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A New Class of S-Bridged Pentanuclear Complexes with a Triple Helical Chirality. Crystal Structure of $[\{Rh^{III}(aet)_3\}_2(Hg^{II}Cl_2)_3]$ (aet = 2-aminoethanethiolate)

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The reactions of *fac(S)*-$[Rh(aet)_3]$ (aet = 2-aminoethanethiolate) with HgX_2 (X = Cl or NO_3) gave twisted-ellipsoid-type S-bridged pentanuclear complexes with a triple helical chirality, in which two Δ- or Λ-*fac(S)*-$[Rh(aet)_3]$ subunits are linked by three mercury atoms. The crystal structure of $[\{Rh(aet)_3\}_2(HgCl_2)_3]$ was determined by X-ray crystallography.

As a part of systematic investigations of S-bridged polynuclear complexes with 2-aminoethanethiolate (aet) or L-cysteinate (L-cys),[1-3] we have recently reported that the reactions of *fac(S)*-$[M(aet)_3]$ (M = Co(III), Rh(III), or Ir(III)) with M' = Zn^{2+} or Cd^{2+} in water produce novel cage-type S-bridged polynuclear complexes with a "defective" $[M'_3O]^{4+}$ or a "complete" $[M'_4O]^{6+}$ core, $[\{M(aet)_3\}M'_{3\text{ or }4}O]^{4+\text{ or }6+}$, which are commonly spontaneously resolved for M' = Zn^{2+}.[2)] These results are in striking contrast to the fact that the reactions with a metal ion M" = Fe^{3+}, Co^{2+}, or Ni^{2+}, which prefers to take an octahedral geometry, give the well-known linear-type S-bridged trinuclear complexes $[M''\{M(\text{aet or L-cys-}N,S)_3\}_2]^{n+\text{ or }n-}$.[1,4)] Here we report that the reactions of *fac(S)*-$[Rh(aet)_3]$ with HgX_2 (X = Cl or NO_3), which is geometrically analogous to ZnX_2 and CdX_2, result in the formation of a new class of S-bridged pentanuclear complexes showing a triple helical chirality.

To a yellow suspension of *fac(S)*-$[Rh(aet)_3]$ (0.10 g) in 15 cm^3 of water was added $HgCl_2$ (0.14 g) in 65 cm^3 of water. The mixture was stirred at room temperature for 30 min, whereupon the suspension became a clear pale yellow solution. Slow evaporation of this reaction solution gave pale yellow crystals (**1**) in 37% yield.[5)] The plasma emission spectral analysis indicated that **1** contains Rh and Hg in a ratio of 2 : 3. X-Ray structural analysis of **1** revealed the presence of a discrete complex molecule and water ones.[6)] The entire complex molecule has a crystallographically imposed C_2 symmetry, the Hg1 atom lying on the two-fold axis

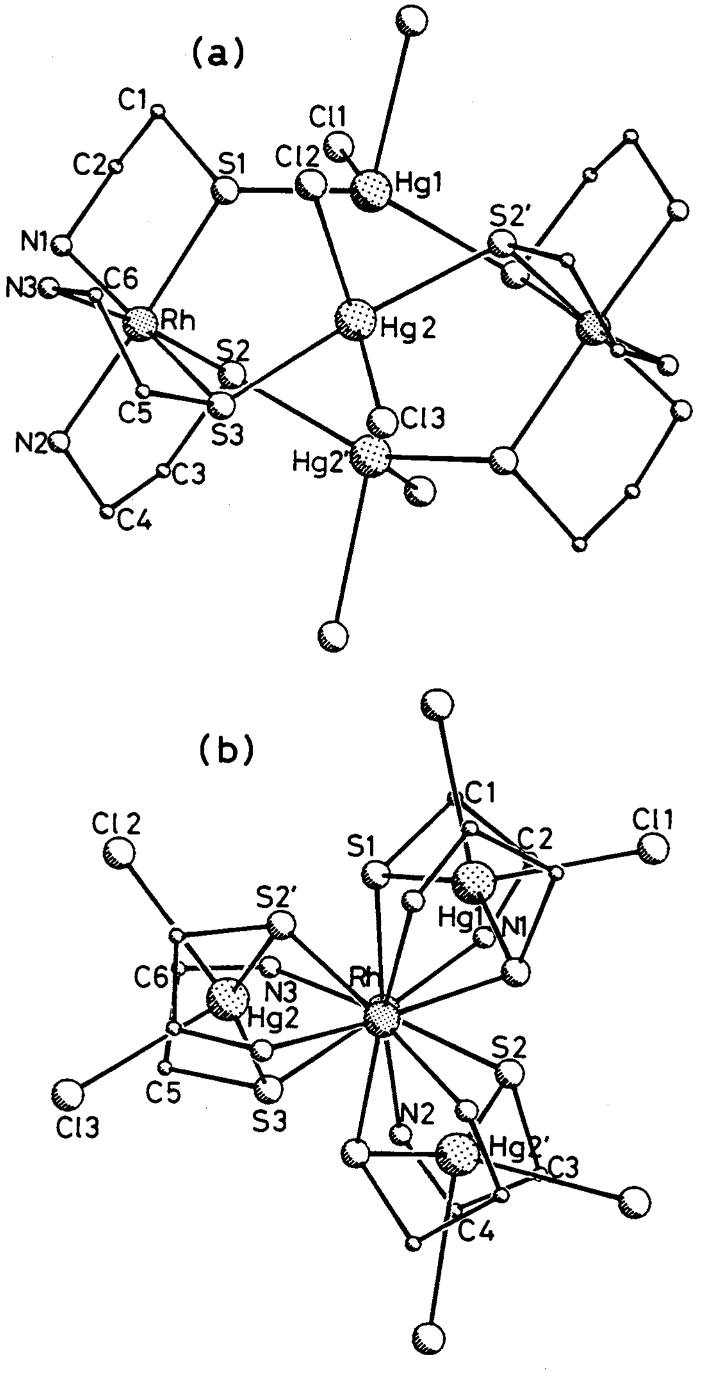

Fig. 1. Perspective view of the complex molecule **1** with the atomic labeling scheme; (a) view down close to a C_2 axis, (b) view down close to a C_3 axis.

(Fig. 1). The entire complex molecule consists of two approximately octahedral *fac(S)*-[Rh(aet)$_3$] subunits and three $HgCl_2$ moieties. The two *fac(S)*-[Rh(aet)$_3$] subunits are linked by the three Hg atoms to give a twisted-ellipsoid-type S-bridged pentanuclear structure, in which five metals form an approximately regular trigonal-bipyramid (average Rh-Hg = 3.970 (1) Å, Hg-Hg = 3.854 (1) Å, Hg-Rh-Hg = 58.08 (2)°, Hg-Hg-Rh = 60.96 (2)°). Each Hg atom is situated in a highly distorted tetrahedral environment coordinated by two thiolato S atoms from the two terminal *fac(S)*-[Rh(aet)$_3$] subunits and two Cl atoms (average S-Hg-S = 147.6 (1)° and Cl-Hg-Cl = 88.8 (4)°). The Hg-S bonds (average 2.443 (4) Å) are much shorter than those in tetrahedral $[Hg(thiolato\text{-}S)_4]^{2-}$ (2.52 - 2.55 Å) [7a,b] and are close to the values observed for Hg-S bonds in digonal $[Hg(thiolato\text{-}S)_2]$ (2.32 - 2.35 Å).[7a,c] On the other hand, the Hg-Cl bonds (average 2.648 (5) Å) are distinctly longer than those found in tetrahedral $[HgCl_4]^{2-}$ (2.39 - 2.53 Å).[7a] Accordingly, it is assumed that in **1** the Cl atoms only weakly coordinate to Hg(II) because of the tendency for Hg(II) to maximize bonding to the S atoms.

The space group of $I4_1/a$ and $Z = 8$ [6] indicates the selective formation of racemic compound for **1**, having the ΔΔ or ΛΛ configuration for the two *fac(S)*-[Rh(aet)$_3$] subunits (Fig. 1). All the six bridging sulfur atoms are fixed to the S configuration for the ΔΔ isomer and R one for the ΛΛ isomer. All the aet chelate rings take a distinct gauche form with the 'ob' conformation (δ conformation for Δ and λ one for Λ), which is in contrast to the 'lel' conformational aet rings observed in the linear-type and cage-type S-bridged polynuclear complexes.[1-4] Besides these three formal chiralities, **1** possesses a novel chirality due to the helical structure of the three Rh-S-Hg-S-Rh chains; the ΔΔ isomer adopts the left-handed helical configuration and the ΛΛ isomer does the right-handed helical one. It is noted that no helical structure has been found in the linear-type and cage-type S-bridged polynuclear complexes,[1-4] and furthermore the triple helical structure is extremely rare for the metal complexes,[8] although mono[9a,b] and double helical structures[9c-j] have been observed in several inorganic compounds.

Optical resolution of the complex molecule **1** was unsuccessful because of its sparing solubility in any solvents. The reaction of *fac(S)*-[Rh(aet)$_3$] (0.10 g) with $Hg(NO_3)_2 \cdot H_2O$ (0.20 g) in water gave a pale yellow complex **2** in 50 % yield, which is soluble in water.[10] The elemental and plasma emission spectral analytical data are consistent with the formulation $[Rh(aet)_3]_2[Hg(NO_3)_2]_3(H_2O)_5$ and the electronic absorption spectrum of **2** [10] is quite similar to the qualitative absorption spectrum of **1**. Moreover, in the ^{13}C NMR spectrum **2** gives only two signals due to two kinds of methylene carbon atoms of the aet ligands.[10] Taking these facts into consideration, it is suggested that **2** takes the twisted-ellipsoid-type S-bridged pentanuclear structure with a D_3 symmetry as found in **1**. This is supported by the fact that **2** was optically resolved with use of d-tartrate as the resolving agent.[10] Efforts to prepare single crystals of **2** are currently underway.

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5) Anal. Found: C, 8.69; H, 2.99; N, 4.98%. Calcd for $C_{12}H_{36}N_6S_6Cl_6Rh_2Hg_3 \cdot 8H_2O$: C, 8.89; H, 3.23; N, 5.18%.

6) Crystal data for $[\{Rh(C_2H_6NS)_3\}_2(HgCl_2)_3] \cdot 8H_2O$ at 293 K: tetragonal, $I4_1/a$, a = 15.083(1), c = 37.043(4) Å, V = 8427(1) Å^3, Z = 8, D_c = 2.56 g cm^{-3}, D_m = 2.59 g cm^{-3}, λ(Mo Kα) = 0.71069 Å, μ = 118.75 cm^{-1}, R = 0.0580, R_w = 0.0633 for 2927 reflections. The structure was solved by the same procedures as described in previous papers (Ref. 2). Selected bond lengths (Å) and angles (deg) (averaged): Rh-S, 2.321(4); Rh-N, 2.108(13); Hg-S, 2.443(4); Hg-Cl, 2.648(5); S-Rh-S, 93.3(1); N-Rh-N, 90.3(5); Cl-Hg-Cl, 88.8(4); S-Hg-Cl, 101.6(2); S-Hg-S, 147.6(1); Rh-S-Rh, 112.9(2).

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10) Anal. Found: C, 8.35; H, 2.53; N, 9.37; Rh, 12.42; Hg, 35.53%. Calcd for $C_{12}H_{36}N_{12}O_{18}S_6Rh_2Hg_3 \cdot 5H_2O$: C, 8.34; H, 2.69; N, 9.74; Rh, 11.92; Hg, 34.85%. Visible-UV spectrum, H_2O solvent [σ_{max}, 10^3 cm^{-1} (log (ε/ mol^{-1}dm^{3}cm^{-1}))]: 29.0 (3.20 sh), 38.9 (4.46 sh), 44.4 (4.86 sh), 49.50 (5.07). sh denotes a shoulder. CD spectrum, H_2O solvent [σ_{max}, 10^3 cm^{-1} ($\Delta\varepsilon$, mol^{-1}dm^{3}cm^{-1})]: 28.74 (-2.79), 32.90 (+3.94), 38.40 (-4.70), 43.63 (-10.02). ^{13}C NMR in D_2O (500 MHz, ppm from DSS): 39.01 ($-CH_2S$) and 52.90 ($-CH_2NH_2$).

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