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Crystal Structures and Spectroscopic Characterization of Linear-Type *S*-Bridged Trinuclear Complexes $\Delta\Lambda$- and $\Delta\Delta/\Lambda\Lambda$-$[\mathrm{Re}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\mathrm{aet})_3\}_2]^{3+}$ (aet = 2-Aminoethanethiolate)

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The reduction of an acidic mixture of *fac*(*S*)-$[\mathrm{Rh}^{\mathrm{III}}(\mathrm{aet})_3]$ (aet = 2-aminoethanethiolate) and $\mathrm{NH_4Re^{VII}O_4}$ gave the first linear-type *S*-bridged trinuclear complexes containing a d^4 metal ion, $[\mathrm{Re}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\mathrm{aet})_3\}_2]^{3+}$. The *meso* (**1a**) and *racemic* (**1b**) isomers were selectively isolated by using HCl and HBr solutions, respectively, although both isomers were formed in each case. The crystal structures of $\mathbf{1a}\mathrm{Cl(ReO_4)_2{\cdot}4H_2O}$ and $\mathbf{1b}\mathrm{(ClO_4)_3}$ were determined by X-ray crystallography. Both complex cations consist of two terminal *fac*(*S*)-$[\mathrm{Rh}^{\mathrm{III}}(\mathrm{aet})_3]$ units and a central rhenium atom, which is situated in an octahedral environment with the $\mathrm{Re^{III}S_6}$ chromophore. **1b** was optically resolved by a column chromatographic method and characterized by CD spectroscopy. **1a** and **1b** were fairly stable in water, even under aerobic conditions, unlike in the case of previously reported $[\mathrm{Mo}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\mathrm{aet})_3\}_2]^{3+}$. The Re(III) ion, which is incorporated into the *S*-bridged polynuclear structure, indicated a lower magnetic moment (1.32 μ_B for **1b**) at room temperature than the spin-only value for the d^4 electronic configuration. The ^{1}H and ^{13}C NMR spectra of **1a** and **1b** showed paramagnetic shifts compared with those of the corresponding diamagnetic complexes, $[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Rh}^{\mathrm{III}}(\mathrm{aet})_3\}_2]^{3+}$. **1a** and **1b** were also characterized on the basis of the IR and UV-vis absorption spectra and the molar conductivities.

Rhenium, which is located between the early and late transition metals, can take a variety of oxidation numbers in complexes from -1 to $+7$ (d^8 to d^0). Various coordination structures of the complexes have been reported, depending on the oxidation number.[1] Therefore, rhenium ion is known for its characteristic stereochemistry compared with other metal ions. For example, Re(III) complexes tend to form metal-metal multiple bonds such as quadruple bonds,[2] and Re(V) complexes can form a linear-type dinuclear unit, O=Re–O–Re=O.[3,4] Many rhenium complexes with phosphorus or nitrogen donor ligands have been widely investigated so far.[4,5] However, rhenium complexes containing coordinated sulfur atoms are still rare, except for sulfide cluster compounds.[6,7]

Recently, we reported that metalloligands, *fac*(*S*)-$[\mathrm{M(aet)_3}]$ (M = $\mathrm{Rh^{III}}$, $\mathrm{Ir^{III}}$; aet = 2-aminoethanethiolate), can react with not only the late transition metal ions (d^5–d^{10} electronic configurations)[8–15] but also the early transition ones (d^1–d^3), to form *S*-bridged polynuclear complexes.[16–18] These complexes involving the V(III),[16] Cr(III),[17] or Mo(III–V)[18] ions indicated unique reactivity and electrochemistry due to the relatively weak affinity of these metal ions toward thiolato sulfur atoms and an electromagnetic interaction in the polynuclear structures by fewer d electrons. Especially, the molybdenum ion incorporated into the *S*-bridged polynuclear structure exhibited different oxidation numbers depending on the metalloligands.[18] Further, the Mo(V) complex, which has a non-linear $\mathrm{Mo_2O_2}(\mu\text{-O})$ core, was formed by spontaneous oxidation of the unstable Mo(III) complex.[18] Although rhenium often shows similar properties to molybdenum, which is located in a diagonal position to the upper left, the electrochemistry of rhenium is more complicate than that of molybdenum.

In this work, we attempted some reactions between $\mathrm{NH_4Re^{VII}O_4}$ and *fac*(*S*)-$[\mathrm{Rh}^{\mathrm{III}}(\mathrm{aet})_3]$ using a reducing agent in order to obtain novel *S*-bridged polynuclear complexes. As a result of this research, we found fairly stable *S*-bridged trinuclear complexes involving a Re(III) ion. The synthesis, characterization and properties of the first linear-type trinuclear complexes with d^4 metal ions are described on the basis of X-ray crystallography and some spectroscopy.

Results and Discussion

Formation. Linear-type *S*-bridged $\mathrm{Rh^{III}Re^{III}Rh^{III}}$ trinuclear complexes, *meso*- and *racemic*-$[\mathrm{Re\{Rh(aet)_3\}_2}]^{3+}$ (**1a** and **1b**), were obtained as dark-red crystals by the reaction of *fac*(*S*)-$[\mathrm{Rh(aet)_3}]$ with $\mathrm{NH_4ReO_4}$ in acidic solutions using a reducing agent, $\mathrm{SnCl_2{\cdot}2H_2O}$. Although an equimolar $\mathrm{SnCl_2{\cdot}2H_2O}$ was added to each solution containing Re(VII) ions, and all rhenium ions were expected to be reduced to the $+5$ oxidation state; rhenium ions incorporated into the *S*-bridged polynuclear structure actually took the $+3$ not $+5$ oxidation state. This is inconsistent with the fact that the dinuclear Re(V) complex, $[\{\mathrm{ReO(5,8\text{-}dithiadodecane)_2Cl_2}\}_2\mathrm{O}]$,[3] was obtained from the reaction using an equimolar reducing agent, $\mathrm{SnCl_2{\cdot}2H_2O}$, and the fact that the Re(III) complex, $[\mathrm{Re(thiourea\text{-}}S)_6]^{3+}$,[19] required double the molar quantity of the reducing agent. Consequently, Re(VII) ions remained in the solutions, and some of them were used as counter anions for crystallization in the case of the HCl solution.

When each of the reaction mixtures in HCl and HBr solutions was passed through an SP-Sephadex C-25 column, two yellow bands containing **1a** and **1b** were eluted. This indicates that both **1a** and **1b** were formed in each reaction in the acidic solutions. However, the crystals of **1a** were selectively isolated from the reaction mixture in a HCl solution, while the crystals of **1b** were obtained by a corresponding method using HBr. The ratios of *meso* and *racemic* isomers in each acidic solution were obtained by a column chromatographic technique. Namely, these analyses indicated values of *meso*:*racemic* = 1.3:1 in a HCl solution and 1:1.9 in a HBr solution. These facts seem to indicate that the difference in the acidic solvents affects the selectivity of stereoisomerism for the formation ratio, because the calculated structural energies for the linear-type *S*-bridged complexes, $[M'\{M(aet)_3\}_2]^{n+}$, showed little differences between these isomers.[18] Further, the crystallization of the isomers may be not only due to the formation ratio, but also a combination of the existence of perrhenate anions and a difference in the solubility between their chloride and bromide salts. In the present reaction, the total yields of **1a** and **1b** were below 50% based on column chromatography. Therefore, it seems that some compounds, which may be the Re(V) species, are also formed. However, they could not be isolated by both methods of crystallization and column chromatography.

Crystal Structures. Perspective drawings of the entire complex cations, **1a** and **1b**, are given in Figs. 1 and 2, respectively. Their selected bond distances and angles are listed in Tables 1 and 2. Both complex cations **1a** and **1b** are $Rh^{III}Re^{III}Rh^{III}$ trinuclear complexes, which consist of two approximately octahedral *fac*(*S*)-[Rh(aet)$_3$] units and one rhenium atom; the overall structures are similar to each other. Namely, three thiolato sulfur atoms in each terminal *fac*(*S*)-[Rh(aet)$_3$] unit coordinate to the central rhenium atom, forming an octahedral $Re^{III}S_6$ chromophore. Plasma emission spectral analyses indicated values of Re:Rh = 3:2 for the crystal of **1a** and 1:2 for the crystal of **1b**. These values and the results of X-ray analyses indicate that the crystal of **1a** contains two perrhenate anions and one chloride anion as counter ions, whereas the crystal of **1b** revealed the presence of three perchlorate anions, in which the averaged Cl–O distances (1.41(5) Å) are shorter than the averaged Re–O distances (1.71(1) Å). The total number of anions implies that both of the entire complex cations are trivalent; these facts indicate that the rhenium ion in **1a** and **1b** is in oxidation state +3. The molar conductivities of **1a**Cl(ReO$_4$)$_2$ and **1b**Br$_3$ in water (350 and 394 S cm^2 mol^{-1}, respectively) are in good agreement with those of the 1:3 electrolyte of *meso*-$[Cr\{Rh(aet)_3\}_2](NO_3)_3$ and *racemic*-$[Cr\{Rh(aet)_3\}_2]Br_3$ (352 and 377 S cm^2 mol^{-1}, respectively).[17] Accordingly, it is reasonable to assume that **1a** and **1b** have *S*-bridged $Rh^{III}Re^{III}Rh^{III}$ trinuclear structures in both solid and solution states, and it can be considered that the relatively low oxidation state of Re(III) are stabilized by the *fac*(*S*)-[Rh(aet)$_3$] units.

Considering the absolute configurations (Δ and Λ) of the two terminal *fac*(*S*)-[Rh(aet)$_3$] units, three isomers ($\Delta\Delta$, $\Lambda\Lambda$, and $\Delta\Lambda$) are possible for $[Re\{Rh(aet)_3\}_2]^{3+}$. The cation **1a** consists of the $\Delta\Lambda$ (*meso*) isomer, with a crystallographic inversion center located on the central rhenium atom. On the other hand, the cation **1b** consists of the $\Delta\Delta$ and $\Lambda\Lambda$ (*racemic*) isomers. All of the bridging sulfur atoms in **1a** and **1b** are fixed to the *S* configuration for the Δ unit and the *R* configuration for the Λ unit, which corresponds to the results in $\Delta\Lambda$-$[M'\{Rh(aet)_3\}_2]^{3+}$ (M′ = Cr^{III}, V^{III}) and $\Delta\Delta/\Lambda\Lambda$-$[M'\{Rh(aet)_3\}_2]^{n+}$ (M′ = Ni^{II}, Mo^{III}).[15–18]

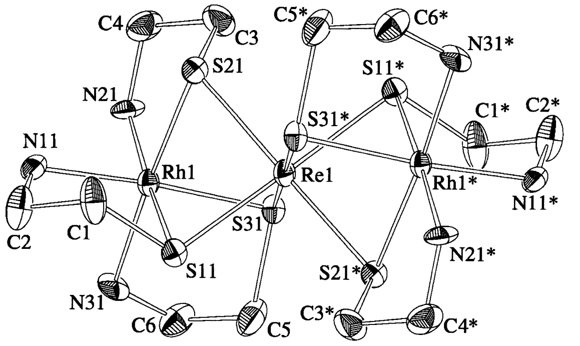

Fig. 1. Perspective view of $\Delta\Lambda$-$[Re\{Rh(aet)_3\}_2]^{3+}$ (**1a**) with the atomic labeling scheme (50% probability ellipsoids). The disordered S(*n*2) and N(*n*2) atoms are omitted for clarity.

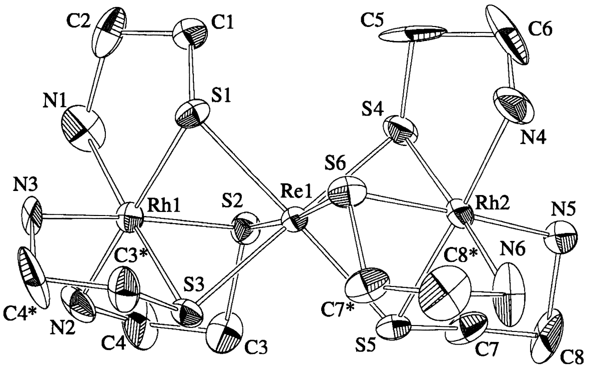

Fig. 2. Perspective view of $\Delta\Delta/\Lambda\Lambda$-$[Re\{Rh(aet)_3\}_2]^{3+}$ (**1b**) with the atomic labeling scheme (30% probability ellipsoids). The overlapped $\Lambda\Lambda$ isomer is omitted for clarity.

In the present work, the crystal structures of both *meso* and *racemic* isomers were first determined in a series of linear-type *S*-bridged trinuclear complexes, $[M'\{M(aet)_3\}_2]^{n+}$. Moreover, this is the first example in which a d^4 metal ion or a third transition series metal ion is incorporated into the *S*-bridged polynuclear structures. Although the Re···Rh distances (2.8248(9) Å for **1a** and average 2.840(2) Å for **1b**) and the S–Re–S (average 86.5(2)° for **1a** and average 85.6(3)° for **1b**) and Re–S–Rh (average 73.7(2)° for **1a** and average 74.3(3)° for **1b**) angles indicate slight differences between the isomers, the Re–S distances (average 2.383(6) Å for **1a** and average 2.386(9) Å for **1b**) and other distances and angles are quite similar to each other. These facts suggest that the distances and angles are almost independent on the absolute configurations of two terminal *fac*(*S*)-[Rh(aet)$_3$] units. On the other hand, all of the bond distances and angles around the Rh(III) ions in **1a** and **1b** are within the ranges of those in $[M'\{Rh(aet)_3\}_2]^{n+}$ (M′ = Cr^{III}, Ni^{II}, V^{III}, or Mo^{III}).[15–18] However, the Re···Rh distances (averages 2.8248(9) and 2.840(2) Å) in these complexes are shorter

Table 1. Selected Bond Distances (Å) and Angles (°) for $\Delta\Lambda$-$[Re\{Rh(aet)_3\}_2]^{3+}$ (**1a**)

Re(1)···Rh(1)	2.8248(9)		
Re(1)–S(11)	2.383(6)	Re(1)–S(12)	2.396(6)
Re(1)–S(21)	2.387(5)	Re(1)–S(22)	2.369(6)
Re(1)–S(31)	2.385(6)	Re(1)–S(32)	2.378(6)
Rh(1)–S(11)	2.331(5)	Rh(1)–S(12)	2.340(6)
Rh(1)–S(21)	2.335(5)	Rh(1)–S(22)	2.332(6)
Rh(1)–S(31)	2.324(5)	Rh(1)–S(32)	2.317(5)
Rh(1)–N(11)	2.11(2)	Rh(1)–N(12)	2.16(3)
Rh(1)–N(21)	2.12(2)	Rh(1)–N(22)	2.14(2)
Rh(1)–N(31)	2.14(2)	Rh(1)–N(32)	2.12(2)
S(11)–Re(1)–S(21)	86.5(2)	S(12)–Re(1)-S(22)	86.6(2)
S(11)–Re(1)–S(31)	86.2(2)	S(12)–Re(1)–S(32)	86.7(2)
S(21)–Re(1)–S(31)	86.8(2)	S(22)–Re(1)–S(32)	86.4(2)
S(11)–Rh(1)–S(21)	89.0(2)	S(12)–Rh(1)–S(22)	88.7(2)
S(11)–Rh(1)–S(31)	88.8(2)	S(12)–Rh(1)–S(32)	89.4(2)
S(21)–Rh(1)–S(31)	89.4(2)	S(22)–Rh(1)–S(32)	88.7(2)
N(11)–Rh(1)–N(21)	93.5(8)	N(12)–Rh(1)–N(22)	94.5(9)
N(11)–Rh(1)–N(31)	90.7(9)	N(12)–Rh(1)–N(32)	92.5(9)
N(21)–Rh(1)–N(31)	94.8(8)	N(22)–Rh(1)–N(32)	92.2(10)
Re(1)–S(11)–Rh(1)	73.6(2)	Re(1)–S(12)–Rh(1)	73.2(2)
Re(1)–S(21)–Rh(1)	73.5(1)	Re(1)–S(22)–Rh(1)	73.9(2)
Re(1)–S(31)–Rh(1)	73.7(2)	Re(1)–S(32)–Rh(1)	74.0(2)

Table 2. Selected Bond Distances (Å) and Angles (°) for $\Delta\Delta/\Lambda\Lambda$-$[Re\{Rh(aet)_3\}_2]^{3+}$ (**1b**)

Re(1)···Rh(1)	2.840(2)	Re(1)···Rh(2)	2.839(2)
Re(1)–S(1)	2.402(8)	Re(1)–S(4)	2.361(9)
Re(1)–S(2)	2.361(9)	Re(1)–S(5)	2.373(8)
Re(1)–S(3)	2.395(9)	Re(1)–S(6)	2.424(9)
Rh(1)–S(1)	2.321(9)	Rh(2)–S(4)	2.318(9)
Rh(1)–S(2)	2.289(9)	Rh(2)–S(5)	2.330(9)
Rh(1)–S(3)	2.356(9)	Rh(2)–S(6)	2.275(10)
Rh(1)–N(1)	2.08(3)	Rh(2)–N(4)	2.13(3)
Rh(1)–N(2)	2.10(3)	Rh(2)–N(5)	2.16(4)
Rh(1)–N(3)	2.09(2)	Rh(2)–N(6)	2.18(3)
S(1)–Re(1)–S(2)	86.3(3)	S(4)–Re(1)–S(5)	87.0(3)
S(1)–Re(1)–S(3)	84.6(3)	S(4)–Re(1)–S(6)	84.7(3)
S(2)–Re(1)–S(3)	86.7(3)	S(5)–Re(1)–S(6)	84.5(3)
S(1)–Rh(1)–S(2)	89.9(3)	S(4)–Rh(2)–S(5)	89.0(3)
S(1)–Rh(1)–S(3)	87.3(3)	S(4)–Rh(2)–S(6)	89.1(4)
S(2)–Rh(1)–S(3)	89.3(3)	S(5)–Rh(2)–S(6)	88.9(3)
N(1)–Rh(1)–N(2)	85(1)	N(4)–Rh(2)–N(5)	95(1)
N(1)–Rh(1)–N(3)	97(1)	N(4)–Rh(2)–N(6)	92(1)
N(2)–Rh(1)–N(3)	97(1)	N(5)–Rh(2)–N(6)	94(1)
Re(1)–S(1)–Rh(1)	73.9(2)	Re(1)–S(4)–Rh(2)	74.7(3)
Re(1)–S(2)–Rh(1)	75.3(3)	Re(1)–S(5)–Rh(2)	74.3(2)
Re(1)–S(3)–Rh(1)	73.4(2)	Re(1)–S(6)–Rh(2)	74.3(3)

than those of the Cr···Rh (2.9328(2) Å)[17] and Ni···Rh (average 2.9451(5) Å),[15] while they are similar to those of the V···Rh (2.838(1) Å)[16] and Mo···Rh (average 2.860(3) Å)[18] in the corresponding trinuclear complexes. The short Re···Rh distances are thought to be caused by the acute Re–S–Rh angle and the obtuse S–Re–S one. Additionally, the Re–S distances (averages 2.383(6) and 2.386(9) Å) in $[Re\{Rh(aet)_3\}_2]^{3+}$ are shorter than the M′–S distances (averages 2.4110(8)–2.44(1) Å) in the corresponding complexes.[15–18] These Re–S distances are also shorter than those in the mononuclear rhenium(III) complex $[Re(thiourea\text{-}S)_6]^{3+}$ (average 2.421(2) Å)[19] and octa(μ_3-sulfido)hexarhenium(III) cluster complexes having terminal pyridine ligands (averages 2.398–2.401 Å).[7] This indicates that the thiolato sulfur atoms of the *fac*(*S*)-$[Rh(aet)_3]$ units make relatively strong Re–S bonds.

Properties. Figure 3 shows the IR spectra of **1a**$Cl(ReO_4)_2$ and **1b**Br_3, together with those of the starting materials, *fac*(*S*)-$[Rh(aet)_3]$ and NH_4ReO_4. Reflecting the structural similarity

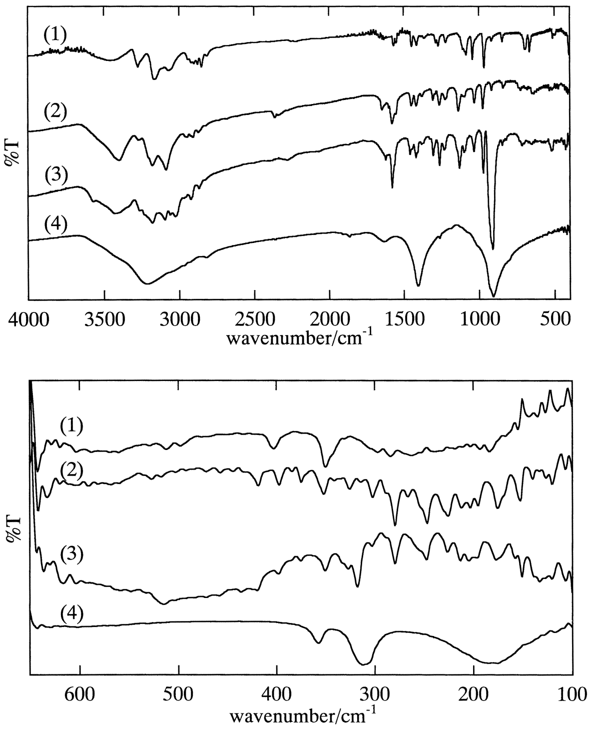

Fig. 3. IR spectra of (1) *fac*(*S*)-[Rh(aet)$_3$], (2) $\Delta\Delta/\Lambda\Lambda$-[Re{Rh(aet)$_3$}$_2$]Br$_3$·1.5H$_2$O (**1b**Br$_3$·1.5H$_2$O), (3) $\Delta\Lambda$-[Re{Rh(aet)$_3$}$_2$]Cl(ReO$_4$)$_2$·4H$_2$O (**1a**Cl(ReO$_4$)$_2$·4H$_2$O), and (4) NH$_4$ReO$_4$.

between the complex cations, the overall IR spectral patterns of **1a** and **1b** are quite similar to each other. However, only **1a** exhibits a characteristic strong band at 910 cm^{-1}, which indicates a vibration mode of the Re=O bond.[20] Similarly, the band at 317 cm^{-1} probably arises from ReO$_4^-$, compared with a curve of NH$_4$ReO$_4$ in the corresponding region. These facts support that **1a** has ReO$_4^-$ as counter anions, whereas **1b** does not. Bands due to the vibration of the NH$_2$ group appear around 3400 cm^{-1}, and that of the CH$_2$ group around 2900 cm^{-1}. The bands from the bending mode are observed around 1600 cm^{-1} for the NH$_2$ group and 1400 cm^{-1} for the CH$_2$ one. These bands in **1a** and **1b** are almost the same as those in the starting *fac*(*S*)-[Rh(aet)$_3$]. This also supports that the terminal units retain their structure during the formation of linear-type *S*-bridged complexes. In addition, [Re{Rh(aet)$_3$}$_2$]$^{3+}$ showed a similar spectrum to [Co{Rh(aet)$_3$}$_2$]$^{3+}$ over the whole region. Although the vibration mode of Re–S bond is observed at ca. 400 cm^{-1},[21] it is difficult to assign the bands depending on the M′–S bonds. This fact implies that the M′–S bonds in the linear-type *S*-bridged trinuclear systems, [M′{Rh(aet)$_3$}$_2$]$^{n+}$, are tightly fixed by the terminal *fac*(*S*)-[Rh(aet)$_3$] units.

The UV-vis absorption and CD spectra of **1a** and **1b** are shown in Fig. 4. **1b** was optically resolved into the $(+)^{\mathrm{CD}}_{350}$ and $(-)^{\mathrm{CD}}_{350}$ isomers, which exhibit the enantiomeric CD spectra to each other, by using the SP-Sephadex C-25 column chromatographic method. **1a** was not optically resolved by a similar method. These results are in agreement with the X-ray crystallographic results, which indicated that **1a** as a *meso* and **1b** as a *racemic* isomer. The absorption spectral patterns of these isomers are similar to each other over the whole region, although the intensity of the bands at 17 and 28 × 10^3 cm^{-1} is slightly different. This reflects the configurational difference between the isomers, because the ReO$_4^-$ counter anions indicated few absorption bands over the whole region. The most intense band in the UV region corresponds well to the sulfur-to-rhodium charge transfer band of the terminal *fac*(*S*)-[Rh(aet)$_3$] units, as observed in previous complexes, which have *fac*(*S*)-[Rh(aet)$_3$] units.[9–18] Similarly, the band at ca. 28 × 10^3 cm^{-1} is a d–d transition band of Rh(III) ion. Taking into account that the *fac*(*S*)-[Rh(aet)$_3$] unit has few absorption bands in the energy region lower than 25 × 10^3 cm^{-1},[9] four bands from 12 to 25 × 10^3 cm^{-1} are assigned to be arising from the central Re^{III}S$_6$ chromophore. Since the Re(III) ion belongs to the group of 5d ions, which is known to occur in strong crystal field octahedral coordination,[19] these bands are thought to depend on a (t$_{2g}$)^4 configuration. In addition, the band at ca. 38 × 10^3 cm^{-1} is assigned to be a sulfur-to-rhenium charge transfer band when compared with the band of *fac*(*S*)-[Rh(aet)$_3$] in the corresponding region. The CD bands are observed in a region where the Re(III) ion indicates absorption bands. This implies that the absolute configuration of asymmetric sulfur atoms from the *fac*(*S*)-[Rh(aet)$_3$] units affects the environment around central rhenium ion. On the other hand, the CD spectral behavior of $(-)^{\mathrm{CD}}_{350}$-**1b** is consistent with that of a reaction product obtained from a similar reaction using optically active Λ-*fac*(*S*)-[Rh(aet)$_3$].[10] Accordingly, $(+)^{\mathrm{CD}}_{350}$-**1b** and $(-)^{\mathrm{CD}}_{350}$-**1b** are assigned to $\Delta\Delta$- and $\Lambda\Lambda$-[Re{Rh(aet)$_3$}$_2$]$^{3+}$, respectively. This is supported by the fact that $\Delta\Delta$-[M′{Rh(aet)$_3$}$_2$]$^{3+}$ (M′ = Cr^{III}, Co^{III}) indicated positive CD bands in the higher energy region.[9,17] For the UV-vis absorption and CD spectra of **1a** and **1b**, no significant changes with time were observed for at least a few hours. This indicates that the trinuclear structures are fairly stable in water, even under an aerobic condition, retaining the oxidation state. This result is highly different from the

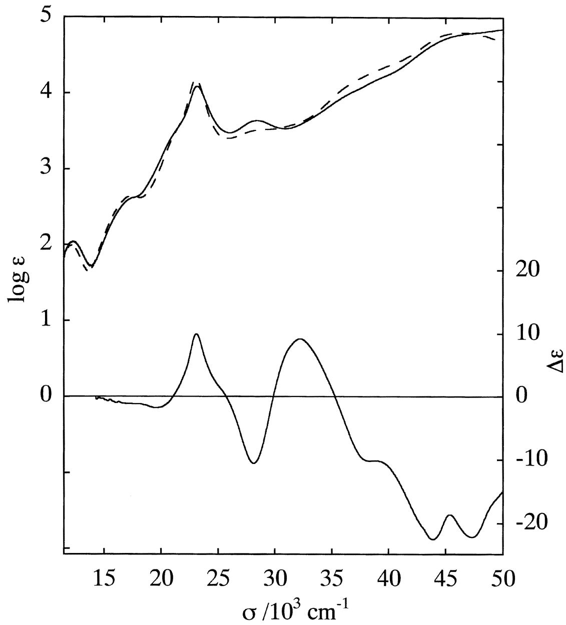

Fig. 4. UV-vis absorption and/or CD spectra of $\Delta\Lambda$-[Re{Rh(aet)$_3$}$_2$]$^{3+}$ (**1a**; - - - -) and $\Lambda\Lambda$-[Re{Rh(aet)$_3$}$_2$]$^{3+}$ ($(-)^{\mathrm{CD}}_{350}$-**1b**; ———).

Table 3. NMR Spectral Data of $[M\{Rh(aet)_3\}_2]^{3+}$ ($M = Re^{III}$, Co^{III})

Complexes	^{1}H NMR chemical shifts$^{a)}$ (coupling constants/Hz)		^{13}C NMR chemical shifts$^{a)}$	
	NCH_2	SCH_2	NCH_2	SCH_2
$\Delta\Lambda$-$[Re\{Rh(aet)_3\}_2]^{3+}$ (**1a**)	4.88 (d, 22.5), 3.39 (dd, 23.4, 10.1)	2.81 (d, 11.3), 2.00 (td, 13.3, 3.6)	57.61	52.16
$\Delta\Delta/\Lambda\Lambda$-$[Re\{Rh(aet)_3\}_2]^{3+}$ (**1b**)	4.87 (d, 13.1), 3.29 (dd, 25.1, 11.7)	2.84 (d, 12.7), 1.78 (td, 13.2, 3.3)	57.10	55.04
$\Delta\Lambda$-$[Co\{Rh(aet)_3\}_2]^{3+}$	3.15 (d, 11.2), 2.73 (dd, 22.5, 13.9)	2.49 (d, 13.2), 1.86 (td, 13.5, 3.3)	49.89	34.40
$\Delta\Delta/\Lambda\Lambda$-$[Co\{Rh(aet)_3\}_2]^{3+}$	3.16 (d, 12.9), 2.73 (dd, 23.7, 10.5)	2.39 (d, 11.2), 1.73 (td, 13.5, 3.6)	50.11	34.62

a) ppm from DSS in D_2O.

fact that the previously reported $[Mo\{Rh(aet)_3\}_2]^{3+}$ was unstable in water.[18]

Mononuclear Re(III) complexes with a distorted octahedral coordination sphere often show lower magnetic moments (1.6–2.1 μ_B) than the spin-only value for the $(t_{2g})^4$ configuration.[5] Moreover, $[Re(S_2CC_6H_5)(S_3CC_6H_5)_2]$, which is a rare example having a $Re^{III}S_6$ chromophore, indicated diamagnetism probably due to a significantly distorted octahedral structure, and the NMR spectra of this complex showed no paramagnetic shifts.[21] The Re(III) ion in the trinuclear complexes is situated in a relatively less distorted octahedral environment, and **1b** indicated paramagnetism, but very low magnetic susceptibility ($\chi_M = 230 \times 10^{-6}$ cm^3 mol^{-1}) at room temperature. Considering a diamagnetic correction,[22] an effective magnetic moment for the Re(III) ion is 1.32 μ_B. The ^{1}H NMR spectra of **1a** and **1b** in D_2O displayed six sets of sharp signals due to the aet ligands, while the ^{13}C NMR spectra exhibited two sharp signals. This means that the S_6 or D_3 symmetrical *S*-bridged trinuclear structures observed in the crystals are retained in their aqueous solution. From C–H correlation spectroscopy (COSY) of **1b**, the proton signals at δ 4.87 and 3.29 were coupled with the carbon signal at δ 57.10, while the signals at δ 2.84 and 1.78 were coupled with the signal at δ 55.04. Moreover, the signals at δ 4.87 and 3.29 indicated coupling with those of NH_2 protons in H–H COSY. Accordingly, it can be assigned that the carbon signal at δ 57.10 is due to a CH_2 group neighbored on the N atom and that the signal at δ 55.04 is due to that neighbored on S atom. A similar H–H coupling pattern was also observed in **1a**, although the signal at δ 4.88 was somewhat unclear because of an overlapping of the HDO signals. The chemical shifts of the CH_2 groups in **1a** and **1b** are summarized in Table 3, together with those in the corresponding diamagnetic complexes $[Co\{Rh(aet)_3\}_2]^{3+}$. These assignments of signals including NH_2 protons (δ 5.29, 5.06 for **1a** and δ 5.36, 5.05 for **1b**) were confirmed by H–H COSY. Both the ^{1}H and ^{13}C NMR spectra of the present Re(III) complexes indicated some paramagnetic shifts. Namely, most signals shift to a lower field, compared with the Co(III) complexes. Especially, the signals of carbon neighboring sulfur atoms, which coordinate to the Re(III) ion, indicate significant lower shifts (17.76 ppm for $\Delta\Lambda$ isomer and 20.42 ppm for $\Delta\Delta/\Lambda\Lambda$ isomer). As well as in the case of the Co(III) complexes, all of the reported chemical shifts of the carbon signals of SCH_2 groups in complexes containing the *fac*(*S*)-$[Rh(aet)_3]$ units and diamagnetic metal ions were in the range of δ 39.01–33.86.[11–13] These facts imply that the paramagnetic Re(III) ion affects the environment around it. However, the degree of paramagnetic shifts in **1a** and **1b** seems to be smaller than those in the other paramagnetic Re(III) complexes.[5] It can be considered that the NMR spectral behavior depends on the lower magnetic moment of the Re(III) ion in the $Rh^{III}Re^{III}Rh^{III}$ structure.

Experimental

Materials. 2-Aminoethanethiol, $RhCl_3 \cdot nH_2O$, NH_4ReO_4, and $SnCl_2 \cdot 2H_2O$ were purchased from Tokyo Kasei Kogyo Co., Ltd., N. E. Chemcat Co., Ltd., Soekawa Chemical Co., Ltd., and Koso Chemical Co., Ltd., respectively. $Na_2[Sb_2(R,R\text{-tartrato})_2] \cdot 5H_2O$ was prepared by a general procedure from $Na_2(R,R\text{-}H_3\text{tartrato})_2 \cdot H_2O$ and Sb_2O_3. The other reagents were obtained from Wako Pure Chemical Ind. Ltd., and all of the chemicals were of reagent grade and were used without further purification.

Preparation of Complexes. ***$\Delta\Lambda$*-$[Re\{Rh(aet)_3\}_2]^{3+}$ (1a):** *fac*(*S*)-$[Rh(aet)_3]$[12,17,23] (0.17 g, 0.50 mmol) and NH_4ReO_4 (0.14 g, 0.50 mmol) were dissolved in a 1 mol dm^{-3} HCl solution. To the yellow solution was added $SnCl_2 \cdot 2H_2O$ (0.12 g, 0.52 mmol), and the dark-red mixture was stirred at room temperature for 1.5 h. After unreacted materials were filtered off, the solution was left standing at room temperature for a few days. Dark-red plates ($\mathbf{1a}Cl(ReO_4)_2 \cdot 4H_2O$) were collected by filtration; one of the crystals was used for X-ray analysis. Yield: 0.028 g (8%). Anal. Found: C, 10.28; H, 3.10; N, 5.80; Re, 35.80, Rh, 14.20%. Calcd for $[Re\{Rh(NH_2CH_2CH_2S)_3\}_2]Cl(ReO_4)_2 \cdot 4H_2O$: C, 9.89; H, 3.04; N, 5.77; Re, 38.35, Rh, 14.13%. UV-vis absorption spectrum in H_2O: [ν_{max}, 10^3 cm^{-1} (log ε, 10^3 mol^{-1} dm^3 cm^{-1})]: 12.20 (1.99), 17.45 (2.64), 20.8 (3.3 sh), 23.05 (4.17), 28.3 (3.5 sh), 37.0 (4.2 sh), 46.60 (4.80). The sh label denotes a shoulder.

The dark-red reaction mixture was also poured onto an SP-Sephadex C-25 column. Two yellow bands (**1a** and **1b**) were eluted in this order with a 0.3 mol dm^{-3} NaCl aqueous solution. Some dark-red bands were adsorbed and not eluted with even a saturated NaCl aqueous solution. The estimated yields were 21% for **1a** and 16% for **1b**.

***$\Delta\Delta/\Lambda\Lambda$*-$[Re\{Rh(aet)_3\}_2]^{3+}$ (1b):** This complex was prepared by a procedure similar to that used for the corresponding complex **1a**, using a 1 mol dm^{-3} HBr solution instead of a HCl solution. Yield: 0.025 g (9%). Anal. Found for the bromide salt: C, 12.55; H, 3.43; N, 7.23; Re, 16.10, Rh, 18.72%. Calcd for $[Re\{Rh(NH_2CH_2CH_2S)_3\}_2]Br_3 \cdot 1.5H_2O$: C, 12.92; H, 3.52; N, 7.53; Re, 16.23, Rh, 17.94%. UV-vis absorption spectrum in H_2O: [ν_{max}, 10^3 cm^{-1} (log ε, 10^3 mol^{-1} dm^3 cm^{-1})]: 12.32 (2.04), 17.5 (2.6 sh), 20.7 (3.4 sh), 23.16 (4.08), 28.44 (3.64), 37.6 (4.1 sh), 45.3 (4.7 sh). The sh label denotes a shoulder. From the SP-Sephadex C-25 column chromatography using this reaction mixture, two yellow bands containing **1a** and **1b** were observed. A crystal ($\mathbf{1b}(ClO_4)_3$) suitable for X-ray analysis was obtained by adding an excess of $NaClO_4$ to an aqueous solution of $\mathbf{1b}Br_3$. Anal. Found for the perchlorate salt: C, 12.43; H, 3.20; N, 7.14%. Calcd for $[Re\{Rh(NH_2CH_2CH_2S)_3\}_2](ClO_4)_3$: C, 12.56; H, 3.16; N, 7.33%.

1b was optically resolved by SP-Sephadex C-25 column chromatography. Two yellow bands, $(+)^{\mathrm{CD}}_{350}$-**1b** and $(-)^{\mathrm{CD}}_{350}$-**1b**, were partially separated by eluting with a 0.15 mol dm^{-3} $Na_2[Sb_2(R,R\text{-tartrato})_2]\cdot 5H_2O$ aqueous solution. The $(+)^{\mathrm{CD}}_{350}$-**1b** and $(-)^{\mathrm{CD}}_{350}$-**1b** parts were eluted and fractionated with a 0.3 mol dm^{-3} NaCl aqueous solution. CD spectrum in H_2O for $(-)^{\mathrm{CD}}_{350}$-isomer: [$\nu_{\max}$, 10^3 cm^{-1} ($\Delta\varepsilon$, 10^3 mol^{-1} dm^3 cm^{-1})]: 17.4 (−1.2 sh), 19.52 (−1.82), 23.12 (+9.86), 28.15 (−10.58), 32.26 (+9.11), 38.40 (−10.22), 43.90 (−22.62), 47.30 (−22.25). The $\Delta\varepsilon$ values of each eluate containing the $(+)^{\mathrm{CD}}_{350}$-**1b** and $(-)^{\mathrm{CD}}_{350}$-**1b** isomers were evaluated on the basis of the absorption spectral data of **1b**$Br_3\cdot 1.5H_2O$.

***ΔΛ*- and *ΔΔ/ΛΛ*-[Co{Rh(aet)$_3$}$_2$]$^{3+}$:** Nitrate salts of these complexes were prepared by methods reported in a previous paper.[9]

Measurements. Elemental analyses (C, H, and N) were performed by the Chemical Analysis Center of the University of Tsukuba. The concentrations of Re and Rh in the complexes were determined with a NIPPON Jarrell-Ash ICPA-575 ICP spectrophotometer using NH_4ReO_4 and $RhCl_3\cdot nH_2O$ as references. The IR spectra were recorded on a JASCO FT/IR-550 spectrometer using KBr disks in the range of 4000–400 cm^{-1} and polyethylene pellets in the range of 650–100 cm^{-1}. The UV-vis absorption and CD spectra were recorded with a JASCO V-560 spectrophotometer and a JASCO J-600 spectropolarimeter in aqueous solution, respectively. The ^1H and ^{13}C NMR spectra were recorded with a BRUKER AM-500 or a JEOL EX-270 NMR spectrometer in D_2O and the sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as an internal reference. The molar conductances of the complexes were measured with a HORIBA conductivity meter (DS-14) in aqueous solution. The magnetic measurements were performed by using a Sherwood Scientific MSB-AUTO susceptibility balance. All of the measurements were carried out at room temperature.

Crystallography. Unit-cell and intensity data for **1a**$Cl(ReO_4)_2\cdot 4H_2O$ and **1b**$(ClO_4)_3$ were collected on a Rigaku AFC-7S four-circle diffractometer (Mo-$K\alpha$ radiation, ω-2θ scan mode, $2\theta_{\max} = 55°$, and 296 K). The crystallographic data and experimental parameters are summarized in Table 4. The structures were determined by a direct method (SIR 92),[24] and refined by full-matrix least-squares techniques. All of the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were not included in the calculations. In **1a**$Cl(ReO_4)_2\cdot 4H_2O$ all S and N atoms exhibited disorder; they appeared to be distributed in two different locations (S(*mn*) and N(*mn*); *n* = 1 and 2). Re(1) and Cl(1) atoms were constrained to the special positions. These atoms were refined with a site occupancy factor of 0.5. Since all [Rh(aet)$_3$] units in the reported *S*-bridged polynuclear complexes take octahedral *fac*(*S*) geometries,[9–18] two possible structures, namely, *racemic* (*ΔΔ* and *ΛΛ*) isomer with a trigonal prism Re(III) ion or *meso* (*ΔΛ*) isomer with an octahedral Re(III) ion, can be assumed. Taking into account some spectrochemical data, including column chromatography, because the central Re(1) atom is situated on the octahedral environment, the cation **1a** must be achiral. Therefore, we should choose a structure with the disordered positions for the *meso* isomer, which is associated with the crystallographic inversion center located on the central Re(1) atom. On the other hand, in **1b**$(ClO_4)_3$ two sets of atom peaks corresponding to a pair of enantiomers co-exist in each of four sites in the unit cell. This behavior is often observed in the *racemic* isomer of the *S*-bridged polynuclear complexes, such as *ΔΔ/ΛΛ*-[Mo{Rh(aet)$_3$}$_2$]$^{3+}$ [18] and *ΔΔ/ΛΛ*-[Ag$_3${M(aet)$_3$}$_2$]$^{3+}$ (M = Co^{III}, Rh^{III}).[11,25] Six of the seven O atoms bound to the Cl(2) atom were disordered. Re(1), Rh(1,2), Cl(1), O(1) and C(1,2,5,6) atoms were constrained to the special positions. The site-occupancy factor of each atom was fixed to 0.5, except for the Cl(2), O(5) and C(3,4,7,8) atoms. All of the calculations were performed on an Indigo II computer using the teXsan crystallographic software package.[26] The final atomic coordinates with equivalent isotropic thermal parameters (Tables S1 and S2), anisotropic thermal parameters (Tables S3 and S4), and complete bond distances and angles (Tables S5–S8) have been deposited as Document No. 74039 at the Office of the Editor of Bull. Chem. Soc. Jpn.. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and

Table 4. Crystallographic Data for *ΔΛ*-[Re{Rh(aet)$_3$}$_2$]$Cl(ReO_4)_2\cdot 4H_2O$ (**1a**$Cl(ReO_4)_2\cdot 4H_2O$) and *ΔΔ/ΛΛ*-[Re{Rh(aet)$_3$}$_2$]$(ClO_4)_3$ (**1b**$(ClO_4)_3$)

	1a$Cl(ReO_4)_2\cdot 4H_2O$	**1b**$(ClO_4)_3$
Formula	$C_{12}H_{44}ClN_6O_{12}Re_3Rh_2S_6$	$C_{12}H_{36}Cl_3N_6O_{12}ReRh_2S_6$
Formula weight	1456.76	1147.18
Cryst dimens/mm	0.63 × 0.38 × 0.05	0.23 × 0.30 × 0.30
Cryst system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (No. 2)	*P*nma (No. 62)
a/Å	9.249(2)	16.485(8)
b/Å	12.821(5)	13.387(4)
c/Å	9.067(2)	14.692(5)
α/°	110.70(2)	
β/°	119.35(1)	
γ/°	73.64(2)	
V/Å^3	868.9(4)	3242(3)
Z	1	4
D_{calcd}/g cm^{-3}	2.784	2.350
μ(Mo $K\alpha$)/cm^{-1}	118.36	54.24
Measured reflcns	4294	4359
Independent reflcns, R_{int}	3987, 0.025	3890, 0.027
Observed reflcns ($> 2\sigma I_0$)	3226	2039
Parameters	247	298
Final *R*, R_w	0.066, 0.088	0.070, 0.082

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