Syntheses and Some Properties of S-Bridged Pentanuclear Co(III)–Hg(II) or Rh(III)–Hg(II) Complexes with 2-Aminoethanethiolate. Crystal Structures of $[\{Rh(aet)_3\}_2(HgCl_2)_3]$ and $[\{Rh(aet)_3\}_2Hg_3(NO_3)_4](NO_3)_2$

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S-Bridged pentanuclear complexes $[\{Rh(aet)_3\}_2(HgCl_2)_3]$ (**1**) and $[\{M(aet)_3\}_2Hg_3(NO_3)_4]^{2+}$ (M=Rh(III), **2** and Co(III), **3**) were newly prepared by the reaction of *fac*(*S*)-$[M(aet)_3]$ with $HgCl_2$ or $Hg(NO_3)_2$; where aet denotes 2-aminoethanethiolate. The crystal structures of **1** and **2** were determined by X-ray diffraction methods. These complexes consist of two *fac*(*S*)-$[M(aet)_3]$ subunits, three Hg atoms, six chlorides (for **1**) or nitrates (for **2**), and water molecules, in which the configuration of the five metals is an approximately regular trigonal-bipyramid. Each Hg atom in these complexes takes a highly distorted tetrahedral geometry. There are three kinds of nitrates in $[\{Rh(aet)_3\}_2Hg_3(NO_3)_4](NO_3)_2$, bridged bidentate, monodentate, and anion. Both **1** and **2** possess a novel chirality due to the helical structures of three Rh–S–Hg–S–Rh chains. Although **1** was insoluble in water, **2** and **3** were optically resolved by fractional precipitation. These complexes were characterized by their absorption, CD, and NMR spectra. The coordinated nitrates in **2** and **3** were readily replaced by water molecules when dissolved in water. The stabilities of the S-bridged pentanuclear complexes are also discussed.

We have previously reported the preparations and properties of two types of S-bridged polynuclear complexes, which are formed by the reactions of *fac*(*S*)-$[M(aet)_3]$ (M=Co(III), Rh(III), Ir(III); aet=2-aminoethanethiolato, $NH_2CH_2CH_2S^-$) with various metal ions.[1—5] These suggest that the S-bridged polynuclear structures formed are highly dependent on the coordination geometry of the reacting metal ions. Namely, the reactions with Co^{3+}, Fe^{3+}, or Ni^{2+} ions, which prefer to take an octahedral geometry, give linear-type S-bridged trinuclear complexes.[1,2] While, in the reactions with Co^{2+}, Zn^{2+}, or Cd^{2+} ions, which prefer to take a tetrahedral geometry, T-cage-type S-bridged penta- or octanuclear complexes are formed.[3—5] The latter complexes exhibit stereoselective aggregation of the chiral *fac*(*S*)-$[M(aet)_3]$ subunits, giving a T-symmetrical structure. In order to explore a new class of S-bridged polynuclear structures, we have extended our studies to investigate the reaction with mercury(II), which can take not only a tetrahedral geometry but also a linear one.[6] It was found that the reaction of *fac*(*S*)-$[Rh(aet)_3]$ with $HgCl_2$ gave a novel pentanuclear complex, $[\{Rh(aet)_3\}_2(HgCl_2)_3]$ (**1**), having triple-helical chirality; the crystal structure of **1** has been presented as a preliminary report.[7] The unique S-bridged structure of **1** prompted us to prepare a series of pentanuclear complexes composed of two *fac*(*S*)-$[M(aet)_3]$ (M=Co(III) and Rh(III)) subunits and three mercury(II) ions. In this paper, we report the preparations and the stereochemical and spectrochemical properties of these S-bridged pentanuclear complexes, which were characterized by a combination of X-ray diffraction, plasma emission spectral and elemental analyses, molar conductivities, and absorption, CD and NMR spectra.

Experimental

Materials. All reagents were purchased from Wako Pure Chemical Ind., Co., Ltd., and used without further purification.

Preparation of Complexes. 1) $[\{Rh(aet)_3\}_2(HgCl_2)_3]$ (1). To a suspension containing 0.10 g (0.30 mmol) of *fac*(*S*)-$[Rh(aet)_3]$[4c,8] in 130 cm^3 of water was added 0.14 g (0.52 mmol) of $HgCl_2$. The mixture was stirred at room temperature for 20 min, and a small amount of white precipitate was filtered out. The pale yellow filtrate was allowed to stand at room temperature for a week, and the resulting pale yellow crystals ($\mathbf{1}\cdot 8H_2O$) were collected by filtration. Yield: 0.18 g (74%). Found: C, 8.71; H, 2.79; N, 4.95; Rh, 12.19; Hg, 36.96%. Calcd for $[\{Rh(aet)_3\}_2(HgCl_2)_3]\cdot 8H_2O = C_{12}H_{36}N_6S_6Cl_6Rh_2Hg_3\cdot 8H_2O$: C, 8.89; H, 3.24; N, 5.18; Rh, 12.69; Hg, 37.12%.

Attempts at optical resolution of the complex molecule **1** were unsuccessful because of its limited solubility in any solvents.

2) $[\{Rh(aet)_3\}_2Hg_3(NO_3)_4]^{2+}$ (2). This complex (**2**$(NO_3)_2\cdot 5H_2O$) was prepared by a procedure similar to that used for **1**, using 30 cm^3 of water and the same molar quantity of $Hg(NO_3)_2\cdot H_2O$ instead of $HgCl_2$. Yield: 0.21 g (81%). Found: C, 8.44; H, 2.49; N, 9.59; Rh, 11.92; Hg, 34.91%. Calcd for $[\{Rh(aet)_3\}_2Hg_3(NO_3)_4](NO_3)_2\cdot 5H_2O = C_{12}H_{36}N_{12}O_{18}S_6Rh_2Hg_3\cdot 5H_2O$: C, 8.35; H, 2.69; N, 9.74; Rh, 11.92; Hg, 34.85%.

3) $[\{Co(aet)_3\}_2Hg_3(NO_3)_4]^{2+}$ (3). To a suspension containing 0.30 g (1.04 mmol) of *fac*(*S*)-$[Co(aet)_3]$[3b,9a] in 120 cm^3 of water was added 0.60 g (1.75 mmol) of $Hg(NO_3)_2\cdot H_2O$. The mixture was stirred at room temperature for 20 min, and a small amount of insoluble material was filtered off. To the filtrate was added a solution containing 2.40 g (28.2 mmol) of $NaNO_3$ in 50 cm^3 of water and this was allowed to stand at room temperature for 1 d. The resulting dark red crystals (**3**$(NO_3)_2\cdot 3H_2O\cdot NaNO_3$) were collected by filtration. Yield: 0.55 g (63%). Found: C, 8.52; H, 2.54; N, 10.09; Co, 6.97; Hg, 36.36%. Calcd for $[\{Co(aet)_3\}_2Hg_3(NO_3)_4](NO_3)_2\cdot 3H_2O\cdot NaNO_3 = C_{12}H_{36}N_{12}O_{18}S_6Co_2Hg_3\cdot 3H_2O\cdot NaNO_3$: C, 8.54; H, 2.51; N, 9.96; Co, 6.98; Hg, 35.66%.

Optical Resolution. **4) $(-)^{CD}_{350}$-$[\{Rh(aet)_3\}_2Hg_3(NO_3)_4]^{2+}$ ($(-)^{CD}_{350}$-2).** A solution containing 0.16 g (0.30 mmol) of $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$ in 150 cm^3 of water was added to a solution containing 0.21 g (0.12 mmol) of **2**$(NO_3)_2\cdot 5H_2O$ in 600 cm^3 of water. The mixture was allowed to stand at room temperature for 2 d and the resulting white floating precipitate was collected by filtration. Yield: 0.18 g (97% as a diastereomer). Found: C, 14.08; H, 2.57; N, 2.75; Rh, 5.54; Hg, 20.65%. Calcd for $[\{Rh(aet)_3\}_2Hg_3][Sb_2(C_4H_2O_6)_2]_3\cdot 13H_2O = C_{36}H_{48}N_6O_{36}S_6Rh_2Sb_6Hg_3\cdot 13H_2O$: C, 13.92; H, 2.40; N, 2.71; Rh, 6.63; Hg, 19.38%.

A solution containing 6.0 g (71 mmol) of $NaNO_3$ in 20 cm^3 of water was added to a suspension containing 0.18 g (0.058 mmol) of the diastereomer in 18 cm^3 of water. The solution was allowed to stand at room temperature for a few days and then the optically inactive pale yellow needle crystals that appeared were removed by filtration. The filtrate was kept at room temperature for a further 10 d. The resulting optically active pale yellow needle crystals ($(-)^{CD}_{350}$-**2**$(NO_3)_2\cdot 5H_2O\cdot NaNO_3$), which showed a negative CD sign at 350 nm, were collected by filtration. Yield: 0.02 g (19% from the diastereomer). Found: C, 8.02; H, 2.43; N, 9.86; Rh, 10.34; Hg, 31.24%. Calcd for $[\{Rh(aet)_3\}_2Hg_3(NO_3)_4](NO_3)_2\cdot 5H_2O\cdot NaNO_3 = C_{12}H_{36}N_{12}O_{18}S_6Rh_2Hg_3\cdot 5H_2O\cdot NaNO_3$: C, 7.96; H, 2.56; N, 10.05; Rh, 11.36; Hg, 33.22%.

5) $(-)^{CD}_{350}[\{Co(aet)_3\}_2Hg_3(NO_3)_4]^{2+}$ ($(-)^{CD}_{350}$-3). A solution containing 0.32 g (0.60 mmol) of $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$ in 150 cm^3 of water was added to a solution containing 0.46 g (0.27 mmol) of **3**$(NO_3)_2\cdot 3H_2O\cdot NaNO_3$ in 900 cm^3 of water. The mixture was allowed to stand at room temperature for 1 d and the resulting dark red powder was collected by filtration. Yield: 0.39 g (90% as a diastereomer). Found: C, 13.27; H, 2.61; N, 2.80%. Calcd for $[\{Co(aet)_3\}_2Hg_3][Sb_2(C_4H_2O_6)_2]_{2.75}(NO_3)_{0.5}\cdot 20H_2O = C_{34}H_{47}N_{6.5}O_{34.5}S_6Co_2Sb_{5.5}Hg_3\cdot 20H_2O$: C, 13.43; H, 2.88; N, 2.99%.

The diastereomer (0.22 g, 0.068 mmol) was dissolved in 100 cm^3 of 1 $mol\,dm^{-3}$ HNO_3. The solution was stirred at room temperature for 2 h and a small amount of insoluble material was filtered off. The filtrate was kept at room temperature for 1 d. The resulting red crystals ($(-)^{CD}_{350}$-**3**$(NO_3)_2\cdot 7H_2O$), which showed a negative CD sign at 350 nm, were collected by filtration. Yield: 0.01 g (9% from the diastereomer). Found: C, 8.99; H, 2.66; N, 9.65; Co, 6.40; Hg, 36.22%. Calcd for $[\{Co(aet)_3\}_2Hg_3(NO_3)_4](NO_3)_2\cdot 7H_2O = C_{12}H_{36}N_{12}O_{18}S_6Co_2Hg_3\cdot 7H_2O$: C, 8.61; H, 3.01; N, 10.04; Co, 7.04; Hg, 35.94%.

Ligand Substitution of $[\{Rh(aet)_3\}_2Hg(NO_3)_4]^{2+}$ (2). To a solution containing 0.10 g (0.058 mmol) of **2**$(NO_3)_2\cdot 5H_2O$ in 10 cm^3 of water was added 0.10 g (1.71 mmol) of NaCl, whereupon the solution soon became a white suspension. This was stirred at room temperature for 1 h, and the white powder was then collected by filtration. The results of ICP and elemental analyses of this powder were identical to those of $[\{Rh(aet)_3\}_2(HgCl_2)_3]\cdot 8H_2O$ (**1**$\cdot 8H_2O$). Yield: 0.09 g (96%).

Measurements. The electronic absorption spectra were recorded with a JASCO UVIDEC-505 or Ubest-55 spectrophotometer. The CD spectra were recorded with a JASCO J-600 spectropolarimeter. All the measurements were carried out in aqueous solutions at room temperature. The ^{13}C NMR spectra were recorded with a Bruker AM-500 NMR spectrometer at probe temperature in D_2O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. The concentrations of Co, Rh, and Hg in the complexes were determined with a Jarrell-Ash ICPA-575 ICP spectrophotometer. The molar conductances of the complexes were measured with a Horiba conductivity meter, DS-14, in aqueous solutions at room temperature.

Crystallography. X-Ray Data Collections. Single crystals of **1**$\cdot 8H_2O$ and **2**$(NO_3)_2\cdot 5H_2O$ were used for data collection on an Enraf–Nonius CAD4 diffractometer with graphite-monochromatized Mo $K\alpha$ (0.71073 Å) radiation. Unit cell parameters were determined by least-squares refinement of 25 reflections. Crystal data and experimental parameters are listed in Table 1. The intensity data were collected by the ω–2θ scan technique, and the scan rate varied from 1 to 5° min^{-1} (on ω). The intensities were corrected for Lorentz and polarization. An empirical absorption correction based on a series of ψ scans was applied. The independent reflections with $F_o > 3\sigma(F_o)$ were considered as 'observed' and used for structure determinations.

Determinations of Crystal Structures. The positions of the rhodium, mercury, and some donor atoms were determined by the direct method. The difference Fourier maps based on these atomic positions revealed the other non-hydrogen atoms.[10] The structures were refined by a full-matrix least-squares refinement of the positional parameters, the anisotropic thermal parameters of the non-hydrogen atoms in **1** and **2**, the nitrate anion (N(3n) and O(3*m*); m=1—3) and water oxygen atom (O(1w)) in **2**, and the isotropic thermal parameters of the other non-hydrogen atoms (program SHELX76[11] was used). The neutral atomic scattering factors were taken from the literature.[12] The occupancy factors for some atoms are listed in Tables 2 and 3. All the calculations were performed on the FACOM M1800/20 computer at the Computer Center of the University of Tsukuba and on a VAX computer using MOLEN.[10] The final atomic coordinates for non-hydrogen atoms are also given in Tables 2 and 3.[13]

Table 1. Crystallographic Data

Formula	$C_{12}H_{52}N_6O_8S_6Cl_6Rh_2Hg_3$	$C_{12}H_{42}N_{12}O_{21}S_6Rh_2Hg_3$
Formula weight	1621.24	1726.51
Cryst. system	Tetragonal	Monoclinic
Space group	$I4_1/a$ (No. 88)	$P2/c$ (No. 13)
a/Å	15.083 (1)	17.974 (4)
b/Å		8.369 (1)
c/Å	37.043 (4)	24.761 (5)
β/deg		146.462 (5)
V/Å^3	8427 (1)	2057.7 (7)
Z	8	2
D_{calcd}/g cm^{-3}	2.556	2.788
Cryst. dimens./mm	0.10×0.25×0.25	0.13×0.21×0.23
μ(Mo $K\alpha$)/cm^{-1}	118.8	118.3
Transm. coeff.	0.792—0.994	0.723—1.000
Temp/K	296	296
λ(Mo Kα)/Å	0.71073	0.71073
$R^{\mathrm{a)}}$	0.058	0.050
$R_{\mathrm{w}}^{\mathrm{b)}}$	$0.063^{\mathrm{c)}}$	$0.064^{\mathrm{d)}}$
Reflection measured	8170	4531
Reflection used	2927	3612

a) $R=\sum|(|F_o|-|F_c|)|/\sum(|F_o|)$. b) $R_w=(\sum w(|F_o|-|F_c|)^2/\sum w(|F_o|^2)^{1/2}$.
c) $w=2.61/(\sigma^2(F_o)+(1.13\times10^{-3})|F_o|^2)$. d) $w=1.00/(\sigma^2(F_o)+(4.89\times10^{-3})|F_o|^2)$.

Table 2. Final Atomic Coordinates, Equivalent Isotropic Thermal Parameters (B_{eq}/Å^2),[a)] and Occupancy Factors (Occ) of [{Rh(aet)$_3$}$_3$-(HgCl$_2$)$_3$]·8H$_2$O (**1**)

Atom	x	y	z	B_{eq}	Occ
Hg(1)	1.0	0.0	0.35629(2)	2.66(3)	1/2
Hg(2)	0.90546(4)	−0.08804(4)	0.26717(2)	2.47(3)	
Rh	0.84935(7)	0.15755(7)	0.29513(3)	1.70(5)	
Cl(1)	1.0597(4)	0.1125(5)	0.4048(2)	7.0(4)	
Cl(2)	0.8750(3)	−0.1647(4)	0.2031(1)	4.2(2)	
Cl(3)	0.7627(3)	−0.1718(3)	0.2899(1)	3.0(2)	
S(1)	0.8502(2)	0.0442(2)	0.3377(1)	2.1(2)	
S(2)	0.8722(3)	0.0615(3)	0.2468(1)	2.3(2)	
S(3)	0.9987(2)	0.1852(3)	0.3028(1)	2.3(2)	
N(1)	0.8196(9)	0.2413(8)	0.3389(3)	2.6(6)	
N(2)	0.7132(8)	0.1389(8)	0.2848(4)	2.6(6)	
N(3)	0.8511(9)	0.2684(9)	0.2604(4)	2.7(6)	
C(1)	0.8165(12)	0.1046(13)	0.3776(5)	3.8(9)	
C(2)	0.8515(10)	0.2019(11)	0.3743(4)	2.8(7)	
C(3)	0.7591(12)	0.0496(12)	0.2302(5)	3.7(9)	
C(4)	0.6940(10)	0.0568(11)	0.2638(5)	3.2(8)	
C(5)	1.0064(12)	0.2881(12)	0.2764(6)	4.3(10)	
C(6)	0.9418(14)	0.2888(13)	0.2473(7)	5.3(11)	
O(1w)	0.820(2)	0.424(2)	0.1140(8)	0.17(1)[b)]	
O(2w)	0.774(2)	0.347(3)	0.1382(10)	0.22(1)[b)]	
O(3w)	0.069(2)	0.375(2)	0.1772(8)	0.17(1)[b)]	
O(4Aw)	0.029(3)	0.420(3)	0.086(1)	0.17(2)[b)]	2/3
O(4Bw)	0.288(6)	0.433(6)	0.345(2)	0.17(3)[b)]	1/3

a) $B_{\mathrm{eq}}=(8\pi^2/3)\sum_i\sum_j U_{ij}\,a_i^*\,b_j^*\,\boldsymbol{a}_i\cdot\boldsymbol{b}_j$. b) Isotropic thermal parameters (U/Å^2).

Results and Discussion

X-Ray Crystal Structures. Perspective drawings of **1** and **2** are shown in Figs. 1 and 2 (also see Fig. 3 about the coordinated nitrates). Selected bond distances and angles are listed in Tables 4 and 5. **1** and **2** consist of two approximately octahedral *fac*(S)-[Rh(aet)$_3$] subunits, three Hg atoms, and six chlorides (for **1**) or four nitrates (for **2**). Both complexes have a very similar framework except for the chlorides and nitrates around the Hg atoms. For example, they have crystallographically imposed C_2 symmetry, the Hg(1) atom lying on the 2-fold axis. Two *fac*(S)-[Rh(aet)$_3$] subunits are linked by the three Hg atoms to give an S-bridged pentanuclear structure. The configuration of the five metal atoms is an approximate regular trigonal-bipyramid, although **2** is somewhat elongated along the Rh···Rh axis compared with the structure of **1** (average Rh–Hg = 3.970(1) Å, Hg–Hg = 3.854(1) Å, Rh–Rh′ = 6.576(2) Å, Hg–Rh–Hg = 58.08(2)°, Hg–Hg–Rh = 60.96(2)°, Hg–Hg–Hg = 60.00(2)° for **1**; Rh–Hg = 3.945(2) Å, Hg–Hg=3.662(2) Å, Rh–Rh′=6.656(2) Å, Hg–Rh–Hg= 55.32(3)°, Hg–Hg–Rh=62.32(3)° for **2**).

The Rh–S and Rh–N distances (average 2.321(4) and 2.108(13) Å for **1**; average 2.331(3) and 2.105(9) Å for **2**, respectively) in the *fac*(S)-[Rh(aet)$_3$] subunits are in good agreement with those in the corresponding subunits of the T-cage-type polynuclear complexes (Tables A and B).[3a,4c,13)] The S–Rh–S and N–Rh–N angles (average 93.3(1) and 90.3(5)° for **1**; average 95.8(1) and 91.2(4)° for **2**, respectively) also indicate that the N$_3$S$_3$ octahedral structures around the Rh atoms in **1** and **2** are also comparable with those in the T-cage-type polynuclear complexes (Tables A and B).[3a,4c,13)]

For each Hg atom in **1**, two coordination sites are occupied by two thiolato S atoms (average Hg–S=

Table 3. Final Atomic Coordinates, Equivalent Isotropic Thermal Parameters (B_{eq}/Å^2), $^{a)}$ and Occupancy Factors (Occ) of [{Rh(aet)$_3$}$_3$Hg$_3$(NO$_3$)$_4$](NO$_3$)$_2$·3H$_2$O (**2**)

Atom	x	y	z	B_{eq}	Occ
Hg(1)	0.5	0.80186(7)	0.25	1.36(3)	1/2
Hg(2)	0.61318(4)	0.18166(5)	0.26027(3)	1.46(2)	
Rh	0.76400(7)	0.05508(9)	0.49255(5)	0.83(3)	
S(1)	0.7906(2)	0.0492(3)	0.4150(2)	1.20(9)	
S(2)	0.6071(3)	−0.1522(3)	0.3998(2)	1.34(9)	
S(3)	0.6076(2)	0.2619(3)	0.4000(2)	1.14(9)	
N(1)	0.9168(8)	0.2327(11)	0.5822(6)	1.2(3)	
N(2)	0.9082(8)	−0.1264(10)	0.5845(6)	0.9(3)	
N(3)	0.7547(9)	0.0640(10)	0.5715(6)	1.6(4)	
C(1)	0.9327(10)	0.1919(13)	0.4935(7)	1.8(5)	
C(2)	0.9267(12)	0.3142(11)	0.5368(9)	1.6(4)	
C(3)	0.7224(13)	−0.3210(13)	0.4784(10)	1.6(5)	
C(4)	0.8586(13)	−0.2829(13)	0.5339(9)	2.1(5)	
C(5)	0.5975(15)	0.2872(17)	0.4688(11)	3.1(6)	
C(6)	0.6275(12)	0.1362(17)	0.5159(8)	2.3(5)	
N(1n)	0.7702(9)	0.0080(13)	0.2558(7)	2.1(4)	
N(2n)	0.7070(10)	0.5515(11)	0.3097(7)	1.9(4)	
N(3n)	1.0	0.6009(17)	0.25	2.0(5)	1/2
O(11)	0.8416(9)	0.1005(13)	0.3230(7)	3.3(4)	
O(12)	0.8168(10)	−0.0846(13)	0.2466(7)	3.4(4)	
O(13)	0.6498(9)	0.0024(18)	0.1940(7)	4.5(5)	
O(21)	0.7458(10)	0.4311(12)	0.3117(8)	4.0(5)	
O(22)	0.6128(10)	0.5338(11)	0.2879(8)	3.6(4)	
O(23)	0.7548(12)	−0.3205(11)	0.3288(9)	4.3(6)	
O(31)	1.0	0.7519(16)	0.25	2.5(5)	1/2
O(32)	0.9173(10)	0.5303(10)	0.1712(6)	2.6(4)	
N(4n)	0.280(4)	0.346(5)	0.370(3)	0.17(2)$^{b)}$	1/2
O(41)	0.301(4)	0.227(4)	0.412(3)	0.08(1)$^{b)}$	1/2
O(42)	0.172(5)	0.337(6)	0.280(3)	0.17(2)$^{b)}$	1/2
O(43)	0.383(3)	0.426(4)	0.424(2)	0.091(9)$^{b)}$	1/2
O(1w)	0.0	0.198(2)	0.25	8.3(13)	1/2
O(2w)	0 195(3)	0.450(3)	0.272(2)	0.068(7)$^{b)}$	1/2
O(3w)	0.350(6)	0.239(7)	0.430(4)	0.14(2)$^{b)}$	1/2

a) $B_{eq}=(8\pi^2/3)\sum_i\sum_j U_{ij}\,a_i^*\,b_j^*\,\boldsymbol{a}_i\cdot\boldsymbol{b}_j$. b) Isotropic thermal parameters (U/Å^2).

2.443(4) Å and S–Hg–S=147.6(1)°) from the two terminal *fac*(*S*)-[Rh(aet)$_3$] subunits. The Hg–S distances are much shorter than those found in tetrahedral [Hg(thiolato-S)$_4$]$^{2-}$ (2.52—2.55 Å)$^{14,15)}$ and are longer than those in diagonal [Hg(thiolato-S)$_2$] (2.32—2.35 Å).$^{14,16)}$ The remaining two coordination sites of the Hg atoms are occupied by the Cl atoms (average Hg–Cl=2.648(5) Å and Cl–Hg–Cl=88.8(4)°). The Hg–Cl distances are distinctly longer than those in tetrahedral [HgCl$_4$]$^{2-}$ (2.39—2.53 Å).$^{14)}$ These facts indicate, therefore, that each Hg atom in **1** is situated in a highly distorted tetrahedral environment and the Cl atoms weakly coordinate to the Hg atom because of the tendency of the Hg atom to maximize bonding to the S atoms.

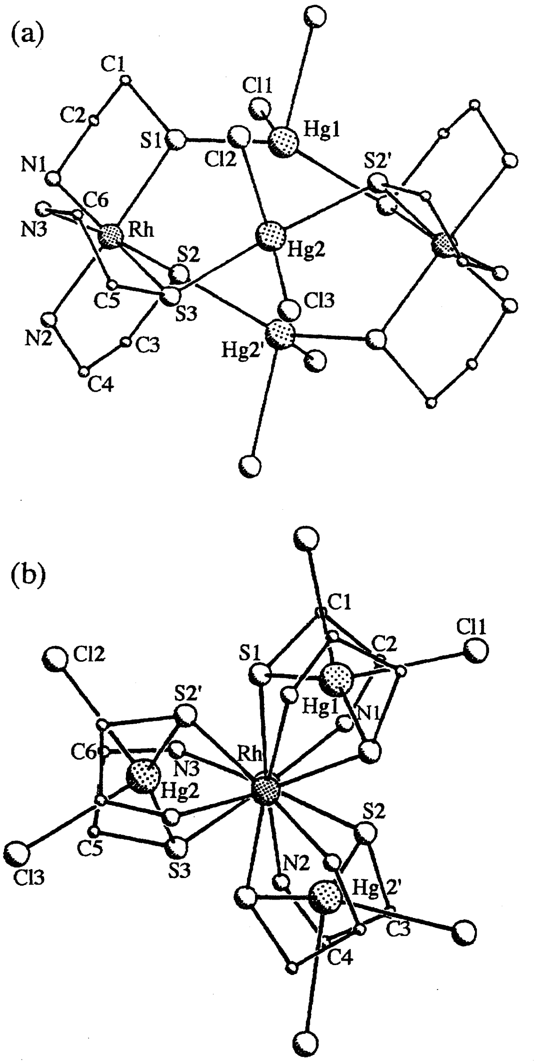

Fig. 1. Perspective view of **1** with the atomic labeling scheme: view down close to a C_2 axis (a) and a C_3 axis (b).

A geometrical tendency similar to **1** is observed for each Hg atom in **2**. However, the Hg–S distances (average 2.388(5) Å) in **2** are shorter than those in **1**, and the S–Hg–S angles (average 161.0(2)°) in **2** are closer to 180° than those in **1**. The remaining two coordination sites of the Hg atoms are occupied by the O atoms from the nitrate ions. There are three kinds of nitrates in [{Rh(aet)$_3$}$_2$Hg$_3$(NO$_3$)$_4$](NO$_3$)$_2$ in terms of the coordination modes; that is, the bidentate nitrates which bridge the two cationic complex units, monodentate nitrates, and nitrate anions. As shown in Fig. 3, each cationic complex unit of **2** is infinitely linked by the bidentate nitrates to from a infinite one-dimensional chain. One of the three Hg atoms, Hg(1), is coordinated by the O atoms from the two bidentate nitrates (Hg(1)–O(22)=2.618(9) Å and O(22)–Hg(1)–O(22)′=62.0(4)°). Each of the other two Hg atoms, Hg(2) and Hg(2)′, is coordinated by the O atoms (O(13)–Hg(2)–O(21)=99.1(3)°) from the bidentate (Hg(2)–O(21)=2.57(1) Å and monodentate nitrates (Hg(2)–O(13)=2.68(1) Å). The Hg–O distances (2.57—2.68 Å) in **2** are much longer than those in Hg(OHg)$_4$Br$_2$(2.24(3) Å)$^{17)}$ where the Hg atom is situated in an approxi-

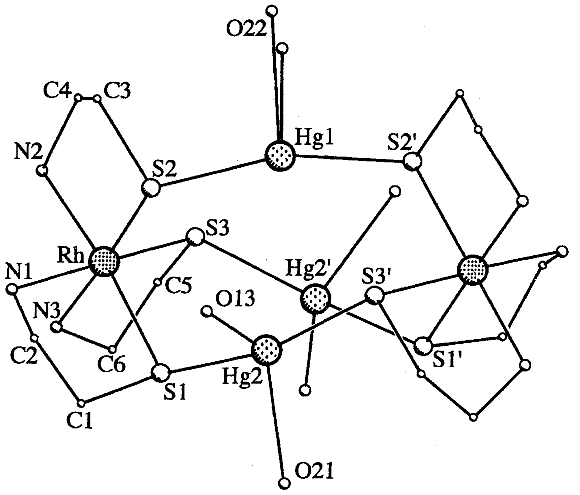

Fig. 2. Perspective view of **2** with the atomic labeling scheme.

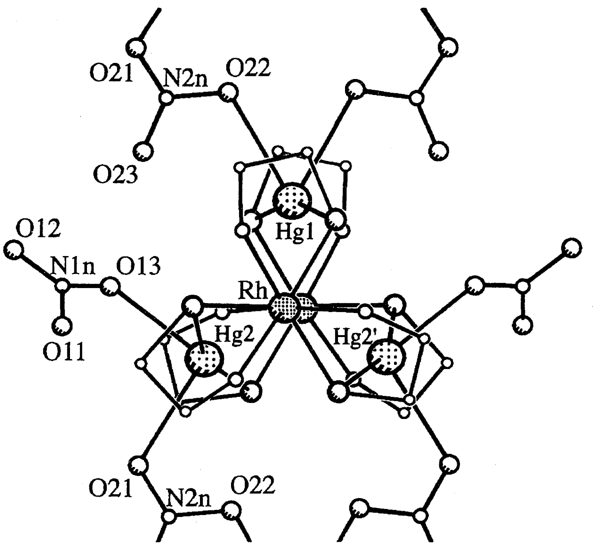

Fig. 3. The portion of the infinite one-dimension chain in $[\{Rh(aet)_3\}_2Hg_3(NO_3)_4]^{2+}$ (**2**).

Table 4. Selected Bond Distances (Å) and Angles (°) for $[\{Rh(aet)_3\}_3(HgCl_2)_3]\cdot 8H_2O$ (**1**)

(a) Bond distances			
Hg(1)–S(1)	2.455(4)	Rh–S(1)	2.326(4)
Hg(2)–S(2)	2.430(4)	Rh–S(2)	2.328(4)
Hg(2)–S(3)	2.445(4)	Rh–S(3)	2.309(4)
Hg(1)–Cl(1)	2.632(5)	Rh–N(1)	2.104(13)
Hg(2)–Cl(2)	2.679(4)	Rh–N(2)	2.108(12)
Hg(2)–Cl(3)	2.634(4)	Rh–N(3)	2.111(13)
(b) Bond angles			
S(1)–Hg(1)–S(1)$^{a)}$	147.4(1)	Cl(2)–Hg(2)–Cl(3)	86.3(1)
S(2)–Hg(2)–S(3)	147.8(1)	S(1)–Rh–N(1)	85.5(4)
Cl(1)–Hg(1)–S(1)	109.4(2)	S(2)–Rh–N(2)	85.5(4)
Cl(1)–Hg(1)–S(1)$^{a)}$	93.0(2)	S(3)–Rh–N(3)	85.4(4)
Cl(2)–Hg(2)–S(2)	95.2(2)	S(1)–Rh–N(3)	174.8(4)
Cl(2)–Hg(2)–S(3)	108.7(1)	S(2)–Rh–N(1)	176.1(4)
Cl(3)–Hg(2)–S(2)	112.0(1)	S(3)–Rh–N(2)	175.6(4)
Cl(3)–Hg(2)–S(3)	91.4(1)	Hg(1)–S(1)–Rh	113.3(2)
Cl(1)–Hg(1)–Cl(1)$^{a)}$	93.8(2)	Hg(2)–S(2)–Rh	111.7(2)

a) The symmetric operation is $(-x, -y, z)$.

Table 5. Selected Bond Distances (Å) and Angles(°) for $[\{Rh(aet)_3\}_3Hg_3(NO_3)_4](NO_3)_2\cdot 3H_2O$ (**2**)

(a) Bond distances			
Hg(1)–S(2)	2.389(2)	Rh–S(1)	2.334(2)
Hg(2)–S(1)	2.390(2)	Rh–S(2)	2.333(3)
Hg(2)–S(3)	2.386(2)	Rh–S(3)	2.327(3)
Hg(1)–O(22)	2.618(9)	Rh–N(1)	2.125(8)
Hg(2)–O(13)	2.680(12)	Rh–N(2)	2.091(9)
Hg(2)–O(21)	2.569(10)	Rh–N(3)	2.098(9)
(b) Bond angles			
S(2)–Hg(1)–S(2)$^{a)}$	161.5(1)	O(13)–Hg(2)–O(21)	99.1(3)
S(1)–Hg(2)–S(3)	160.7(2)	S(1)–Rh–N(1)	84.4(2)
S(2)–Hg(1)–O(22)	101.6(2)	S(2)–Rh–N(2)	85.2(2)
S(2)–Hg(1)–O(22)$^{a)}$	94.3(2)	S(3)–Rh–N(3)	85.5(3)
S(1)–Hg(2)–O(13)	92.4(3)	S(1)–Rh–N(3)	175.9(3)
S(1)–Hg(2)–O(21)	97.8(2)	S(2)–Rh–N(1)	176.3(3)
S(3)–Hg(2)–O(13)	93.2(2)	S(3)–Rh–N(2)	175.4(3)
S(3)–Hg(2)–O(21)	99.5(2)	Hg(2)–S(1)–Rh	113.2(1)
O(22)–Hg(1)–O(22)$^{a)}$	62.0(4)	Hg(1)–S(2)–Rh	113.4(1)

a) The symmetric operation is $(-x, y, 1/2 - z)$.

mately regular O_4-tetrahedral geometry. Two kinds of Hg–O distances are found in $[Hg(OCOCF_3)_2(1,4\text{-dioxane})_2(OH_2)_2]$ (2.08(1) and 2.64(1)—2.75(1) Å)[18] and $HgSO_4\cdot H_2O$ (2.179(2)—2.228(2) and 2.501(1)—2.514(1) Å),[19] where the Hg atom is situated in an O_6-octahedral geometry. The Hg–O distances in **2** are within the range of 2.5—2.75 Å observed for the longer Hg–O distances in those complexes, in spite of the fact that the Hg atoms are situated in a distorted tetragonal geometry. This range is shorter than 2.86 Å, which is the sum of the van der Waals redii.[20] These facts suggest, accordingly, that the O atoms in the nitrates coordinate to the Hg atoms, though very weakly. The Hg–O bonds will be weaker than the Hg–Cl ones, since the geometry around the Hg atoms in **2** is more distorted than that in **1**. Namely, the affinities of the Hg–O bonds in $[\{Rh(aet)_3\}_2Hg_3(NO_3)_4]^{2+}$ (**2**) are much weaker than the affinities of the Hg–Cl bonds in $[\{Rh(aet)_3\}_2(HgCl_2)_3]$ (**1**). This is responsible for the fact that the five metal atoms take the elongate-strained framework in **2**.

The space group ($I4_1/a$ for **1** and $P2/c$ for **2**) and Z indicate the selective formations of the racemic compounds for **1** and **2**, having the $\Delta\Delta$ or $\Lambda\Lambda$ configuration for the arrangements (Δ or Λ) of the three chelate rings of the two *fac*(S)-$[Rh(aet)_3]$ subunits. All six bridging sulfur atoms are fixed to the S configuration for the $\Delta\Delta$ isomer and the R configuration for the $\Lambda\Lambda$ isomer. All the aet chelate rings take a distinct gauche form with the 'ob (oblique for C_3 axis)' conformation (δ conformation for Δ and λ for Λ), which is in contrast to the 'lel (parallel)' conformational aet rings observed in linear-type and T-cage-type S-bridged polynuclear complexes.[1—5,9)] Besides these three formal chiralities, **1** and **2** possess a novel chirality due to the helical structure of the three Rh–S–Hg–S–Rh chains; the $\Delta\Delta$ isomer adopts a left-handed helical configuration and the $\Lambda\Lambda$ isomer forms a right-handed helical one. It is noted that no helical structure has been found in the linear-type and T-cage-type S-bridged polynuclear complexes, [1—5,9)] and furthermore a triple helical structure is extremely rare for metal complexes,[21)] although mono[22)] and double helical structures[23)] have been observed in several inorganic compounds. Further, it is also noted that the one-dimensional chains composed of the $\Delta\Delta$ or $\Lambda\Lambda$ isomers for **2** align regularly to give $\Delta\Delta$ or $\Lambda\Lambda$ sheets, which alternately arrange in the crystals (Fig. 3).

Properties. The measurements of the molar conductivities of $[\{M(aet)_3\}_2Hg_3(NO_3)_4](NO_3)_2$ (M=Rh(III), **2** and Co(III), **3**) dissolved in water gave values of 833.95 (for **2**) and 803.09 $\Omega^{-1}\,cm^2\,mol^{-1}$ (for **3**), which are close to the values of the known hexavalent complexes.[3c)] These suggest that the solutions containing **2** and **3** consist of a hexavalent cation and six nitrate anions. The ^{13}C NMR spectrum exhibits only two signals due to two kinds of methylene carbon atoms of aet (δ=39.01 ($-CH_2S$) and 52.90 ($-CH_2NH_2$) for **2**; δ= 39.69 and 51.99 for **3**), it being a D_3 symmetrical structure. Further, the ligand substitutions resulted in $[\{Rh(aet)_3\}_2(HgCl_2)_3]$ being obtained as a white powder from an aqueous solution of $[\{Rh(aet)_3\}_2Hg_3(NO_3)_4](NO_3)_2$ by adding a large excess NaCl. Similar ligand substitutions were observed for the optical resolution of $[\{M(aet)_3\}_2Hg_3(NO_3)_4]^{2+}$ using the $[Sb_2(d\text{-tart})_2]^{2-}$ resolving reagent to give $[\{M(aet)_3\}_2Hg_3][Sb_2(d\text{-tart})_2]_n(NO_3)_m$ (n=3 for M=Rh(III); and n= 2.75 and m=0.5 for M=Co(III)) in the crystalline state. Taking these facts and the X-ray structural studies into consideration, the nitrates, which coordinate to the Hg atom in the crystalline state, seem to be displaced by water molecules, $[\{M(aet)_3\}_2Hg_3(H_2O)_6]^{6+}$, while retaining the structure of the framework.

$[\{Co(aet)_3\}_2Hg_3(H_2O)_6]^{6+}$ exhibits spin-allowed d–d absorption bands (18—25×10^3 cm^{-1}) and sulfur-to-metal charge transfer (SMCT) bands (33—40×10^3 cm^{-1}) (Fig. 4 and Table 6). Similar absorption spectral behavior (ca. 30×10^3 cm^{-1} and ca. 50×10^3 cm^{-1}, respectively) is also observed for the $Rh^{III}{}_2Hg^{II}{}_3$ complexes (Fig. 4 and Table 6). In these complexes, the two types of absorption bands are in a higher energy region than the corresponding bands of $[\{M(aet)_3\}_4Zn_4O]^{6+}$,[3a,3b,4c)] although the absorption spectral pattern of the $Co^{III}{}_2Hg^{II}{}_3$ complex coincides well with the T-cage-type octanuclear complex (Fig. 4).[3b)] This indicates that the electronic states of the *fac*(S)-$[M(aet)_3]$ subunits are somewhat affected by whether the subunits coordinate to the Hg(II) or Zn(II) atoms. The CD spectra for the $(-)^{CD}_{350}$ isomers of $[\{M(aet)_3\}_2Hg_3(H_2O)_6]^{6+}$ (M=Rh(III), **2** and Co(III), **3**) show a negative and a positive band in the d–d absorption band region and a negative and a positive band in the SMCT band region (Fig. 4). Although these CD bands coincide well with the corresponding T-cage-type octanuclear complexes, the negative CD bands at ca. 39×10^3 cm^{-1} for **2** and ca. 34×10^3 cm^{-1} for **3** are quite different from that of $\Delta\Delta\Delta\Delta$-$[\{M(aet)_3\}_4Zn_4O]^{6+}$ (Table 6).[3a,3b,4c)] These absorption and CD spectral properties seem to reflect the difference of the structures between trigonal-bipyramid-type and T-cage-type complexes, that is, the trigonal-bipyramid-type structure has triple-helical chirality, not observed in the T-cage-type structure. Nevertheless, the signs of the CD bands in the d–d absorption and SMCT band regions are in agreement with those of $\Delta\Delta\Delta\Delta$-$[\{M(aet)_3\}_4Zn_4O]^{6+}$.[3a,3b,4c)] This agreement seems to reflect that the absolute configurations around the sulfur donor atoms and the *fac*(S)-$[M(aet)_3]$ subunits (S for Δ and R for Λ) are similar to each other in the two structure types. Therefore, these facts indicate that the $(-)^{CD}_{350}$ isomers for **2** and **3** can be assigned to $\Delta\Delta$-$[\{M(aet)_3\}_2Hg_3(H_2O)_6]^{6+}$.

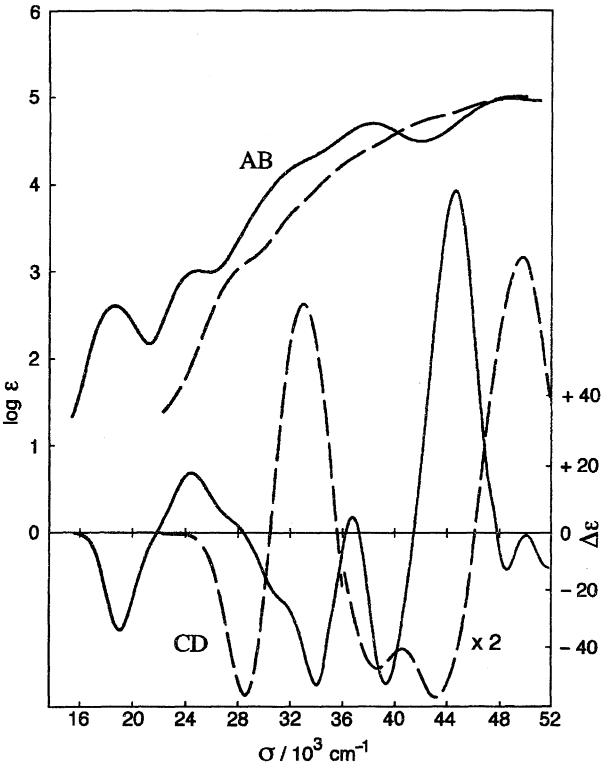

Fig. 4. Absorption and CD spectra of $(-)^{CD}_{350}$-$\Delta\Delta$-$[\{M(aet)_3\}_2Hg_3(H_2O)_6]^{6+}$: M=Co(III) (—) and Rh(III) (- - -).

Syntheses and Properties. The reactions of *fac*(S)-$[M(aet)_3]$ with $HgCl_2$ or $Hg(NO_3)_2$ gave the novel trigonal-bipyramid-type S-bridged pentanuclear complexes $[\{Rh(aet)_3\}_2(HgCl_2)_3]$ (**1**) or [{M-

Table 6. Absorption and CD Spectral Data of the Complexes

	Absorption maxima $\sigma/10^3\ \mathrm{cm}^{-1}$ $(\log \varepsilon/\mathrm{mol}^{-1}\ \mathrm{dm}^3\ \mathrm{cm}^{-1})$	CD extrema $\sigma/10^3\ \mathrm{cm}^{-1}$ $(\Delta\varepsilon/\mathrm{mol}^{-1}\ \mathrm{dm}^3\ \mathrm{cm}^{-1})$
$(-)^{\mathrm{CD}}_{350}$-$\Delta\Delta$-$[\{\mathrm{Rh(aet)_3}\}_2\mathrm{Hg_3}]^{6+}$	28.60 (3.10 sh[a])	28.57 (−37.42)
	31.85 (3.63 sh)	32.98 (+52.67)
(**2**)	36.36 (4.27 sh)	38.70 (−62.61)
	43.25 (4.78 sh)	43.14 (−75.95)
	49.95 (4.99)	49.70 (+126.7)
$(-)^{\mathrm{CD}}_{350}$-$\Delta\Delta$-$[\{\mathrm{Co(aet)_3}\}_2\mathrm{Hg_3}]^{6+}$	18.66 (2.61)	19.03 (−22.41)
	24.94 (3.01)	24.46 (+13.70)
(**3**)	33.22 (4.29)	34.01 (−35.09)
	38.31 (4.70)	36.76 (+3.55)
	48.78 (4.99)	39.37 (−34.79)
		44.64 (+78.52)

a) sh denote a shoulder.

$(\mathrm{aet})_3\}_2\mathrm{Hg_3(NO_3)_4}](\mathrm{NO_3})_2$ (M=Rh(III), **2** and Co(III), **3**), of which the structures of the Rh(III) complexes were determined by X-ray structure analysis. The crystals were not spontaneously resolved, but the intramolecular stereoselectivity is recognized on their formation, that is, two *fac*(*S*)-[M(aet)$_3$] subunits have the same absolute configurations in the complex. Molecular model constructions reveal that the lone pair of electrons on the thiolato-S atoms from the two *fac*(*S*)-[M(aet)$_3$] subunits are oriented inconveniently for coordination to the one Hg atom with distorted tetrahedral geometry, when the absolute configurations of the two subunits are different from each other. Therefore, this seems to give the result that only the racemates were formed, and the selective formation in the crystal of the infinite one-dimensional chains and their sheets in the nitrate complex $[\{\mathrm{Rh(aet)_3}\}_2\mathrm{Hg_3(NO_3)_4}]^{2+}$ are regarded as intermolecular aggregation of the chirality.

Between the trigonal-bipyramid-type and T-cage-type structures, the following two common features are recognized: (i) all the *fac*(*S*)-[M(aet)$_3$] subunits in these structures have the same absolute configurations and have bond distances and angels similar to each other, and (ii) the three S atoms from one *fac*(*S*)-[M(aet)$_3$] subunit are bonded to the three different metal atoms. There features lead to the emphasis that the two structures are closely related to each other from the view point of formation. Both $\mathrm{Rh^{III}}_2\mathrm{Hg^{II}}_3$ complexes **1** and **2** are dissolved in alkaline aqueous solution easily with yellow coloration. A similar yellow complex is also formed by the reaction of *fac*(*S*)-[Rh(aet)$_3$] with HgO, which is assigned to the T-cage-type complex [{Rh-

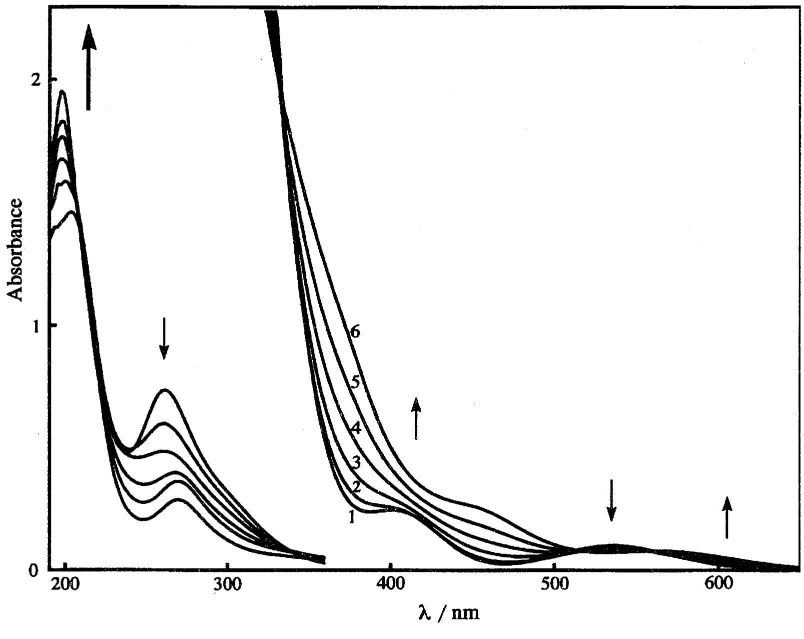

Fig. 5. Absorption spectral change with time of $[\{\mathrm{Co(aet)_3}\}_2\mathrm{Hg_3(H_2O)_6}]^{6+}$ (**3**) in water at 23 °C: Curves 1—6 were measured at 0, 2, 4, 6, 8, 10 d, respectively.

$(aet)_3\}_4Hg_4O]^{6+}$ ($Rh^{III}_4Hg^{II}_4$). As shown in Fig. 5, the absorption spectral changes with time of $[\{Co(aet)_3\}_2Hg_3(H_2O)_6]^{6+}$ suggest that the trigonal-bipyramid-type pentanuclear structure changes to a T-cage-type octanuclear one. All the Zn(II), Cd(II), and Hg(II) atoms tend to take tetrahedral geometry, and the Hg(II) atom changes further to linear geometry.[6)] Thus, all the reactions of *fac*(*S*)-[M(aet)$_3$] with the tetrahedrally geometrical metal ions under the appropriate conditions gave T-cage-type S-bridged octanuclear complexes. In addition, the reaction with the Hg^{2+} ion also gave trigonal-bipyramid-type pentanuclear $M^{III}_2Hg^{II}_3$ complexes **1**, **2**, and **3**. Accordingly, these facts indicate that the trigonal-bipyramid-type and T-cage-type structures are interchangeable with each other, in relation to the arrangements around the Hg(II) atom and the common features between the two types of structures. They also mean that the properties of the metal ions incorporated in the *fac*(*S*)-[M(aet)$_3$] subunits influence the structure of the polynuclear complexes significantly.

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