Stoichiometric Interconversion of S-Bridged $Rh^{III}_2Ag^{I}_3$ Pentanuclear and $Rh^{III}_4Ag^{I}_5$ Nonanuclear Structures: Synthesis and Structural Characterization of $[Ag_3\{Rh(aet)_3\}_2]^{3+}$ and $[Ag_5\{Rh(aet)_3\}_4]^{5+}$ (aet = 2-Aminoethanethiolate)

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The reaction of *fac(S)*-[Rh(aet)$_3$] (aet = 2-aminoethanethiolate) with 1.5 molar equiv of $AgBF_4$ in water gave an S-bridged pentanuclear complex, [Ag$_3${Rh(aet)$_3$}$_2$](BF$_4$)$_3$ (**1**(BF$_4$)$_3$), while the reaction with 1.2 molar equiv of $AgBF_4$ produced an S-bridged nonanuclear complex, [Ag$_5${Rh(aet)$_3$}$_4$](BF$_4$)$_5$ (**2**(BF$_4$)$_5$). The crystal structures of **1**(BF$_4$)$_3$ and **2**(BF$_4$)$_5$ were determined by X-ray crystallography: **1**(BF$_4$)$_3$·H$_2$O crystallizes in the orthorhombic space group *Pnma* with $a = 16.609(3)$ Å, $b = 13.352(4)$ Å, $c = 15.771(3)$ Å, $V = 3497(1)$ Å^3, $Z = 4$, and $R = 0.056$. **2**(BF$_4$)$_5$·4H$_2$O crystallizes in the monoclinic space group $P2_1/c$ with $a = 15.665(5)$ Å, $b = 14.003(2)$ Å, $c = 31.900(9)$ Å, $\beta = 94.19(1)°$, $V = 6979(3)$ Å^3, $Z = 4$, and $R = 0.068$. In **1** each of three Ag^I atoms is linearly coordinated by two thiolato sulfur atoms from two octahedral *fac(S)*-[Rh(aet)$_3$] units. In **2** each of four Ag^I atoms is trigonally coordinated by three thiolato sulfur atoms from three *fac(S)*-[Rh(aet)$_3$] units, while the remaining Ag^I atom is linearly coordinated by two thiolato sulfur atoms from two *fac(S)*-[Rh(aet)$_3$] units. **2** was readily converted to **1** by reaction with Ag$^+$, while the conversion of **1** to **2** was achieved by the reaction with *fac(S)*-[Rh(aet)$_3$].

Introduction

It has been recognized that the octahedral tris(thiolato) complexes *fac(S)*-[M(aet)$_3$] and *fac(S)*-[M(L-cys-*N,S*)$_3$]$^{3-}$ (M = Co^{III}, Rh^{III}, Ir^{III}; aet = 2-aminoethanethiolate; L-cys = L-cysteinate), can function as S-donating tridentate ligands to a variety of metal ions to form S-bridged polynuclear complexes.[1−18] Recent our studies have shown that the structures of these polynuclear complexes can be made to vary by changes in metal ions incorporated with *fac(S)*-[M(aet)$_3$] or *fac(S)*-[M(L-cys-*N,S*)$_3$]$^{3-}$.[13−18] For example, the reactions of *fac(S)*-[M(aet)$_3$] with ZnX$_2$ (X = Cl, Br, NO$_3$) in water were found to produce a new class of cage-type S-bridged octanuclear complexes, [Zn$_4$O{M(aet)$_3$}$_4$]$^{6+}$,[14,15] of which the stereochemical behavior is quite different from that of the well-known linear-type trinuclear complexes [M′{M(aet)$_3$}$_2$]$^{n+}$ (M′ = Fe^{III}, Co^{III}, Ni^{II}).[1−5,8−12] Furthermore, we have found that the trigonal-bipyramid-type pentanuclear complexes [Hg$_3$Cl$_6${M(aet)$_3$}$_2$] and [Hg$_3$(NO$_3$)$_4${M(aet)$_3$}$_2$]$^{2+}$ are formed by the reactions of *fac-(S)*-[M(aet)$_3$] with HgX$_2$ (X = Cl, NO$_3$) in water.[17] In this pentanuclear structure, each of three Hg^{II} atoms has a significantly distorted tetrahedral geometry with an expanded S−Hg−S angle, which suggests that Ag^I is an appropriate candidate for forming this kind of pentanuclear structure. Thus, we have extended our work to employ Ag$^+$ as a reacting metal ion, in order to better understand the key to the control of S-bridged polynuclear structures derived from the octahedral tris(thiolato) complexes. In this paper we report that the reaction of *fac(S)*-[Rh(aet)$_3$] with 1.5 molar equiv of AgBF$_4$ gives a trigonal-bipyamid-type pentanuclear complex, [Ag$_3${Rh(aet)$_3$}$_2$]$^{3+}$ (**1**), while the reaction with 1.2 molar equiv of AgBF$_4$ leads to the isolation of an unexpected S-bridged nonanuclear complex, [Ag$_5${Rh(aet)$_3$}$_4$]$^{5+}$ (**2**), which is interconvertible to **1** in a rational manner. The results presented here first show that the slight modification of molar ratios of a reacting metal ion to a mononuclear thiolato complex makes possible the control of the structures and properties of the resulting S-bridged polynuclear complexes.

Experimental Section

Preparation of Complexes. [Ag$_3${Rh(aet)$_3$}$_2$](BF$_4$)$_3$ (1(BF$_4$)$_3$). To a stirred yellow suspension of *fac(S)*-[Rh(aet)$_3$][14b] (0.10 g, 0.30 mmol) in 10 cm^3 of water was dropwise added an aqueous solution of AgBF$_4$ (0.09 g, 0.46 mmol) at room temperature, which gave a clear yellow

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Table 1. Crystallographic Data[a] for $\mathbf{1}(BF_4)_3\cdot H_2O$ and $\mathbf{2}(BF_4)_5\cdot 4H_2O$

	$\mathbf{1}(BF_4)_3\cdot H_2O$	$\mathbf{2}(BF_4)_5\cdot 4H_2O$
chem formula	$C_{12}H_{38}B_3N_6OF_{12}S_6Rh_2Ag_3$	$C_{24}H_{80}B_5N_{12}O_4F_{20}S_{12}Rh_4Ag_5$
fw	1264.7	2370.8
cryst color	yellow	orange-yellow
cryst size, mm	0.25 × 0.25 × 0.12	0.25 × 0.12 × 0.10
space group	*P*nma (No. 62)	$P2_1/c$ (No. 14)
a, Å	16.609(3)	15.665(5)
b, Å	13.352(4)	14.003(2)
c, Å	15.771(3)	31.900(9)
β, deg		94.19(1)
V, Å^3,	3497(1)	6979(3)
Z	4	4
ρ_{calc}, g cm^{-3}	2.40	2.26
μ, cm^{-1}	29.8	27.1
transm coeff	0.88−1.00	0.89−1.00
R^b	0.056	0.068
$R_w{}^c$	0.057	0.070

[a] $T = 23$ °C; λ(Mo Kα) = 0.710 73 Å. [b] $R = \sum(|F_o| - |F_c|)/\sum(|F_o|)$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$.

solution by way of a reddish solution. The yellow reaction solution was allowed to stand at room temperature for 3 days, and the resulting yellow crystals, one of which was used for X-ray analysis, were collected by filtration. Yield: 0.14 g (73%). Anal. Calcd for $[Rh_2Ag_3(C_2H_6NS)_6](BF_4)_3\cdot H_2O$: C, 11.40; H, 3.03; N, 6.65; Rh, 16.27; Ag, 25.59. Found: C, 11.55; H, 3.12; N, 6.72; Rh, 16.22; Ag, 25.46. Visible−UV spectrum in H_2O [σ_{max}, 10^3 cm^{-1} (log ϵ, mol^{-1} dm^3 cm^{-1})]: 26.67 (3.11), 38.5 (4.3 sh), 45.25 (4.85). The sh label denotes a shoulder.

$[Ag_5\{Rh(aet)_3\}_4](BF_4)_5$ (2(BF$_4$)$_5$). To a stirred yellow suspension of *fac(S)*-[Rh(aet)$_3$][14b] (0.10 g, 0.30 mmol) in 10 cm^3 of water was dropwise added an aqueous solution of $AgBF_4$ (0.074 g, 0.38 mmol) at room temperature, which gave a clear dark-red solution. The dark-red reaction solution was allowed to stand at room temperature for 1 week, and the resulting orange-yellow crystals, one of which was used for X-ray analysis, were collected by filtration. Yield: 0.15 g (84%). Anal. Calcd for $[Rh_4Ag_5(C_2H_6NS)_{12}](BF_4)_5\cdot 4H_2O$: C, 12.16; H, 3.40; N, 7.09; Rh, 17.36; Ag, 22.75. Found: C, 12.00; H, 3.40; N, 6.91; Rh, 17.17; Ag, 23.02. Visible−UV spectrum in H_2O [σ_{max}, 10^3 cm^{-1} (log ϵ, mol^{-1} dm^3 cm^{-1})]: 21.60 (3.23), 27.40 (3.75), 38.5 (4.5 sh), 44.84 (5.11). The sh label denotes a shoulder.

Measurements. The electronic absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer at room temperature. The ^{13}C NMR spectra were recorded with a Bruker AM-500 NMR spectrometer at the probe temperature. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. The 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 Nippon Jarrel-Ash ICPA-575 ICP spectrophotometer.

X-ray Structure Determination. Single-crystal X-ray diffraction experiments were performed on an Enraf-Nonius CDA4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 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 range of 15 < 2θ <20°. The intensity data were collected by the ω-2θ scan mode up to 2θ = 52° for $\mathbf{1}(BF_4)_3\cdot H_2O$ and 2θ = 50° for $\mathbf{2}(BF_4)_5\cdot 4H_2O$. The intensities were corrected for Lorentz and polarization. Empirical absorption corrections based on a series of ψ scans were also applied. The 2657 independent reflections with $I > 2\sigma(I)$ of the measured 3861 reflections were considered as "observed" and used for structure determination of $\mathbf{1}(BF_4)_3\cdot H_2O$ and the 5580 independent reflections with $F_o > 3\sigma(F_o)$ of the measured 12 559 reflections were used for $\mathbf{2}(BF_4)_5\cdot 4H_2O$.

The positions of Rh, Ag, and S atoms for $\mathbf{1}(BF_4)_3\cdot H_2O$ were determined by direct methods, and the remaining non-H atom positions were found by successive difference Fourier techniques.[19] The structure was refined by full-matrix least-squares techniques using the teXsan crystallographic software package.[19] The systematic absences led to the choice of the space group $Pna2_1$ (No. 33) or *Pnma* (No. 62) for $\mathbf{1}(BF_4)_3\cdot H_2O$. At first the structure was solved by using the space group $Pna2_1$, which showed that two sets of atom peaks corresponding to a pair of enantiomers co-exist in each of four sites in unit cell. When the entire coordinate set obtained by the $Pna2_1$ refinement was translated, one Ag and two Rh atoms were put almost on the mirror (*x*, 0.25, *y*) and the remaining two Ag atoms and two sets of donor atoms were put on symmetry-equivalent positions in the space group *Pnma*. Thus, the space group was deduced to be *Pnma*, and this assignment was confirmed by the eventual structure refinement. The structure was refined using anisotropic thermal parameters for all the non-H atoms, and H atoms were not included in the calculations. Ag1, Rh1, Rh2, C11, C12, and C21 atoms of the complex cation, B1 and F12 atoms of one BF_4^- anion, and a water O atom (O1) were constrained to the special positions of symmetry *m* (*x*, 0.25, *z*). The site occupancy factor of each atom was fixed to 0.5, except for Ag2, C13, C14, B2, F13, F21, F22, F23, F24, and F25.

The positions of Rh, Ag, and several S atoms for $\mathbf{2}(BF_4)_5\cdot 4H_2O$ were determined by direct methods, and the remaining non-H atom positions were found by successive difference Fourier techniques.[20] The structure was refined by full-matrix least-squares techniques using the MOLEN crystallographic software package.[20] O and B atoms were refined isotropically, and all other non-H atoms were refined anisotropically. Four of the six O atoms were refined with a site occupancy factor of 0.5. One of the five B atoms could not be found from a difference map probably because of disorder of the BF_4^- anion, and this atom beside the H atoms was not included in the calculations.

Results and Discussion

Treatment of ca. 1.5 molar equiv of $AgBF_4$ to the yellow aqueous suspension of *fac(S)*-[Rh(aet)$_3$] at room temperature gave a clear yellow solution, from which yellow crystals ($\mathbf{1}(BF_4)_3$) were isolated in a reasonable yield. The elemental and plasma emission analyses of this yellow complex are in good agreement with the proposed formula, $[Ag_3\{Rh(aet)_3\}_2](BF_4)_3\cdot H_2O$, and its structure was determined by X-ray analysis. Perspective drawings of the complex cation **1** are given in Figure 1 and its selected bond distances and angles are listed in Table 2. The complex cation **1** consists of two approximately octahedral *fac(S)*-[Rh(aet)$_3$] units and three Ag atoms. The two *fac(S)*-[Rh(aet)$_3$] units are linked by three Ag atoms to give an S-bridged pentanuclear structure, in which five metals form a trigonal-bipyramid (average Ag−Ag = 3.067(2) Å, Ag−Rh = 3.859(2) Å, Ag−Rh−Ag = 46.92(3)°, Ag−Ag−Rh = 66.4(3)°). This S-bridged Rh_2Ag_3 pentanuclear structure corresponds with the S-bridged Rh_2Hg_3 structure observed in $[Hg_3Cl_6\{Rh(aet)_3\}_2]$ and $[Hg_3(NO_3)_4\{Rh(aet)_3\}_2]^{2+}$.[17] However, in **1** each Ag atom has a nearly linear geometry (average S−Ag−S = 176.3(2)°) coordinated by two thiolato S atoms from two *fac(S)*-[Rh(aet)$_3$] units, which is distinct from the four-coordinated Hg atoms in $[Hg_3Cl_6\{Rh(aet)_3\}_2]$ (average S−Hg−S = 147.6(1)°, Cl-Hg-Cl = 88.8(4)°) and $[Hg_3(NO_3)_4\{Rh(aet)_3\}_2]^{2+}$ (average S−Hg−S = 161.0(2)°, O−Hg−O = 86.7(4)°). The two *fac(S)*-[Rh(aet)$_3$] units in **1** have the same chiral configuration to form the ΔΔ and ΛΛ isomers; the latter isomer is illustrated in Figure 1. In the unit cell the ΔΔ and ΛΛ isomers co-exist in each of four sites with a site occupancy of 0.5, which indicates that crystal **1** is not a racemic compound but a rare example of a solid solution.[21] The helical structure due to the three Rh−S−Ag−S−Rh chains is left-handed for the ΔΔ isomer and right-handed for the ΛΛ isomer. These chiral properties are quite similar to those found in $[Hg_3Cl_6\{Rh(aet)_3\}_2]$ and $[Hg_3(NO_3)_4\{Rh(aet)_3\}_2]^{2+}$.[17] However, it

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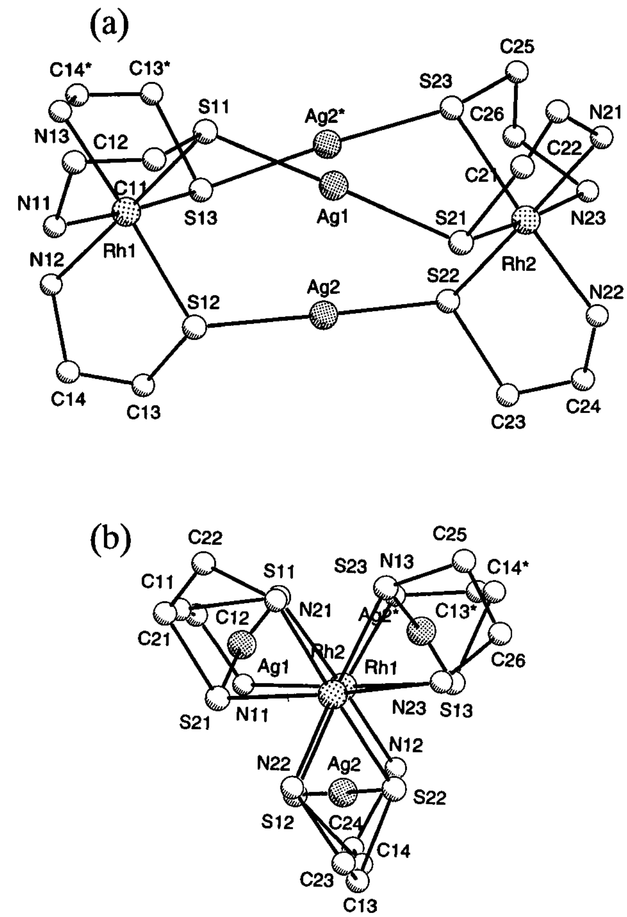

Figure 1. Perspective views of the complex cation **1** (the ΛΛ isomer) with the atomic labeling scheme. The overlapped ΔΔ isomer is omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

	Distances		
Ag1−S11	2.398(6)	Rh−N12	2.13(2)
Ag1−S21	2.362(6)	Rh1−N13	2.16(2)
Ag2−S12	2.388(6)	Rh2−S21	2.293(6)
Ag2−S22	2.355(6)	Rh2−S22	2.286(6)
Rh1−S11	2.322(6)	Rh2−S23	2.363(7)
Rh1−S12	2.342(6)	Rh2−N21	2.19(2)
Rh1−S13	2.308(6)	Rh2−N22	2.06(2)
Rh1−N11	2.12(2)	Rh2−N23	2.17(2)
	Angles		
S11−Ag1−S21	174.1(2)	N12−Rh1−N13	90.0(8)
S12−Ag2−S22	178.6(2)	S21−Rh2−S22	94.3(2)
S13−Ag2*−S23	176.3(3)	S21−Rh2−S23	93.5(2)
S11−Rh1−S12	94.7(2)	S22−Rh2−S23	94.1(2)
S11−Rh1−S3	93.1(2)	N21−Rh2−N22	95.3(9)
S12−Rh1−S13	91.8(2)	N21−Rh2−N23	90.2(8)
N11−Rh1−N12	91.9(8)	N22−Rh2−N23	91(1)
N11−Rh1−N13	92(1)		

should be noted that in **1** the aet chelate rings adopt a mixture of the *ob* and *lel* conformations. This is in contrast to the fact that all the aet rings are fixed to the *ob* conformation in $[Hg_3Cl_6\{Rh(aet)_3\}_2]$ and $[Hg_3(NO_3)_4\{Rh(aet)_3\}_2]^{2+}$.[17]

When *fac(S)*-$[Rh(aet)_3]$ was reacted with ca. 1.2 molar equiv of $AgBF_4$ in water at room temperature, a yellow suspension turned to a clear dark red solution, from which orange-yellow needle crystals (**2**$(BF_4)_5{\cdot}4H_2O$) were isolated in high yield. X-ray structural analysis revealed that the complex cation **2** consists of four approximately octahedral *fac(S)*-$[Rh(aet)_3]$ units and five Ag atoms (Figure 2 and Table 3). This is compatible with the plasma emission analysis, which gave the value Rh:Ag = 4:5. Each of four Ag atoms is situated in a distorted trigonal planar environment coordinated by three thiolato S atoms from three different *fac(S)*-$[Rh(aet)_3]$ units. The remaining Ag atom (Ag5) is linearly coordinated by two S atoms from two *fac(S)*-$[Rh(aet)_3]$ units, completing the unprecedented S-bridged nonanuclear structure. The three S atoms in each of the Rh1 and Rh2 units have a normal μ_2-thiolato structure, while one μ_3-thiolato S atom exists besides two μ_2-thiolato atoms in each of the Rh3 and Rh4 units (each of S32 and S42 bridges one Rh and two Ag atoms). Crystal **2** is a racemic compound of a pair of enantiomers, ΔΔ(Rh1, Rh2)ΛΛ(Rh3, Rh4) and ΛΛ-(Rh1, Rh2)ΔΔ(Rh3, Rh4); the former isomer is shown in Figure 2. That is, the chiral configuration of the Rh1 and Rh2 units is opposite to that of the Rh3 and Rh4 units, which forms a quasi-meso-type compound. It is seen from Figure 2 that the formation of the Ag2−S32 and Ag3−S42 bonds is impossible when the Rh3 and Rh4 units have the same chiral configuration as the Rh1 and Rh2 units.

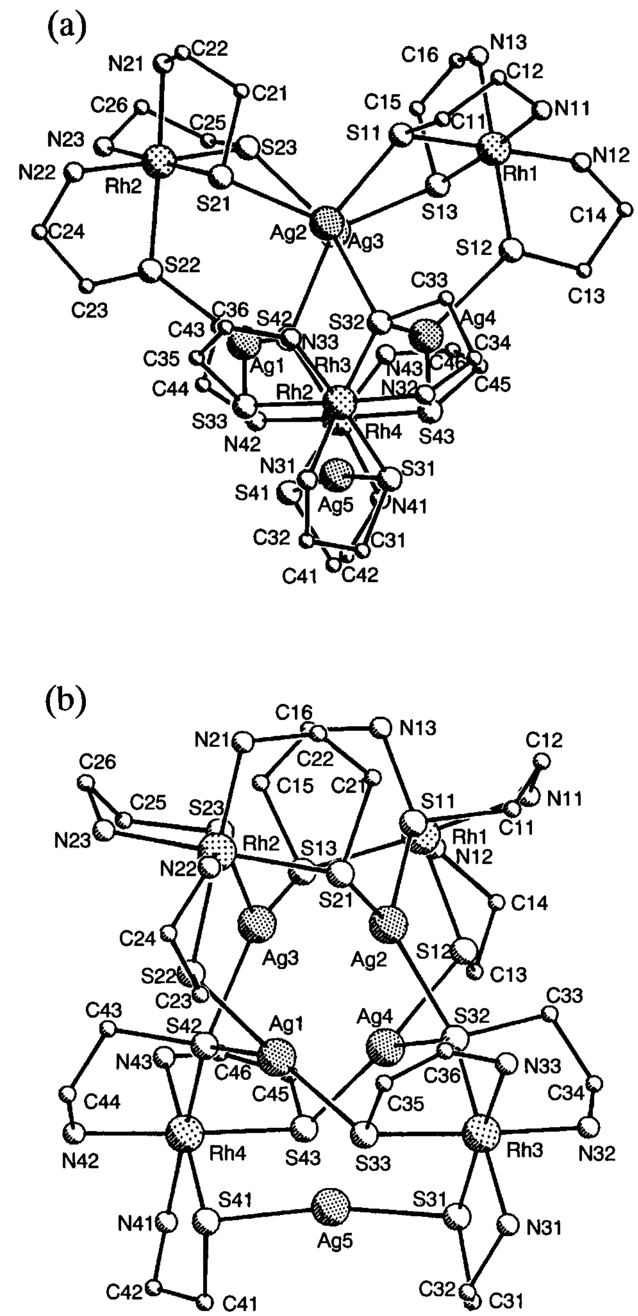

Figure 2. Perspective views of the complex cation **2** with the atomic labeling scheme.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**

Distances			
Ag1−S22	2.548(6)	Rh1−N13	2.12(2)
Ag1−S33	2.460(6)	Rh2−S21	2.306(7)
Ag1−S42	2.545(6)	Rh2−S22	2.314(6)
Ag2−S11	2.521(7)	Rh2−S23	2.316(7)
Ag2−S21	2.469(7)	Rh2−N21	2.10(2)
Ag2−S32	2.487(6)	Rh2−N22	2.16(2)
Ag3−S13	2.464(8)	Rh2−N23	2.13(2)
Ag3−S42	2.488(6)	Rh3−S32	2.306(6)
Ag4−S12	2.568(7)	Rh3−S33	2.320(7)
Ag4−S32	2.542(6)	Rh3−N31	2.12(2)
Ag4−S43	2.459(6)	Rh3−N32	2.11(2)
Ag5−S31	2.364(6)	Rh3−N33	2.13(2)
Ag5−S41	2.357(6)	Rh4−S41	2.310(7)
Rh1−S11	2.338(8)	Rh4−S42	2.308(6)
Rh1−S12	2.298(6)	Rh4−S43	2.316(6)
Rh1−S13	2.299(8)	Rh4−N41	2.15(2)
Rh1−N11	2.13(2)	Rh4−N42	2.14(2)
Rh1−N12	2.13(2)	Rh4−N43	2.11(2)
Angles			
S22−Ag1−S33	120.9(2)	S21−Rh2−S22	92.1(2)
S22−Ag1−S42	93.0(2)	S21−Rh2−S23	92.6(3)
S33−Ag1−S42	143.3(2)	S22−Rh2−S23	95.8(2)
S11−Ag2−S21	108.9(2)	N21−Rh2−N22	91.2(8)
S11−Ag2−S32	115.3(2)	N21−Rh2−N23	92.9(9)
S21−Ag2−S32	131.2(2)	N22−Rh2−N23	91.1(7)
S13−Ag3−S23	114.0(2)	S31−Rh3−S32	91.2(2)
S13−Ag3−S42	129.8(2)	S31−Rh3−S33	94.0(2)
S23−Ag3−S42	112.7(2)	S32−Rh3−S33	91.8(2)
S12−Ag4−S32	93.0(2)	N31−Rh3−N32	92.1(8)
S12−Ag4−S43	123.0(2)	N31−Rh3−N33	90.1(8)
S32−Ag4−S43	141.5(2)	N32−Rh3−N33	92.2(7)
S31−Ag5−S41	168.8(2)	S41−Rh4−S42	89.5(2)
S11−Rh1−S12	92.9(2)	S41−Rh4−S43	95.0(2)
S11−Rh1−S13	92.8(3)	S42−Rh4−S43	92.3(2)
S12−Rh1−S13	93.2(2)	N41−Rh4−N42	91.7(7)
N11−Rh1−N12	92.6(9)	N41−Rh4−N43	91.8(7)
N11−Rh1−N13	90.9(8)	N42−Rh4−N43	91.8(8)
N12−Rh1−N13	94.3(9)		

As illustrated in Figure 3, the electronic absorption spectrum of **1**$(BF_4)_3 \cdot H_2O$ in water is dominated by a d−d absorption band at 26.67 × 10^3 cm^{-1} and a sulfur-to-rhodium charge transfer band at 45.25 × 10^3 cm^{-1}. A similar absorption spectral feature has been observed for $[Hg_3(NO_3)_4\{Rh(aet)_3\}_2]^{2+}$,[17] although the d−d band (28.60 × 10^3 cm^{-1}) and the charge transfer band (49.95 × 10^3 cm^{-1}) were located at higher energy than those for **1**. No significant absorption spectral change was recognized for **1** at least for several hours. Furthermore, this solution spectrum is essentially the same as the solid state spectrum measured by a diffuse reflectance technique. Considering these facts and the fact that the ^{13}C NMR spectrum of **1**$(BF_4)_3 \cdot H_2O$ in D_2O gives only two sharp signals (δ 35.66 for $-CH_2S$ and 52.54 for $-CH_2NH_2$), it is reasonable to assume that the D_3 symmetrical S-bridged $Rh^{III}{}_2Ag^{I}{}_3$ structure observed in crystal is retained in solution. However, it was found that the $Rh^{III}{}_2Ag^{I}{}_3$ pentanuclear structure of **1** is easily converted to the $Rh^{III}{}_4Ag^{I}{}_5$ nonanuclear structure of **2** by reaction with *fac(S)*-$[Rh(aet)_3]$ in water; the addition of 0.5 molar equiv of *fac(S)*-$[Rh(aet)_3]$ to the yellow aqueous solution of **1**$(BF_4)_3 \cdot H_2O$ at room temperature produced a dark red solution in a few minutes, from which **2**$(BF_4)_5 \cdot 4H_2O$ was isolated in 85% yield. The detailed mechanism of this conversion is not clear at present, but it is obvious that the two-coordinated Ag atoms in **1** are highly reactive toward the thiolato S atoms in *fac(S)*-$[Rh(aet)_3]$, which causes the stoichiometric conversion of the $Rh^{III}{}_2Ag^{I}{}_3$ pentanuclear structure to the $Rh^{III}{}_4Ag^{I}{}_5$ nonanuclear structure.

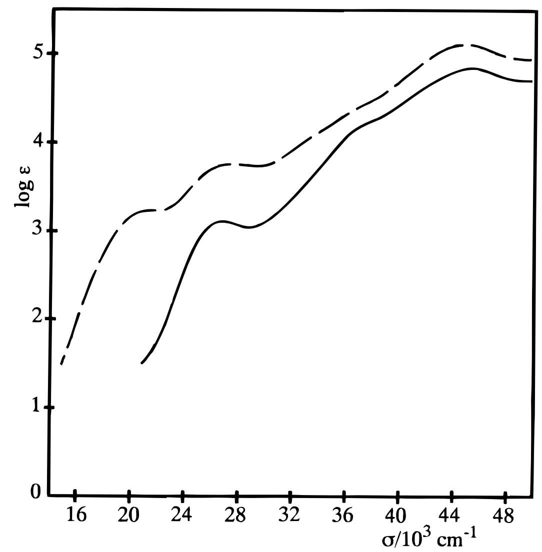

Figure 3. Electronic absorption spectra of **1**$(BF_4)_3$ (—) and **2**$(BF_4)_5$ (− −) in H_2O.

In solid state **2**$(BF_4)_5 \cdot 4H_2O$ is orange-yellow in color and its electronic spectrum is characterized by a near-UV band at 26.74 × 10^3 cm^{-1}. However, on dissolving in water the color turned to orange-red, showing a new visible band at 21.60 × 10^3 cm^{-1} besides a near-UV band at 27.40 × 10^3 cm^{-1} in the absorption spectrum (Figure 3). These facts suggest that the S-bridged $Rh^{III}{}_4Ag^{I}{}_5$ nonanuclear structure of **2** is unstable in solution, converting at least in part to another S-bridged polynuclear structure. The ^{13}C NMR spectrum of **2**$(BF_4)_5 \cdot 4H_2O$ in D_2O, which gives two dominant signals at δ 36.01 and 52.80 besides two clusters of signals at δ 35.7 and 52.3, may support this suggestion. When an aqueous solution of **2**$(BF_4)_5 \cdot 4H_2O$ is treated with 1 molar equiv of $AgBF_4$ at room temperature, the solution color immediately turned from orange-red to yellow, of which the absorption spectrum is identical with that of **1**. This result clearly indicates that the S-bridged $Rh^{III}{}_4Ag^{I}{}_5$ nonanuclear structure of **2** is readily converted to the S-bridged $Rh^{III}{}_2Ag^{I}{}_3$ pentanuclear structure of **1** by reacting with additional Ag^+. This conversion can be understood by the comparison of the crystal structures of **1** and **2** (Figures 1 and 2). That is, the binding of additional Ag atom to S12 and S22, followed by the cleavage of Ag1−S22, Ag2−S32, Ag3−S42, and Ag4−S12 bonds in **2**, leads to the formation of 2 mol of **1**.

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Supporting Information Available: Tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for **1**$(BF_4)_3 \cdot H_2O$ and **2**$(BF_4)_5 \cdot 4H_2O$ and a figure of perspective view of disordered complex cation **1** (13 pages). Ordering information is given on any current masthead page.

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