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Rhodium(III) complexes with thiolate and thioether ligands derived from *fac*(*S*)-[Rh(aet)$_3$] (aet = 2-aminoethanethiolate): selective formation, characterization and properties

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Alkylation of *fac*(*S*)-[Rh(aet)$_3$] (aet = $NH_2CH_2CH_2S^-$) with use of 1,2-dibromoethane in *N*,*N*-dimethylformamide produces *fac*(*S*)-[Rh(aet)(baete)]$^{2+}$ ([**1**]$^{2+}$, baete = $(NH_2CH_2CH_2SCH_2)_2$), in which two of the three thiolato S atoms in *fac*(*S*)-[Rh(aet)$_3$] are linked by an ethylene group. When methyl iodide is used as an alkylating reagent, two of the three thiolato S atoms are methylated to give *fac*(*S*)-[Rh(aet)(mtea)$_2$]$^{2+}$ ([**2**]$^{2+}$, mtea = $NH_2CH_2CH_2SCH_3$). Complexes [**1**]$^{2+}$ and [**2**]$^{2+}$ were optically resolved into the two enantiomers by SP-Sephadex C-25 column chromatography. The synthesis of a trimethylated complex, *fac*(*S*)-[Rh(mtea)$_3$]$^{3+}$ ([**3**]$^{3+}$), has been achieved by treatment of an aqueous solution of [**2**]$^{2+}$ with dimethyl sulfate. Reactions of [**1**]$^{2+}$ or [**2**]$^{2+}$ with Ag$^+$ in a 2 : 1 molar ratio in water produce S-bridged Rh^{III}Ag^{I}Rh^{III} trinuclear complexes, [Ag{Rh(aet)(baete)}$_2$]$^{5+}$ ([**4**]$^{5+}$) and [Ag{Rh(aet)(mtea)$_2$}$_2$]$^{5+}$ ([**5**]$^{5+}$), indicating that [**1**]$^{2+}$ and [**2**]$^{2+}$ act as an S-donating monodentate complex-ligand. These complexes have been characterized by UV-VIS absorption, CD and NMR spectroscopic methods, together with single-crystal X-ray analyses for [**1**]$^{2+}$ and [**3**]$^{3+}$.

Introduction

One of the most attractive properties of thiolato groups coordinated to a metal ion is their high nucleophilicity, which leads to derivatives modified at sulfur atoms, such as coordinated sulfenato, sulfinato, and thioether groups.[1–6] In addition, it has been recognized that the high nucleophilicity of coordinated thiolato groups allows thiolato metal complexes to function as S-donating complex-ligands towards a variety of metal ions to construct S-bridged polynuclear structures.[7–14] To date, the ligating ability of thiolato groups coordinated to cobalt(III) ion has been extensively investigated, and a large number of S-bridged polynuclear complexes with different nuclearities have been prepared based on mono(thiolato)-, bis(thiolato)- and tris(thiolato)-type cobalt(III) complexes containing 2-aminoethanethiolate (aet), L-cysteinate (L-cys), or D-penicillaminate (D-pen).[11–13] On the other hand, reports on the S-bridged polynuclear complexes derived from rhodium(III) complexes with thiolate ligands are relatively few in number and are limited to polynuclear complexes derived from the tris(thiolato)-type *fac*(*S*)-[Rh(aet)$_3$] and *fac*(*S*)-[Rh(L-cys-*N*,*S*)$_3$]$^{3-}$.[14] The limitation is mainly due to the difficulty in preparation of mono(thiolato)- and bis(thiolato)-type rhodium(III) complexes, compared with the corresponding cobalt(III) complexes.[3,14a]

Recently, it has been shown that a non-bridging thiolato donor group in [Pd{Pd(aet)}{Rh(aet)$_2$}{Rh(aet)$_3$}$_2$]$^{4+}$, which was prepared by the reaction of *fac*(*S*)-[Rh(aet)$_3$] with [PdCl$_4$]$^{2-}$, is converted to a thioether group by a methylation reaction.[15] From this observation, we expected that mono(thiolato)- and/or bis(thiolato)-type rhodium(III) species can be derived from tris(thiolato)-type rhodium(III) complexes if one or two of the three thiolato groups are converted to thioether groups by alkylation reactions. Thus, as part of our effort to construct S-bridged polynuclear structures based on chiral thiolato metal octahedrons, we started to investigate alkylation reactions of tris(thiolato)-type rhodium(III) complexes so as to create a new class of rhodium(III) complexes containing both thiolato and thioether groups, which could function as S-donating complex-ligands. Here we report the alkylation of the most typical tris(thiolato)-type rhodium(III) complex, *fac*(*S*)-[Rh(aet)$_3$], with use of 1,2-dibromoethane and methyl iodide, which was found to form dialkylated mono(thiolato)-type rhodium(III) complexes, *fac*(*S*)-[Rh(aet)(baete)]$^{2+}$ ([**1**]$^{2+}$, baete = 1,2-bis(2-aminoethylthio)ethane) and *fac*(*S*)-[Rh(aet)(mtea)$_2$]$^{2+}$ ([**2**]$^{2+}$, mtea = 2-methylthioethylamine). While there have been a number of reports of alkylation for mono(thiolato)- and bis(thiolato)-type metal complexes,[5,6] to the best of our knowledge, this is the first report of alkylation for tris(thiolato)-type complexes. Further conversion of [**2**]$^{2+}$ to the trialkylated *fac*(*S*)-[Rh(mtea)$_3$]$^{3+}$ ([**3**]$^{3+}$) by reaction with dimethyl sulfate, together with the construction of S-bridged Rh^{III}Ag^{I}Rh^{III} trinuclear structures in [Ag{Rh(aet)(baete)}$_2$]$^{5+}$ ([**4**]$^{5+}$) and [Ag{Rh(aet)(mtea)$_2$}$_2$]$^{5+}$ ([**5**]$^{5+}$) by reaction of [**1**]$^{2+}$ or [**2**]$^{2+}$ with Ag^{I} ion are also reported (Scheme 1).

Experimental

Preparation of *fac*(*S*)-[Rh(aet)(baete)]$^{2+}$ ([1]$^{2+}$)

To a yellow suspension of *fac*(*S*)-[Rh(aet)$_3$][14c] (0.20 g, 0.60 mmol) in 20 cm^3 of *N*,*N*-dimethylformamide (DMF) was added 1,2-dibromoethane (0.15 g, 0.80 mmol). The mixture was stirred at 60 °C for 5 h under a dinitrogen atmosphere, during which time the suspension became a clear orange solution. The orange reaction solution was treated with diethyl ether several times to extract DMF and unreacted 1,2-dibromoethane. The remaining orange residue was dissolved in 10 cm^3 of water, several drops of a saturated aqueous solution of NaClO$_4$ were

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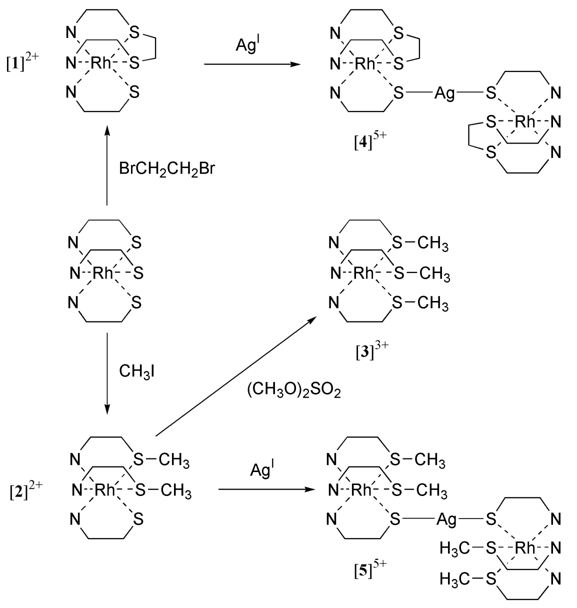

Scheme 1

added to it, and it was stored in a refrigerator for 2 days. The resulting fine orange crystals of [**1**](ClO_4)$_2$·H_2O (0.22 g, 63%) were collected by filtration. Found: C, 16.47; H, 4.11; N, 7.16. [Rh(aet)(baete)](ClO_4)$_2$·H_2O = $C_8H_{24}Cl_2N_3O_9RhS_3$ requires: C, 16.67; H, 4.20; N, 7.29%. Single crystals suitable for X-ray analysis were obtained by recrystallization of the fine crystals from water in a refrigerator.

This complex was obtained in a higher yield with use of SP-Sephadex C-25 cation exchange column chromatography. The orange residue obtained from the reaction of *fac*(*S*)-[Rh(aet)$_3$] (0.20 g) with 1,2-dibromoethane (0.15 g) was dissolved in water and then poured onto an SP-Sephadex C-25 column (2 cm × 20 cm, Na^+ form). After the column had been washed with water, an orange band was eluted with a 0.15 mol dm^{-3} aqueous solution of $NaClO_4$. The eluate was concentrated to a small volume with a rotary evaporator, followed by storing in a refrigerator for 2 days. The resulting orange crystals (0.29 g, 83%) were collected by filtration.

Preparation of *fac*(*S*)-[Rh(aet)(mtea)$_2$]$^{2+}$ ([2]$^{2+}$)

To a yellow suspension of *fac*(*S*)-[Rh(aet)$_3$]^{14c} (0.20 g, 0.60 mmol) in 20 cm^3 of DMF was added CH_3I (0.30 g, 2.1 mmol). The mixture was stirred at 40 °C for 2 h under a dinitrogen atmosphere, during which time the suspension became a clear orange solution. The orange solution was treated with diethyl ether several times to extract DMF and unreacted CH_3I. The remaining red oil was dissolved in 10 cm^3 of water, several drops of a saturated aqueous solution of NaI were added to it, and it was stored in a refrigerator for 3 days. The resulting orange-yellow microcrystals were collected by filtration and then recrystallized from water to give orange-yellow rod-shaped crystals (0.17 g, 42%). Found: C, 14.46; H, 4.45; N, 6.07. [Rh(aet)(mtea)$_2$]I_2·3H_2O = $C_8H_{30}I_2N_3O_3RhS_3$ requires: C, 14.36; H, 4.52; N, 6.28%.

The perchlorate salt of [**2**]$^{2+}$ was isolated by the following method. The red oil obtained from the reaction of *fac*(*S*)-[Rh(aet)$_3$] (0.10 g) with CH_3I (0.16 g) was dissolved in water and then poured onto an SP-Sephadex C-25 column (2 cm × 20 cm, Na^+ form). After the column had been washed with water, a yellow band was eluted with a 0.15 mol dm^{-3} aqueous solution of $NaClO_4$. The eluate was concentrated to a small volume with a rotary evaporator, followed by storing in a refrigerator for 4 days. The resulting orange-yellow needle-like crystals were collected by filtration. The second crop of crystals (0.14 g, 80%) was obtained by storing the filtrate in a refrigerator for several days. Found: C, 16.60; H, 4.31; N, 7.21. [Rh(aet)(mtea)$_2$]-(ClO_4)$_2$·H_2O = $C_8H_{26}Cl_2N_3O_9RhS_3$ requires: C, 16.61; H, 4.53; N, 7.27%.

Optical resolution of [1]$^{2+}$ and [2]$^{2+}$

An aqueous solution of [**1**](ClO_4)$_2$·H_2O (0.04 g) was chromatographed on an SP-Sephadex C-25 column (2 cm × 50 cm, Na^+ form), using a 0.08 mol dm^{-3} aqueous solution of $Na_2[Sb_2(R,R\text{-tartrato})_2]$·5$H_2O$ as an eluent. When the adsorbed band was developed close to the end of the column, the eluent was changed to a 0.15 mol dm^{-3} aqueous solution of $NaClO_4$. The eluate was fractionated in portions of *ca.* 100 cm^3 each. Each fraction was concentrated to a small volume with a rotary evaporator, and the concentrates were used for the CD spectral measurements. The concentration of each fraction was evaluated on the basis of the absorption spectral data of the racemate of [**1**](ClO_4)$_2$·H_2O. It was found from the CD spectral measurements that the earlier several fractions contained the pure $(+)^{CD}_{420}$ isomer, whereas the later several fractions contained the pure $(-)^{CD}_{420}$ isomer.

The optical resolution of [**2**](ClO_4)$_2$·H_2O was carried out using the same column chromatographic method. It was found from the CD spectral measurements that the earlier several fractions contained the pure $(+)^{CD}_{420}$ isomer, whereas the later several fractions contained the pure $(-)^{CD}_{420}$ isomer.

Preparation of *fac*(*S*)-[Rh(mtea)$_3$]$^{3+}$ ([3]$^{3+}$)

To a yellow solution of [Rh(aet)(mtea)$_2$](ClO_4)$_2$·H_2O (0.05 g, 0.09 mmol) in 5 cm^3 of water was added dimethyl sulfate (2 cm^3). The mixture was stirred at room temperature for 10 min, followed by allowing to stand at room temperature for 1 day to give a pale yellow upper layer and a colorless lower layer. The pale yellow layer was separated from the colorless layer and its pH was adjust to *ca.* 7 with a 1 mol dm^{-3} aqueous solution of NaOH. This solution was concentrated to a small volume with a rotary evaporator, a few drops of a saturated aqueous solution of $NaClO_4$ were added to it, and the solution was stored in a refrigerator for 10 days. The resulting, almost colorless, crystalline solid (0.03 g, 46%) was collected by filtration. Found: C, 15.05; H,4.20; N, 5.58. [Rh(mtea)$_3$](ClO_4)$_3$·H_2O·1/4$NaClO_4$ = $C_9H_{29}Cl_3N_3O_{13}RhS_3$·1/4$NaClO_4$ requires: C, 14.94; H, 4.04; N, 5.81%. Single crystals of [**3**](ClO_4)$_3$·H_2O suitable for X-ray analysis were obtained by recrystallization of the solid from water in a refrigerator.

Preparation of [Ag{Rh(aet)(baete)}$_2$](ClO_4)$_5$·2H_2O ([4](ClO_4)$_5$·2H_2O)

To an orange solution of [**1**](ClO_4)$_2$·H_2O (0.10 g, 0.17 mmol) in 5 cm^3 of water was added $AgClO_4$ (0.02 g, 0.1 mmol) dissolved in 2 cm^3 of water. The mixture was stirred at room temperature for 1 h, during which time the color of the solution changed to light yellow. To the reaction solution were added a few drops of a saturated aqueous solution of $NaClO_4$, followed by storing in a refrigerator for 6 days. The resulting light yellow needle crystals (0.048 g, 41%) were collected by filtration. Found: C, 14.02; H, 3.49; N 6.09. [Ag{Rh(aet)(baete)}$_2$](ClO_4)$_5$·2H_2O = $C_{16}H_{48}AgCl_5N_6O_{22}Rh_2S_6$ requires: C, 14.13; H, 3.56; N, 6.18%.

Preparation of [Ag{Rh(aet)(mtea)$_2$}$_2$](ClO_4)$_5$·5H_2O ([5](ClO_4)$_5$·5H_2O)

To an orange solution of [**2**](ClO_4)$_2$·H_2O (0.10 g, 0.17 mmol) in 3 cm^3 of water was added $AgClO_4$ (0.02 g, 0.1 mmol) dissolved in 2 cm^3 of water. The mixture was stirred at room temperature for 30 min, during which time the color of the solution changed to light yellow. To the reaction solution were added a few drops of a saturated aqueous solution of $NaClO_4$, followed by storing in a refrigerator for 6 days. The resulting light yellow needle crystals (0.054 g, 44%) were collected by filtration. Found: C,

Table 1 Crystallographic data for [**1**]$(ClO_4)_2\cdot H_2O$ and [**3**]$(ClO_4)_3\cdot H_2O$

	[**1**]$(ClO_4)_2\cdot H_2O$	[**3**]$(ClO_4)_3\cdot H_2O$
Formula	$C_8H_{24}Cl_2N_3O_9RhS_3$	$C_9H_{29}Cl_3N_3O_{13}RhS_3$
M	576.30	692.80
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/a$ (no. 14)
a/Å	9.368(2)	19.181(4)
b/Å	16.306(2)	14.374(4)
c/Å	13.167(1)	20.233(4)
β/°	96.41(1)	116.93(1)
V/Å^3	1998.6(4)	4973(1)
Z	4	8
T/K	293	298
Radiation, *λ*/Å	0.7107	0.7107
D_c/g cm^{-3}	1.915	1.850
μ(Mo Kα)/cm^{-1}	14.79	13.20
R^a	0.026	0.049
$R_w{}^b$	0.025	0.035

[a] $R = \Sigma|(|F_o| - |F_c|)|/\Sigma(|F_o|)$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

13.49; H, 4.04; N 5.96. [Ag{Rh(aet)(mtea)$_2$}$_2$]$(ClO_4)_5\cdot 5H_2O$ = $C_{16}H_{58}AgCl_5N_6O_{25}Rh_2S_6$ requires: C, 13.55; H, 4.12; N, 5.93%.

CAUTION: Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.

Crystallography

Single-crystal X-ray diffraction experiments for [**1**]$(ClO_4)_2\cdot H_2O$ and [**3**]$(ClO_4)_3\cdot H_2O$ were performed on a Rigaku AFC-7S diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Crystallographic data are summarized in Table 1. Unit cell parameters were determined by a least-squares refinement, using the setting angles of 25 reflections in the ranges of $29° < 2\theta < 30°$ for [**1**]$(ClO_4)_2\cdot H_2O$ and $25° < 2\theta < 29°$ for [**3**]$(ClO_4)_3\cdot H_2O$. The intensity data were collected by the ω–2θ scan technique (2θ <55°). The intensities were corrected for Lorentz and polarization effects. Empirical absorption corrections based on a series of ψ scans were also applied. The 4095 and 6702 independent reflections with $I > 2\sigma(I)$ of the measured 5032 and 12212 reflections were considered as 'observed' and used for structure determinations of [**1**]$(ClO_4)_2\cdot H_2O$ and [**3**]$(ClO_4)_3\cdot H_2O$, respectively.

The positions of Rh, S and some other atoms were determined by direct methods. The remaining non-H atom positions were found by successive difference Fourier techniques. The structures were refined by full-matrix, least-squares techniques using anisotropic thermal parameters for non-H atoms. H atoms for [**1**]$(ClO_4)_2\cdot H_2O$, except for those of a water molecule, were found from difference Fourier maps and were refined using isotropic thermal parameters. H atoms for [**3**]$(ClO_4)_3\cdot H_2O$, except for those of a water molecule, were located and added to calculations but not refined. All calculations were performed using the teXsan crystallographic software package.[16]

CCDC reference numbers 172537 and 172538.

See http://www.rsc.org/suppdata/dt/b1/b107933f/ for crystallographic data in CIF or other electronic format.

Measurements

UV-VIS absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer and the CD spectra were recorded with a JASCO J-700 spectropolarimeter at room temperature. ^1H and ^{13}C NMR spectra were recorded with a JEOL JNM-A500 NMR spectrometer at probe temperature. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as the internal reference. Elemental analyses (C, H, N) were performed by the Analysis Center of the University of Tsukuba. The concentrations of Rh and Ag in the complexes were determined with a SHIADZU ICPS-1000III ICP spectrometer.

Table 2 Selected bond distances (Å) and angles (°) for [**1**]$(ClO_4)_2\cdot H_2O$

Rh–S1	2.3347(7)	Rh–N1	2.106(3)
Rh–S2	2.2930(7)	Rh–N2	2.137(2)
Rh–S3	2.2785(8)	Rh–N3	2.122(3)
S1–Rh–S2	88.83(3)	S2–Rh–N2	86.15(7)
S1–Rh–S3	95.55(3)	S2–Rh–N3	170.09(7)
S1–Rh–N1	84.98(8)	S3–Rh–N1	177.66(8)
S1–Rh–N2	173.02(8)	S3–Rh–N2	89.10(8)
S1–Rh–N3	86.59(8)	S3–Rh–N3	84.01(7)
S2–Rh–S3	87.69(3)	N1–Rh–N2	90.6(1)
S2–Rh–N1	94.61(8)	N1–Rh–N3	93.7(1)
		N2–Rh–N3	99.1(1)

Molar conductivities of the complexes were measured with a Horiba DS-14 conductivity meter at room temperature.

Results and discussion

Crystal structure of *fac*(*S*)-[Rh(aet)(baete)]$^{2+}$ ([**1**]$^{2+}$)

X-Ray structural analysis of [**1**]$(ClO_4)_2\cdot H_2O$ revealed the presence of a complex cation, two perchlorate anions and a water molecule. The number of the perchlorate anions implies that the complex cation is divalent. The structure of the complex cation is shown in Fig. 1(a) and its selected bond distances and angles are listed in Table 2.

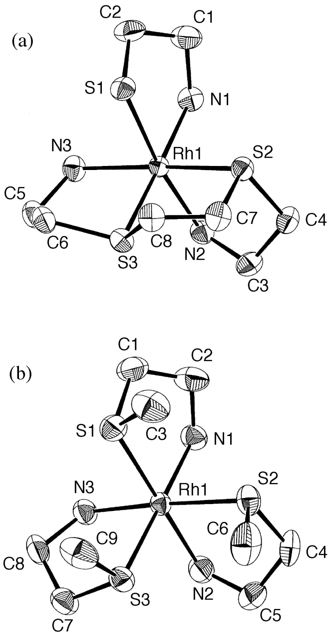

Fig. 1 Perspective views of (a) [Rh(aet)(baete)]$^{2+}$ ([**1**]$^{2+}$) and (b) [Rh(mtea)$_3$]$^{3+}$ ([**3**]$^{3+}$) with the atomic labeling scheme. Ellipsoids represent 50% probability.

The complex cation [**1**]$^{2+}$ consists of a bidentate-*N*,*S* aet ligand and a tetradentate-*N*,*S*,*S*,*N* baete ligand, which surround the Rh^{III} center in an approximately octahedral structure. Two thioether S atoms from the baete ligand and one thiolato S atom from the aet ligand occupy one face of the octahedron to give a *fac*(*S*) isomer, consistent with that of the parental complex *fac*(*S*)-[Rh(aet)$_3$]. As to the tetradentate-*N*,*S*,*S*,*N* baete ligand, two terminal N atoms are located at *cis* positions to form a *cis*-β geometry. As indicated by the space group $P2_1/c$, crystal [**1**]$^{2+}$ is a racemic compound consisting of a pair of enantiomers, Δ and Λ; the former isomer is shown in Fig. 1(a). Both the two asymmetric thioether S atoms have *R* configuration for the Δ isomer and *S* configuration for the Λ isomer. The two *N*,*S*-chelate rings for the baete ligand adopt a gauche form with opposite conformations, *lel* and *ob*, which allow the

Table 3 Selected bond distances (Å) and angles (°) for [**3**]$(ClO_4)_3 \cdot H_2O$

Rh1–S1	2.326(2)	Rh2–S4	2.309(2)
Rh1–S2	2.338(2)	Rh2–S5	2.322(2)
Rh1–S3	2.317(2)	Rh2–S6	2.339(2)
Rh1–N1	2.116(5)	Rh2–N4	2.104(6)
Rh1–N2	2.112(6)	Rh2–N5	2.101(5)
Rh1–N3	2.113(5)	Rh2–N6	2.115(6)
S1–Rh1–S2	98.27(7)	S4–Rh2–S5	96.85(8)
S1–Rh1–S3	96.80(7)	S4–Rh2–S6	97.88(7)
S1–Rh1–N1	85.1(2)	S4–Rh2–N4	86.0(2)
S1–Rh1–N2	175.2(2)	S4–Rh2–N5	87.5(2)
S1–Rh1–N3	87.1(2)	S4–Rh2–N6	175.5(2)
S2–Rh1–S3	95.40(7)	S5–Rh2–S6	96.48(7)
S2–Rh1–N1	87.2(1)	S5–Rh2–N4	176.0(2)
S2–Rh1–N2	84.9(2)	S5–Rh2–N5	85.3(2)
S2–Rh1–N3	174.4(2)	S5–Rh2–N6	86.2(2)
S3–Rh1–N1	176.5(2)	S6–Rh2–N4	85.9(2)
S3–Rh1–N2	86.4(2)	S6–Rh2–N5	174.1(2)
S3–Rh1–N3	85.3(1)	S6–Rh2–N6	85.1(2)
N1–Rh1–N2	91.5(2)	N4–Rh2–N5	92.0(2)
N1–Rh1–N3	91.8(2)	N4–Rh2–N6	90.9(2)
N2–Rh1–N3	89.7(2)	N5–Rh2–N6	89.4(2)

bridging *S*,*S*-chelate ring to have a preferable gauche form, rather than an envelope form. The remaining *N*,*S*-chelate ring for the aet ligand has an unusual *ob* conformation, so as to avoid the steric interaction between the methylene proton on the C8 atom and the lone pair on the S1 atom. This interaction is also decreased by having the obtuse angle of 95.55(3)° for S1–Rh–S3, which is significantly larger than the S1–Rh–S2 angle of 88.83(3)°.

The Rh–S1 distance [2.3347(7) Å] in [**1**]$^{2+}$ is similar to the averaged Rh–S_{aet} distance [2.3217(7) Å] in $[Rh_2(aet)_4(cysta)]^{2+}$ (cysta = cystamine), in which two *fac*(*S*)-[Rh(aet)$_3$] units are linked by a sulfur–sulfur bond.[17] Furthermore, the Rh–S2 and Rh–S3 distances [average 2.2858(8) Å] are within the range of Rh–S distances found in the rhodium(III) complexes with thioether S donor atoms.[18,19] However, it should be noted that the Rh–S2 and Rh–S3 distances are shorter than the Rh–S1 distance, which is in contrast to the observation that the Co–$S_{thioether}$ bond distance [2.267(10) Å] in $[Co(mtea)(en)_2]^{3+}$ is longer than the Co–$S_{thiolato}$ distance [2.226(2) Å] in $[Co(aet)(en)_2]^{2+}$.[5a] The shorter Rh–$S_{thioether}$ bonds compared with the Rh–$S_{thiolato}$ bond in [**1**]$^{2+}$ may be attributed to the structural chelate influence, which allows the inner thioether S atoms to bind with the Rh^{III} center more tightly than the terminal thiolato S atom does. Indeed, it has been shown that in the rhodium(III) complexes with a tetradentate-*S*,*S*,*S*,*S* thioether ligand, the Rh–S bond distances for the inner S atoms are commonly *ca.* 0.05 Å shorter than those for the terminal S atoms.[19] In [**1**]$^{2+}$, the Rh–N2 distance [2.137(2) Å] *trans* to the thiolato S atom is somewhat longer than the Rh–N1 and Rh–N3 distances [average 2.114(3) Å] *trans* to the thioether S atoms. This is consistent with the order of structural *trans*-influence due to S donor atom; $RS^- > R\text{–}S\text{–}R'$.[5a]

Crystal structure of *fac*(*S*)-[Rh(mtea)$_3$]$^{3+}$ ([3]$^{3+}$)

X-Ray structural analysis of [**3**]$(ClO_4)_3 \cdot H_2O$ revealed the presence of two crystallographically independent, yet nearly identical, complex cations, six perchlorate anions and two water molecules. The number of the perchlorate anions implies that each complex cation is trivalent. The structure of one of the two complex cations is shown in Fig. 1(b), and the selected bond distances and angles are listed in Table 3.

The complex cation [**3**]$^{3+}$ consists of three mtea ligands that chelate to the Rh^{III} center through amine N and thioether S atoms to form an approximately octahedral structure. In [**3**]$^{3+}$, the three thioether S atoms occupy one face of the octahedron to give a *fac*(*S*) isomer, as in [**1**]$^{2+}$ and the starting complex *fac*(*S*)-[Rh(aet)$_3$]. The three asymmetric S atoms in [**3**]$^{3+}$ are unified to have *S* configuration for the Δ isomer and *R* configuration for the Λ isomer. Thus, crystal [**3**]$^{3+}$ consists of Δ_{SSS} and Λ_{RRR} isomers, which combine to form the racemic compound; the former isomer is illustrated in Fig. 1(b). All three chelate rings in [**3**]$^{3+}$ adopt a gauche form with the *ob* conformation, which is unusual for tris(chelate)-type metal complexes.[20] Molecular model examinations point out that the steric interaction among the three methyl groups on the facially arranged S atoms is effectively decreased by adopting this conformation in $\Delta_{SSS}/\Lambda_{RRR}$-*fac*(*S*)-[Rh(mtea)$_3$]$^{3+}$. The presence of three methyl groups on one face also affects the S–Rh–S angles in [**3**]$^{3+}$. That is, all the S–Rh–S angles are obtuse [average 96.95(8)°] to give an expanded S_3 face, whereas the N–Rh–N bond angles [average 90.9(2)°] are normal and close to the right angle.

The Rh–S bond distances in [**3**]$^{3+}$ [average 2.325(2) Å] are longer than the Rh–$S_{thioether}$ distances in [**1**]$^{2+}$ [average 2.2858(8) Å]. This is to be expected in view of the difference in environment between the thioether donors in [**1**]$^{2+}$ and [**3**]$^{3+}$. The Rh–N bond distances in [**3**]$^{3+}$ [average 2.110(6) Å], are in good agreement with the averaged Rh–N distance *trans* to the thioether S atoms in [**1**]$^{2+}$ [2.114(3) Å].

Synthesis and characterization of *fac*(*S*)-[Rh(aet)(baete)]$^{2+}$ ([1]$^{2+}$)

The reaction of *fac*(*S*)-[Rh(aet)$_3$] having three thiolato donors with a slight excess of 1,2-dibromoethane in DMF gave an orange solution, from which orange crystals of [**1**]$(ClO_4)_2 \cdot H_2O$ were isolated in a high yield. From the elemental analysis, it was suggested that [**1**]$^{2+}$ is a 1 : 1 adduct of [Rh(aet)$_3$] and $(CH_2CH_2)^{2+}$. X-Ray analysis established that [**1**]$^{2+}$ is a mononuclear rhodium(III) complex, *fac*(*S*)-[Rh(aet)(baete)]$^{2+}$, having two thioether and one thiolato donors in one face. The formation of polynuclear species such as $[Rh_2(aet)_2(baete)_2]^{4+}$, in which two [Rh(aet)$_3$] units are intermolecularly linked by two ethylene groups, was not noticed. Thus, it is seen that two of the three thiolato S atoms in *fac*(*S*)-[Rh(aet)$_3$] are effectively linked by one ethylene group with retention of the *fac*(*S*) geometry.

As shown in Fig. 2(a), the ^{13}C NMR spectrum of [**1**]$^{2+}$ in D_2O gives eight sharp signals for eight methylene carbon atoms in the complex (δ = 31.54, 39.18, 42.16, 43.59, 44.40, 45.65, 52.61 and 53.89). This implies that only the C_1 symmetrical Δ_{RR}/Λ_{SS}-*fac*(*S*) isomer observed in the crystal is formed for [Rh(aet)(baete)]$^{2+}$, the structure of which is retained in solution. The UV-VIS absorption spectrum of [**1**]$^{2+}$ is characterized by a first d–d transition band at *ca.* 32×10^3 cm^{-1} with an explicit shoulder on the lower energy side (*ca.* 26×10^3 cm^{-1}) and a broad sulfur-to-rhodium CT band at *ca.* 44×10^3 cm^{-1} (Fig. 3 and Table 4). This absorption spectral feature is similar to that of *fac*(*S*)-[Rh(aet)$_3$] having the same *fac*(*S*)-$Rh(N)_3(S)_3$ chromophore.[14c] However, the intensity of the shoulder of the d–d band for [**1**]$^{2+}$ is much lower than that for *fac*(*S*)-[Rh(aet)$_3$]. This result suggests that the absorption component of this shoulder is due to thiolato coordination and that its intensity is decreased with decreasing the number of the thiolato groups coordinated to the rhodium(III) center. Similar absorption shoulders have been observed for cobalt(III) complexes with a single thiolato donor at the lower energy side of the first d–d band.[5,21]

Complex [**1**]$^{2+}$ was optically resolved by SP-Sephadex C-25 column chromatography, using $[Sb_2(R,R\text{-tartrato})_2]^{2-}$ as the resolving agent. Although attempts to separate [**1**]$^{2+}$ completely into two enantiomers in the column were unsuccessful, it was confirmed from the absorption and CD spectral measurements that the earlier and later fractions contain the optically pure $(+)^{\mathrm{CD}}_{420}$ and $(-)^{\mathrm{CD}}_{420}$ isomers, respectively, which show CD spectra enantiomeric to each other. As shown in Fig. 3 and Table 4, the CD spectrum of $(+)^{\mathrm{CD}}_{420}$-[**1**]$^{2+}$ exhibits a positive CD band at *ca.* 24×10^3 cm^{-1} in the d–d transition region and a negative CD band at *ca.* 45×10^3 cm^{-1} in the CT transition region. For

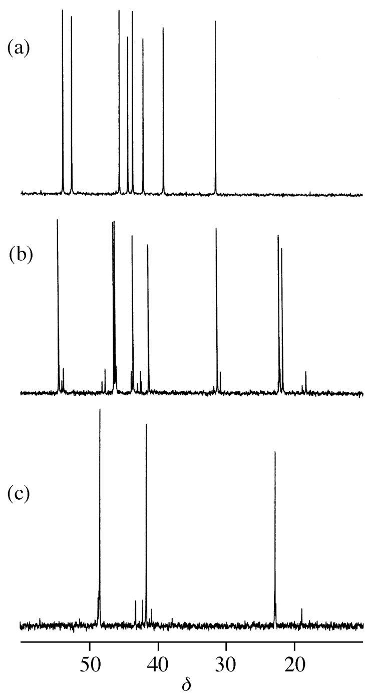

Fig. 2 ^{13}C NMR spectra of (a) $[\mathbf{1}]^{2+}$, (b) $[\mathbf{2}]^{2+}$, and (c) $[\mathbf{3}]^{3+}$ in D_2O.

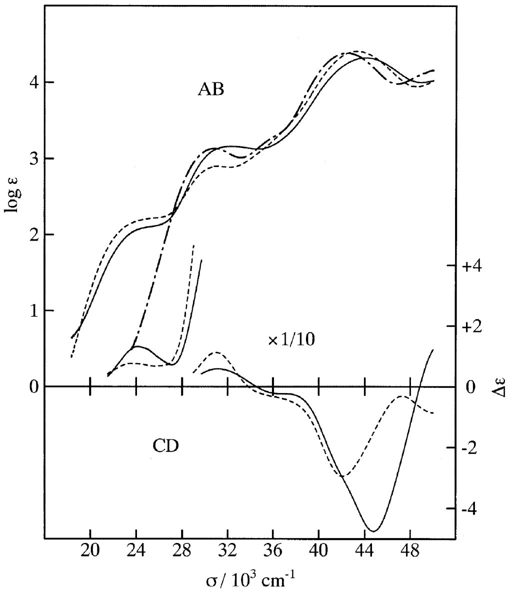

Fig. 3 Electronic absorption and CD spectra of $[\mathbf{1}]^{2+}$ (—), $[\mathbf{2}]^{2+}$ (- - -), and $[\mathbf{3}]^{3+}$ (–•–) in water.

several S-bridged polynuclear complexes consisting of *fac*(*S*)-$[\mathrm{Rh(aet)_3}]$ units and d^{10} metal ions (Zn$^{\rm II}$, Hg$^{\rm II}$, Au$^{\rm I}$), the isomers having the Δ configurational *fac*(*S*)-$[\mathrm{Rh(aet)_3}]$ units commonly give a positive CD band at lower energy side of the d–d absorption band region.[14c,e,i] Thus, it is likely that the $(+)^{\rm CD}_{420}$ and $(-)^{\rm CD}_{420}$ isomers of $[\mathbf{1}]^{2+}$ have the Λ and Δ configurations, respectively.

Synthesis and characterization of *fac*(*S*)-$[\mathrm{Rh(aet)(mtea)_2}]^{2+}$ ($[\mathbf{2}]^{2+}$) and *fac*(*S*)-$[\mathrm{Rh(mtea)_3}]^{3+}$ ($[\mathbf{3}]^{3+}$)

Treatment of *fac*(*S*)-$[\mathrm{Rh(aet)_3}]$ with *ca.* three molar equiv. of CH_3I in DMF gave an orange solution, from which orange-yellow crystals of $[\mathbf{2}]I_2{\cdot}3H_2O$ were directly isolated in a satisfactory yield. When the reaction mixture was chromatographed on a cation-exchange SP-Sephadex C-25 column, a yellow band of $[\mathbf{2}]^{2+}$ was eluted with a 0.15 mol dm^{-3} aqueous solution of $NaClO_4$, and from the eluate orange-yellow crystals of $[\mathbf{2}](ClO_4)_2{\cdot}3H_2O$ were isolated in a high yield. The elemental analysis results of the iodide and perchlorate salts of $[\mathbf{2}]^{2+}$ are consistent with the formulas for the dimethylated complex, $[\mathrm{Rh(aet)(mtea)_2}]^{2+}$, rather than the monomethylated $[\mathrm{Rh(aet)_2(mtea)}]^{+}$ and the trimethylated $[\mathrm{Rh(mtea)_3}]^{3+}$. As shown in Fig. 3, the absorption spectrum of $[\mathbf{2}]^{2+}$ coincides well with that of $[\mathbf{1}]^{2+}$ over the whole region, giving a first d–d transition band at *ca.* 31 × 10^3 cm^{-1} with an explicit shoulder on the lower energy side and a broad sulfur-to-rhodium CT band at *ca.* 43 × 10^3 cm^{-1}. Thus, $[\mathbf{2}]^{2+}$ is assignable to *fac*(*S*)-$[\mathrm{Rh(aet)(mtea)_2}]^{2+}$ having one thiolato and two thioether donor atoms. This assignment is supported by its molar conductivity in water (293 Ω^{-1} cm^2 mol^{-1}), which is in good agreement with that of $[\mathbf{2}]^{2+}$ (294 Ω^{-1} cm^2 mol^{-1}).

Table 4 Absorption and CD spectral data for $[\mathbf{1}]^{2+}$, $[\mathbf{2}]^{2+}$, $[\mathbf{3}]^{3+}$, $[\mathbf{4}]^{5+}$, and $[\mathbf{5}]^{5+}$ in H_2O

Abs max: $\sigma/10^3$ cm^{-1} (log ε/mol^{-1} dm^3 cm^{-1})	CD extrema: $\sigma/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
fac(*S*)-$[\mathrm{Rh(aet)(baete)}]^{2+}$ ($[\mathbf{1}]^{2+}$)	
26.6 (2.17)$^{\rm sh}$	24.1 (+1.3)
32.3 (3.16)	31.1 (+5.8)
44.0 (4.32)	44.8 (−47.5)
fac(*S*)-$[\mathrm{Rh(aet)(mtea)_2}]^{2+}$ ($[\mathbf{2}]^{2+}$)	
26.8 (2.26)$^{\rm sh}$	23.6 (+0.8)
31.1 (2.90)	31.0 (+11.2)
43.3 (4.41)	42.1 (−29.5)
fac(*S*)-$[\mathrm{Rh(mtea)_3}]^{3+}$ ($[\mathbf{3}]^{3+}$)	
30.8 (3.13)	
37.1 (3.41)$^{\rm sh}$	
42.5 (4.38)	
$[\mathrm{Ag\{Rh(aet)(baete)\}_2}]^{5+}$ ($[\mathbf{4}]^{5+}$)	
26.7 (2.61)$^{\rm sh}$	
32.4 (3.49)	
44.1 (4.64)	
$[\mathrm{Ag\{Rh(aet)(mtea)_2\}_2}]^{5+}$ ($[\mathbf{5}]^{5+}$)	
26.6 (2.61)$^{\rm sh}$	
31.1 (3.23)	
43.2 (4.71)	

The sh label denotes a shoulder.

Complex $[\mathbf{2}]^{2+}$ was optically resolved by the same SP-Sephadex C-25 column chromatography as that used for $[\mathbf{1}]^{2+}$. The elution behavior for $[\mathbf{2}]^{2+}$ in the column was similar to that for $[\mathbf{1}]^{2+}$; the developed band was not completely separated into two bands and the earlier and later fractions of the broadened band contained the $(+)^{\rm CD}_{420}$ and $(-)^{\rm CD}_{420}$ isomers, respectively. The CD spectral behavior of $(+)^{\rm CD}_{420}$ -$[\mathbf{2}]^{2+}$ is quite similar to that of $(+)^{\rm CD}_{420}$ -$[\mathbf{1}]^{2+}$ over the whole region (Fig. 3), suggesting that the $(+)^{\rm CD}_{420}$ and $(-)^{\rm CD}_{420}$ isomers of $[\mathbf{2}]^{2+}$ have the Λ and Δ configurations, respectively. However, some notable differences are observed in more minute detail. That is, the CD band for $[\mathbf{1}]^{2+}$ at *ca.* 31 × 10^3 cm^{-1} in the d–d band region has a smaller $|\Delta\varepsilon|$ value, whereas the band at *ca.* 44 × 10^3 cm^{-1} in the sulfur-to-rhodium CT band region has a greater $|\Delta\varepsilon|$ value, compared with the corresponding CD bands for $[\mathbf{2}]^{2+}$. We have previously pointed out that the CD contribution due to asymmetric sulfur atoms is minor in the d–d absorption band region, dominated by the configurational effect due to the skew pair of chelate rings, whereas the asymmetric sulfur atom contributes significantly in the sulfur-to-rhodium CT band region.[14c] Thus, the smaller CD intensity in the d–d region for $[\mathbf{1}]^{2+}$ may be ascribed to the presence of an *S*,*S*-chelate ring, which partially counteracts the configurational effect due to skew pair of the three *N*,*S*-chelate rings. On the other hand, the tightly fixed asymmetric thioether sulfur atoms in $[\mathbf{1}]^{2+}$, contrary to the flexible thioether sulfur atoms in $[\mathbf{2}]^{2+}$, would contribute significantly to the CD spectrum in the CT region, which seems to result in the greater CD intensity.

Considering the chiral configurations (*R* and *S*) of the two asymmetric sulfur atoms, four pairs of diastereomers, Δ_{SS}/Λ_{RR}, Δ_{SR}/Λ_{RS}, Δ_{RS}/Λ_{SR} and Δ_{RR}/Λ_{SS}, are possible for $[\mathbf{2}]^{2+}$. As shown in Fig. 2(b), the ^{13}C NMR spectrum of [**2**]$^{2+}$ in D_2O exhibits eight main signals; the six signals at δ 31.25, 41.23, 43.48, 46.08, 46.28 and 54.30 are due to the six methylene carbon atoms for three $NH_2\mathit{C}H_2\mathit{C}H_2S$ moieties, whereas the remaining two signals at δ 21.71 and 22.21 are due to the two methyl carbon atoms. This suggests that a pair of diastereomers predominantly exist in solution. However, another set of minor signals was found in the ^{13}C NMR spectrum of [**2**]$^{2+}$, even after its recrystallization. Moreover, the ^{1}H NMR spectrum of [**2**]$^{2+}$ shows several minor signals between two main signals (δ 2.39 and 2.55) in the methyl proton region. Accordingly, it is assumed that [**2**]$^{2+}$ exists as a mixture of the diastereomers in solution. The Δ_{SS}/Λ_{RR} isomer may be the dominant species, taking account of the fact that the trimethylated *fac*(*S*)-[Rh(mtea)$_3$]$^{3+}$ adopts the $\Delta_{SSS}/\Lambda_{RRR}$ configuration in the crystal.

In this reaction, the monomethylated [Rh(aet)$_2$(mtea)]$^+$ was not formed, even when *fac*(*S*)-[Rh(aet)$_3$] was treated with CH_3I in a 1 : 1 ratio; the reaction solution contained only [**2**]$^{2+}$, leaving the unreacted solid of *fac*(*S*)-[Rh(aet)$_3$] in the reaction mixture. Moreover, the formation of the trimethylated [Rh(mtea)$_3$]$^{3+}$ was not noticed, even when *fac*(*S*)-[Rh(aet)$_3$] was treated with a large excess CH_3I. These results imply that the monomethylated [Rh(aet)$_2$(mtea)]$^+$, once formed in the reaction solution, is readily methylated by CH_3I to give [**2**]$^{2+}$, but that further methylation is hindered by the presence of two methyl groups on the S_3 face in [**2**]$^{2+}$. However, treatment of a yellow aqueous solution of [**2**]$^{2+}$ with excess dimethyl sulfate gave a pale yellow solution, from which an almost colorless complex ([**3**]$^{3+}$) was isolated as the perchlorate salt. The elemental analysis result is consistent with the formula for the trimethylated [Rh(mtea)$_3$]$^{3+}$, and its structure was determined by X-ray analysis to be *fac*(*S*)-[Rh(mtea)$_3$]$^{3+}$. As shown in Fig. 3, the absorption spectrum of [**3**]$^{3+}$ is characterized by a d–d transition band at *ca.* 31 × 10^3 cm^{-1} and a sulfur-to-rhodium CT band at *ca.* 42 × 10^3 cm^{-1}. These two bands correspond well with the d–d and the CT bands for [**2**]$^{2+}$, although they locate at slightly lower energies than the corresponding bands for [**2**]$^{2+}$. The striking feature of the absorption spectrum of [**3**]$^{3+}$ is the absence of a shoulder at the lower energy side of the d–d transition band. From this result, it is confirmed that the absorption shoulder at *ca.* 26 × 10^3 cm^{-1} observed for each of [**1**]$^{2+}$ and [**2**]$^{2+}$ is due to the presence of the thiolato donor group. It has been recognized for thiolato cobalt(III) complexes that the absorption shoulder at the lower energy side of the d–d transition band disappears on conversion of the thiolato donor group to a thioether group by alkylation,[5] and this spectroscopic behavior has been ascribed to the utilization of lone-pair of electrons in a thiolato sulfur 3p orbital, which interacts anisotropically with two $\mathrm{Co^{III}}$ d(π) orbitals.[5d]

Considering the chiral configurations of the three asymmetric sulfur atoms, four pairs of diastereomers, $\Delta_{SSS}/\Lambda_{RRR}$, $\Delta_{SSR}/\Lambda_{RRS}$, $\Delta_{SRR}/\Lambda_{RSS}$ and $\Delta_{RRR}/\Lambda_{SSS}$, are possible for [**3**]$^{3+}$. As shown in Fig. 2(c), the ^{13}C NMR spectrum of [**3**]$^{3+}$ gives three main signals, at δ 22.90, 41.61 and 48.39, accompanied by several minor signals. Furthermore, in the ^{1}H NMR spectrum, three minor methyl proton signals are observed at δ 2.69, 2.71 and 2.78, besides one main signal at δ 2.76, with an integration ratio of *ca.* 1 : 1 : 1 : 8. The NMR spectral profiles seem to indicate that a major isomer having a C_3 symmetry and a minor isomer having a C_1 symmetry co-exist in solution as a result of the chiral inversion at the thioether sulfur atom, which is slow on the NMR time scale at room temperature. Taking account of the molecular structure of [**3**]$^{3+}$ in crystal, it is likely that the major isomer in solution is $\Delta_{SSS}/\Lambda_{RRR}$, which converts in part to the minor species, tentatively assigned to $\Delta_{SSR}/\Lambda_{RRS}$.

Reactions of *fac*(*S*)-[Rh(aet)(baete)]$^{2+}$ ([1]$^{2+}$) or *fac*(*S*)-[Rh(aet)(mtea)$_2$]$^{2+}$ ([2]$^{2+}$) with $\mathrm{Ag^I}$

Treatment of an orange aqueous solution of [**1**](ClO_4)$_2$ or [**2**](ClO_4)$_2$ with $AgClO_4$ in a 2 : 1 ratio gave a light yellow solution, from which light yellow crystals of [**4**](ClO_4)$_5$·2H_2O or [**5**](ClO_4)$_5$·5H_2O, respectively, were isolated in satisfactory yields. Plasma emission spectral analysis implies that each of [**4**]$^{5+}$ and [**5**]$^{5+}$ contains Rh and Ag atoms in a 2 : 1 ratio, and their elemental analyses are in good agreement with the proposed formulas, [Ag{Rh(aet)(baete)}$_2$](ClO_4)$_5$ and [Ag{Rh(aet)(mtea)$_2$}$_2$](ClO_4)$_5$. As shown in Fig. 4, the UV-VIS absorption spectrum of each complex is dominated by two absorption bands at *ca.* 32 × 10^3 and 44 × 10^3 cm^{-1}, the positions of which are almost identical with those of the corresponding bands for each of the starting complexes [**1**]$^{2+}$ and [**2**]$^{2+}$. Furthermore, the ^{13}C NMR spectral features of [**4**]$^{5+}$ and [**5**]$^{5+}$ in D_2O are essentially the same as those of [**1**]$^{2+}$ and [**2**]$^{2+}$, respectively; [**4**]$^{5+}$ exhibits only eight signals (δ 31.54, 39.18, 42.16, 43.69, 44.40, 45.65, 52.61 and 53.89), whereas [**5**]$^{5+}$ shows several minor signals besides the eight main ones (δ 21.72, 22.24, 31.26, 41.25, 43.51, 46.08, 46.28 and 54.29). The absorption and NMR spectral behavior implies that [**4**]$^{5+}$ and [**5**]$^{5+}$ are composed of the *fac*(*S*)-[Rh(aet)(baete)]$^{2+}$ and *fac*(*S*)-[Rh(aet)(mtea)$_2$]$^{2+}$ units, respectively. Here, it should be noted that the absorption shoulders at *ca.* 26 × 10^3 cm^{-1} for [**4**]$^{5+}$ and [**5**]$^{5+}$ are vaguer than those of [**1**]$^{2+}$ and [**2**]$^{2+}$. This is indicative of the presence of Ag–S bonds, which would diminish an anisotropic π-donor interaction between $\mathrm{Rh^{III}}$ and the thiolato S atom. Accordingly, [**4**]$^{5+}$ and [**5**]$^{5+}$ can be assigned to the S-bridged $\mathrm{Rh^{III}Ag^{I}Rh^{III}}$ trinuclear complexes, [Ag{Rh(aet)(baete)}$_2$]$^{5+}$ and [Ag{Rh(aet)(mtea)$_2$}$_2$]$^{5+}$, respectively, in which the $\mathrm{Ag^I}$ ion is coordinated by two thiolato S atoms from two *fac*(*S*)-[Rh(aet)(baete)]$^{2+}$ or *fac*(*S*)-[Rh(aet)(mtea)$_2$]$^{2+}$ units.

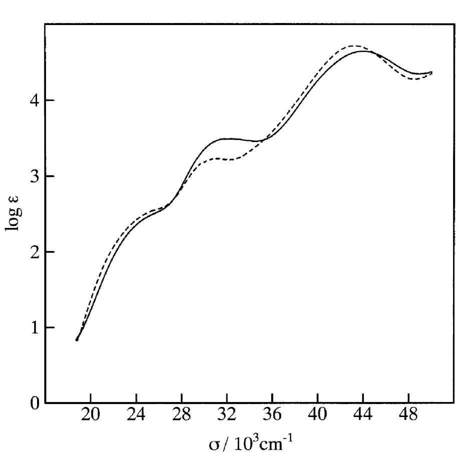

Fig. 4 Electronic absorption spectra of [**4**]$^{5+}$ (—) and [**5**]$^{5+}$ (---) in water.

Concluding remarks

In the present study, it has been found that the alkylation reactions of *fac*(*S*)-[Rh(aet)$_3$] with 1,2-dibromoethane and methyl iodide afford the dialkylated *fac*(*S*)-[Rh(aet)(baete)]$^+$ ([**1**]$^{2+}$) and *fac*(*S*)-[Rh(aet)(mtea)$_2$]$^+$ ([**2**]$^{2+}$), respectively, whereas the monoalkylated and trialkylated species were little formed. Thus, the mono(thiolato)-type rhodium(III) complexes with a *fac*(*S*) geometry were stereoselectively prepared with use of the simple tris(thiolato)-type rhodium(III) complex as the starting complex. To the best of our knowledge, these are the first well-defined mononuclear rhodium(III) complexes containing both thiolate and thioether ligands, and this approach could be applicable to the preparation of a wide range of transition metal complexes with thiolato and thioether donors. Conversion of the dimethylated [**2**]$^{2+}$ to the trimethylated *fac*(*S*)-[Rh(mtea)$_3$]$^{3+}$ ([**3**]$^{3+}$) was unsuccessful by treatment with methyl iodide, but was achieved by treatment with dimethyl sulfate. The thiolato sulfur atom in both [**1**]$^{2+}$ and [**2**]$^{2+}$ was found to have a coordination ability toward the Ag^{I} ion to form S-bridged Rh^{III}Ag^{I}Rh^{III} trinuclear complexes, [Ag{Rh(aet)(baete)}$_2$]$^{5+}$ ([**4**]$^{5+}$) and [Ag{Rh(aet)(mtea)$_2$}$_2$]$^{5+}$ ([**5**]$^{5+}$). Reactions of [**1**]$^{2+}$ or [**2**]$^{2+}$ with other metal ions are currently underway in order to better understand the coordination ability of thiolato sulfur atoms in each of [**1**]$^{2+}$ and [**2**]$^{2+}$ and to construct well-organized S-bridged polynuclear structures composed of the *fac*(*S*)-[Rh(aet)(baete)]$^{2+}$ and *fac*(*S*)-[Rh(aet)(mtea)$_2$]$^{2+}$ octahedral units.

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