta\Delta$ type trinuclear isomers shows a positive CD band as does $\Delta_{\mathrm{LLL}}$-*fac*-$[\mathrm{Rh}(\text{L-cys-}N,S)_3]^{3-}$. Accordingly, it is likely that the absorption and CD spectral contributions in this region of the trinuclear complexes are mainly attributed to the terminal $\mathrm{Rh}^{\mathrm{III}}\mathrm{N}_3\mathrm{S}_3$ chromophore. The intense absorption band (ca. $23.5\times10^3\,\mathrm{cm}^{-1}$) and the shoulder (ca. $18\times10^3\,\mathrm{cm}^{-1}$) of $[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\text{aet or L-cys-}N,S)_3\}_2]^{3+\text{or}3-}$ in the visible region (ca. $15$—$25\times10^3\,\mathrm{cm}^{-1}$) are obviously related to the central $\mathrm{Co}^{\mathrm{III}}\mathrm{S}_6$ chromophore, taking account of the absorption spectral behavior of *fac*-$[\mathrm{Rh}(\text{aet or L-cys-}N,S)_3]^{0\text{or}3-}$ in the corresponding region (Figs. 2 and 6). In the CD spectra, $\Delta\Delta$- or $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\text{aet or L-cys-}N,S)_3\}_2]^{3+\text{or}3-}$ exhibit the intense negative (ca. $17\times10^3\,\mathrm{cm}^{-1}$) and positive (ca. $23\times10^3\,\mathrm{cm}^{-1}$) CD bands in the visible region, while in the corresponding region $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co}^{\mathrm{II}}\{\mathrm{Rh}^{\mathrm{III}}(\text{L-cys-}N,S)_3\}_2]^{4-}$ gives the weak and broad CD bands which are comparable to those of $\Delta_{\mathrm{LLL}}$-*fac*-$[\mathrm{Rh}(\text{L-cys-}N,S)_3]^{3-}$ (Fig. 6). These facts suggest that the six asymmetric sulfur atoms around the central metal ion are fixed more tightly in $\Delta\Delta$- or $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\text{aet or L-cys-}N,S)_3\}_2]^{3+\text{or}3-}$ than in $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co}^{\mathrm{II}}\{\mathrm{Rh}^{\mathrm{III}}(\text{L-cys-}N,S)_3\}_2]^{4-}$, taking into consideration that each sulfur atom in all the present $\Delta\Delta$ type trinuclear isomers is regulated to the *R* configuration.

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