Synthesis and Structure of Unprecedented $Cu^{I}_4Rh^{III}_4$ and $Cu^{I}_4Ir^{III}_4$ S-Bridged Polynuclear Complexes Containing μ_2- and μ_3-Thiolato and Coordinated Disulfide: Spontaneous Reduction of Copper(II) to Trigonal-Planar Copper(I)

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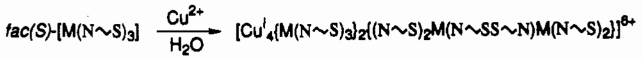
S-Bridged polynuclear metal complexes with 2-aminoethanethiolate (aet) or L-cysteinate (L-cys) have attracted much interest because of their diverse and specific stereochemical behavior.[1-4] For example, a number of linear-type S-bridged trinuclear complexes, $[M'\{M(\text{aet or L-cys-}N,S)_3\}_2]^{n+,n-}$ (M = Co(III) or Rh(III); M′ = Fe(III), Co(III), or Ni(II)), have been prepared by the reactions of *fac*(*S*)-$[M(\text{aet or L-cys-}N,S)_3]^{0,3-}$ with metal ions M′ which prefer to take an octahedral coordination geometry.[2,3] On the other hand, we have recently found that the reactions of *fac*(*S*)-$[M(aet)_3]$ with Zn^{2+} in water give a new class of cage-type polynuclear complexes having a *T* symmetry (*T*-cage), $[\{M(aet)_3\}_4Zn_{3,4}O]^{4+,6+}$, in which each Zn(II) has a tetrahedral geometry coordinated by three thiolato sulfur atoms from three different *fac*(*S*)-$[M(aet)_3]$ subunits and a central oxygen atom.[4] These facts point out that the S-bridged polynuclear structure composed of *fac*(*S*)-$[M(\text{aet or L-cys-}N,S)_3]^{0,3-}$ subunits is highly dependent on the coordination geometry of metal ions incorporated in the polynuclear complexes. In the present communication, we wish to report that the facile reactions of *fac*(*S*)-$[M(aet)_3]$ (M = Rh(III) or Ir(III)) with Cu^{2+} in water give unprecedented cage-type S-bridged octanuclear complexes having a C_2 symmetry (C_2-cage), $[Cu^{I}_4\{M(aet)_3\}_2\{M_2(aet)_4(cysta)\}]^{6+}$ (cysta = cystamine), one of which was characterized by X-ray diffraction (Scheme I).

To a yellow suspension of *fac*(*S*)-$[Rh(aet)_3]$ (0.1 g) in water was added $Cu(NO_3)_2\cdot 3H_2O$ (0.1 g), and the mixture was stirred at room temperature. The suspension became a clear reddish yellow solution within a few minutes, from which fine red crystals (**1**$(NO_3)_6\cdot 6.5H_2O$) were isolated in 45% yield.[5] Single crystals suitable for X-ray analysis (**1**$(NO_3)_2(PF_6)_4\cdot 4H_2O$) were prepared by adding NH_4PF_6 to the reddish yellow reaction solution (yield, 51%).[6] The same reaction of *fac*(*S*)-$[Ir(aet)_3]$ with $Cu(NO_3)_2\cdot 3H_2O$ in water gave reddish brown crystals (**2**$(NO_3)_6\cdot 4H_2O$) in 49% yield.[7]

Scheme I



$$fac(S)\text{-}[M(N\sim S)_3] \xrightarrow[H_2O]{Cu^{2+}} [Cu^{I}_4\{M(N\sim S)_3\}_2\{(N\sim S)_2M(N\sim SS\sim N)M(N\sim S)_2\}]^{6+}$$

X-ray structural analysis of the red complex (**1**$(NO_3)_2(PF_6)_4\cdot 4H_2O$) revealed the presence of a discrete hexavalent complex cation, two nitrate and four hexafluorophosphate anions, and water molecules.[8] As shown in Figure 1, the complex cation **1** consists of four approximately octahedral *fac*(*S*)-$[Rh(C_2H_6NS\text{-}N,S)_3]$ subunits and four copper atoms. This is compatible with the plasma emission spectral analysis, which gave the value of Rh:Zn = 4:4. The four Rh subunits are linked by four copper atoms to form the cage-type S-bridged octanuclear structure. The three sulfur atoms in the Rh1 and Rh2 subunits have a normal μ_2-thiolato structure, bridging one rhodium and one copper atom. On the other hand, three different types of sulfur atoms, μ_2- and μ_3-thiolato and disulfide, are present in the Rh3 and Rh4 subunits. That is, each of S33 and S44 bridges one rhodium and one copper atom, each of S32 and S42 bridges one rhodium and two copper atoms, and S31 and S41 bind to each other (S31–S41 = 2.142 (5) Å) to bridge two rhodium atoms. As a result, the Rh3 and Rh4 subunits coordinate to three copper atoms as do the Rh1 and Rh2 subunits. Here it should be noted that this S-bridged octanuclear structure containing μ_2- and μ_3-thiolato and coordinated disulfide is unprecedented; the coordinated sulfur atoms in all other known S-bridged polynuclear complexes with aet or L-cys ligands have uniformly adopted a μ_2-thiolato structure.[1-4] Each copper atom is situated in an approximately trigonal-planar environment coordinated by three thiolato sulfur

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(5) Anal. Found: C, 13.87; H, 4.12; N, 12.09; Cu, 11.60; Rh, 19.44. Calcd for $[Cu_4\{Rh(aet)_3\}_2\{Rh_2(aet)_4(cysta)\}](NO_3)_6\cdot 6.5H_2O = C_{24}H_{72}N_{18}O_{18}S_{12}Cu_4Rh_4\cdot 6.5H_2O$: C, 13.94; H, 4.14; N, 12.19; Cu, 12.29; Rh, 19.90. This complex was obtained as a microcrystalline product in 91% yield by the addition of a large amount of $NaNO_3$ to the reddish yellow reaction solution. Anal. Found: C, 13.93; H, 3.96; N, 12.28.

(6) Anal. Found: C, 12.21; H, 3.39; N, 8.23; Cu, 10.53; Rh, 16.75. Calcd for $[Cu_4\{Rh(aet)_3\}_2\{Rh_2(aet)_4(cysta)\}](NO_3)_2(PF_6)_4\cdot 4H_2O = C_{24}H_{72}N_{14}O_6F_{24}S_{12}P_4Cu_4Rh_4\cdot 4H_2O$: C, 12.24; H, 3.42; N, 8.33; Cu, 10.79; Rh, 17.48. ^{13}C NMR (500 MHz, D_2O, ppm from DSS): 35.93, 36.79, 44.63, 45.06, 46.96, 51.07, 51.24, 51.68, and 53.76.

(7) Anal. Found: C, 12.21; H, 3.45; N, 10.43; Cu, 10.59; Ir, 31.88. Calcd for $[Cu_4\{Ir(aet)_3\}_2\{Ir_2(aet)_4(cysta)\}](NO_3)_6\cdot 4H_2O = C_{24}H_{72}N_{18}O_{18}S_{12}Cu_4Ir_4\cdot 4H_2O$: C, 12.10; H, 3.39; N, 10.59; Cu, 10.68; Ir, 32.29. ^{13}C NMR (500 MHz, D_2O, ppm from DSS): 34.55, 35.06, 35.72, 43.39, 44.20, 47.14, 48.51, 52.88, 53.04, 53.53, and 54.09.

(8) Crystal data for $[Cu_4\{Rh(C_2H_6NS)_3\}_4](NO_3)_2(PF_6)_4\cdot 4H_2O$ at 293 K: $M_r = 2355.4$, 0.15 × 0.15 × 0.08 mm, triclinic, $P\bar{1}$, $a = 17.688$ (5) Å, $b = 17.919$ (5) Å, $c = 13.431$ (3) Å, $\alpha = 110.32$ (1)°, $\beta = 97.23$ (2)°, and $\gamma = 66.94$ (2)°, $V = 3672$ (2) Å^3, $Z = 2$, $D_{calcd} = 2.13$ g cm^{-3}, λ(Mo Kα) = 0.71073 Å, μ(Mo Kα) = 23.94 cm^{-1}, R (R_w) = 0.0642 (0.0701) for 8601 independent reflections with $F_o > 5\sigma(F_o)$ ($2\theta < 50°$). The structure was solved by direct methods (SIR-88) and difference Fourier techniques and refined by blocked matrix least squares using anisotropic thermal parameters for Rh, Cu, S, P, N, and C atoms and isotropic thermal parameters for O and F atoms. All calculations were performed with use of the programs of SHELX-76. The F atoms of the PF_6^- groups were disordered but were not modeled. Selected bond lengths (Å) and angles (deg) (averaged): Rh–S(μ_2), 2.315 (4); Rh–S(μ_3), 2.348 (4); Rh–S(sulfide), 2.334 (4); Cu–S(μ_2), 2.250 (4); Cu–S(μ_3), 2.285 (4); S–S, 2.142 (4); Rh–N, 2.126 (15); S–Rh1–S, 93.3 (1); S–Rh2–S, 92.9 (1); S–Rh3–S, 94.4 (1); S–Rh4–S, 95.3 (1); N–Rh1–N, 91.3 (5); N–Rh2–N, 91.3 (5); N–Rh3–N, 89.3 (5); N–Rh4–N, 88.9 (5); S–Cu1–S, 118.1 (2); S–Cu2–S, 118.5 (1); S–Cu3–S, 119.0 (2); S–Cu4–S, 119.1 (1).

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atoms from three different *fac*(*S*)-[Rh(C_2H_6NS-*N*,*S*)$_3$] subunits (average S–Cu–S = 118.7 (2)°). The Cu–S bond distances (average 2.268 (4) Å) are within the range (2.22–2.33 Å) observed for three-coordinated (thiolato)copper(I) complexes.[9] Taking these facts and the net charge of the complex cation into consideration, it is suggested that each of four copper atoms in [Cu$_4${Rh(aet)$_3$}$_2${Rh$_2$(aet)$_4$(cysta)}]$^{6+}$ possesses the formal charge +1. The Cu···Cu distances fall in the range 2.947–4.404 Å, indicating that there is no direct interaction between the four Cu(I) atoms.

Ten isomers are possible for **1**,[10] considering the chiral configuration (Δ or Λ) around each *fac*(*S*)-[Rh(C_2H_6NS-*N*,*S*)$_3$] subunit. However, crystal **1** consists of a pair of enantiomers, ΔΔ(Rh1,Rh2) ΛΛ(Rh3,Rh4) and ΛΛ(Rh1,Rh2) ΔΔ(Rh3,Rh4); the former isomer is illustrated in Figure 1. Molecular model constructions reveal that a significant nonbonding interaction among the chelate rings of adjacent *fac*(*S*)-[Rh(C_2H_6NS-*N*,*S*)$_3$] subunits and/or a significant strain on the coordinated sulfur atoms exist in the remaining eight octanuclear isomers. Furthermore, the ^{13}C NMR spectrum of **1** exhibits nine sharp signals due to 24 methylene carbon atoms in the complex.[6] Accordingly, the Δ and Λ isomers of *fac*(*S*)-[Rh(aet)$_3$] are equally incorporated in the present cage-type structure, forming the quasi-meso compound with a C_2 symmetry.[11] This is in contrast to the fact that either Δ- or Λ-*fac*(*S*)-[M(aet)$_3$] is discriminatingly incorporated in the *T*-cage-type [{M(aet)$_3$}$_4$M″$_4$O]$^{6+}$ structure, giving the ΔΔΔΔ or ΛΛΛΛ isomer.[4]

The electronic absorption spectrum of **1** in water, which is dominated by intense near-UV absorption shoulders at ca. 295 nm (log ε = 4.36) and ca. 235 nm (log ε = 4.80), changes little for several hours, indicating that the C_2-cage-type structure of **1** is fairly stable in solution. The absorption spectral behavior of **2** is quite similar to that of **1**, showing intense absorption shoulders at ca. 295 nm (log ε = 4.25) and ca. 235 nm (log ε = 4.69). In addition, **2** exhibits 11 methylene carbon signals in the ^{13}C NMR spectrum.[7] From these facts and elemental and plasma emission spectral analyses (Ir:Cu = 4:4),[7] **2** is confidently assigned as the C_2-cage-type complex having a C_2 symmetry, [Cu$^{I}_4${Ir(aet)$_3$}$_2${Ir$_2$(aet)$_4$(cysta)}]$^{6+}$.

In the present work, it was found that the reactions of *fac*(*S*)-[M(aet)$_3$] (M = Rh(III) or Ir(III)) with Cu^{2+} under moderate conditions result in the formation of unprecedented C_2-cage-type S-bridged octanuclear complexes [Cu$^{I}_4${M(aet)$_3$}$_2${M$_2$(aet)$_4$(cysta)}]$^{6+}$. This result obviously implies that four Cu(II) atoms are readily converted to four trigonal-planar Cu(I) atoms, accompanied by the formation of a sulfur–sulfur bond between the two *fac*(*S*)-[M(aet)$_3$] subunits. Several metal complexes with [Cu^{I}(thiolato-*S*)$_3$]$^{2-}$ units have been prepared from Cu(II) and thiols.[9a–f] In those cases, however, the reduction of Cu(II) to Cu(I) is ascribed to excess free thiols, which are oxidized to form free disulfides. No reducing agents such as free thiols exist in the present reactions. Thus, it is probable that the reduction of Cu(II) to Cu(I) occurs spontaneously owing mainly to the valence specificity of the trigonal-planar copper geometry, which is constrained in the present C_2-cage-type octanuclear structure.

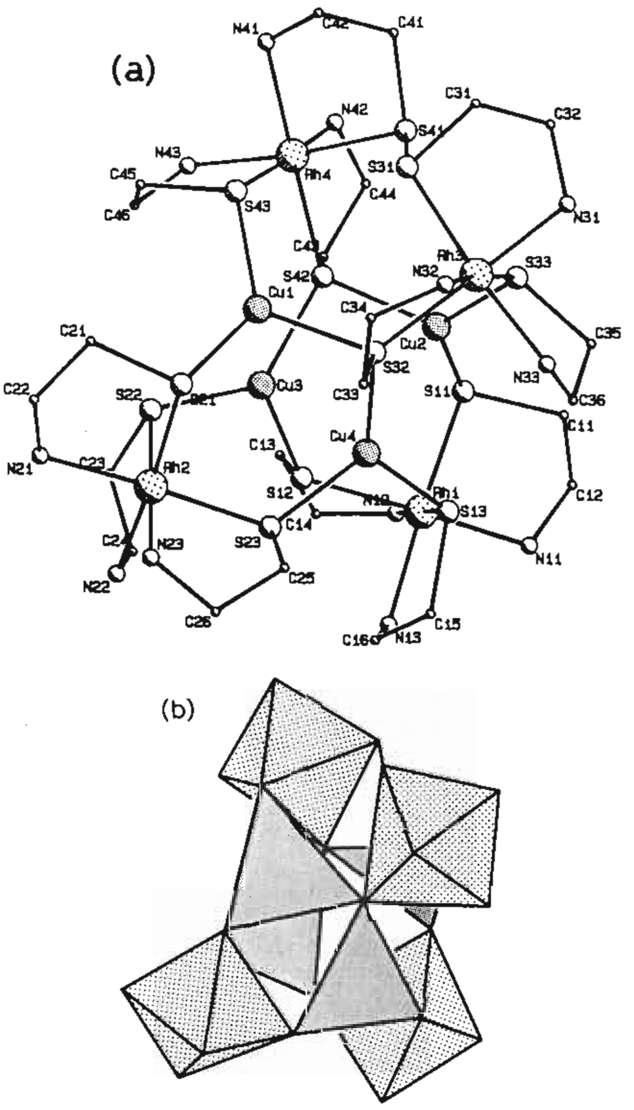

Figure 1. Perspective view of **1** with the atomic labeling scheme (a) and polyhedral representation of **1** (b).

Supplementary Material Available: Tables SI–SV, listing atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters for **1** (8 pages). Ordering information is given on any current masthead page.

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(10) The possible isomers are ΔΔ(Rh1,Rh2) ΔΔ(Rh3,Rh4), ΔΔ(Rh1,Rh2) ΔΛ(Rh3,Rh4), ΔΛ(Rh1,Rh2) ΔΔ(Rh3,Rh4), ΛΛ(Rh1,Rh2) ΔΔ(Rh3,Rh4), ΔΔ(Rh1,Rh2) ΛΛ(Rh3,Rh4), ΔΛ(Rh1,Rh2) ΔΛ(Rh3,Rh4), ΔΛ(Rh1,Rh2) ΛΔ(Rh3,Rh4), ΔΛ(Rh1,Rh2) ΛΛ(Rh3,Rh4), ΛΛ(Rh1,Rh2) ΛΔ(Rh3,Rh4), and ΛΛ(Rh1,Rh2) ΛΛ(Rh3,Rh4).

(11) For the ΔΔ(Rh1,Rh2) ΛΛ(Rh3,Rh4) isomer, the three asymmetric sulfur atoms in the Rh1 and Rh2 subunits all take the *R* configuration (*RRR*), while the μ_2- and μ_3-thiolato and disulfide sulfur atoms in the Rh3 and Rh4 subunits take the *S*, *R*, and *S* configurations, respectively. The three five-membered chelate rings in the Rh1, Rh2, Rh3, and Rh4 subunits take the gauche form with the (lel,lel,ob), (lel,lel,ob), (ob,ob,ob), and (ob,ob,ob) conformations, respectively.