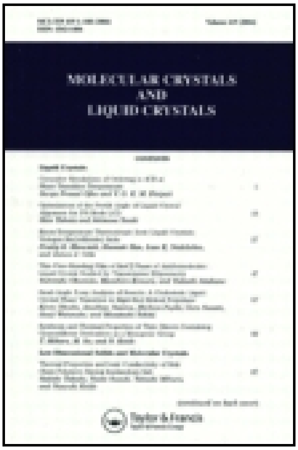

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Spontaneous Reduction of Gold(III) to Gold(I) by Forming Sulfur-Bridged Polynuclear Structure with Octahedral Tris(Thiolato) Complexes

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Spontaneous Reduction of Gold(III) to Gold(I) by Forming Sulfur-Bridged Polynuclear Structure with Octahedral Tris(Thiolato) Complexes

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The reaction of *fac*(*S*)-$[Rh^{III}(aet)_3]$ (aet = 2-aminoethanethiolate) with $[Au^{III}Cl_4]^-$ in water gave an S-bridged pentanuclear complex $[Au^I_3\{Rh^{III}(aet)_3\}_2]^{3+}$ (**1**), accompanied by the spontaneous reduction of Au^{III} to Au^I. The crystal structure of $\mathbf{1}(NO_3)_3\cdot4H_2O$ was determined by X-ray crystallography. In **1** two octahedral *fac*(*S*)-$[Rh(aet)_3]$ units are linked by three linear Au^I atoms to form a trigonal-bipyramid-type $Rh^{III}_2Au^I_3$ pentanuclear structure with an averaged Au^I-Au^I distance of 3.083(5) Å. The two $Rh^{III}_2Au^I_3$ cations contact with each other through one Au^I-Au^I interaction with a distance of 3.311(3) Å. The optically active ΔΔ-**1** was derived from ΔΔΔΔ-$[Zn_3(OH)\{Rh(aet)_3\}_4]^{5+}$ by reacting with $[AuCl_4]^-$ in water.

Keywords: rhodium(III); gold(I); S-bridged polynuclear complex

INTRODUCTION

It has been recognized that *fac*(*S*)-$[M(aet)_3]$ (M = Co^{III}, Rh^{III}, Ir^{III}; aet = 2-aminoethanethiolate) can function as a tridentate-S_3 complex-ligand toward a variety of metal ions to form S-bridged polynuclear complexes.[1-4] Recent our studies have shown that the S-bridged polynuclear structures composed of *fac*(*S*)-$[M(aet)_3]$ units are highly dependent on the coordination geometry of reacting metal ions. That is, the reactions of *fac*(*S*)-$[M(aet)_3]$ with octahedral Co^{III} commonly gave M_2Co^{III} trinuclear complexes $[Co\{M(aet)_3\}_2]^{3+}$,[1] while the reactions with Ag^I, which prefers to take a linear geometry, produced $M_2Ag^I_3$ pentanuclear complexes $[Ag_3\{M(aet)_3\}_2]^{3+}$.[3] Furthermore, it has been found that the reactions with Pd^{II}, which adopts a square-planar geometry, result in the chelate-transfer to produce $M_3Pd^{II}_2$ pentanuclear complexes $[Pd\{Pd(aet)\}\{M(aet)_2\}\{M(aet)_3\}_2]^{4+}$.[4] In these circumstances, it is desirable to investigate the reactions of *fac*(*S*)-$[M(aet)_3]$ with Au^{III}, which prefers to take a square-planar geometry. In this paper, we report that the reaction of *fac*(*S*)-$[Rh(aet)_3]$ with $[Au^{III}Cl_4]^-$ gives an S-bridged $Rh^{III}_2Au^I_3$ pentanuclear complex $[Au_3\{Rh(aet)_3\}_2]^{3+}$ (**1**), in which each Au^I ion has a linear geometry. The structural conversion of ΔΔΔΔ-$[Zn_3(OH)\{Rh(aet)_3\}_4]^{5+}$ to ΔΔ-**1** is also reported.

EXPERIMENTAL

Preparation

$[Au_3\{Rh(aet)_3\}_2](NO_3)_3\cdot 4H_2O$ (**1**$(NO_3)_3\cdot 4H_2O$)
To a yellow suspension of *fac*(*S*)-$[Rh(aet)_3]$ [1b] (0.15 g, 0.45 mmol) in 300 cm^3 of water was added $Na[AuCl_4]\cdot 2H_2O$ (0.16 g, 0.40 mmol). The mixture was stirred at 50 °C for 1 h, which gave a clear yellow solution. After addition of a saturated aqueous solution of $NaNO_3$ (8 cm^3), the reaction solution was allowed to stand at room temperature for 3 d. The resulting light-yellow powder was collected by filtration and washed with methanol. Yield: 0.20 g (99% based on Au). Anal. Found: C, 9.48; H, 2.96; N, 8.13%. Calcd for $[Au_3\{Rh(C_2H_6NS)_3\}_2](NO_3)_3\cdot 4H_2O$: C, 9.53; H, 2.93; N, 8.34%. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the reaction solution at room temperature, after addition of an appropriate amount of $NaNO_3$.

$(-)^{CD}_{375}$-ΔΔ-$[Au_3\{Rh(aet)_3\}_2](NO_3)_3\cdot 4H_2O$ ($(-)^{CD}_{375}$-ΔΔ-**1**$(NO_3)_3\cdot 4H_2O$)
To a solution of ΔΔΔΔ-$[Zn_3(OH)\{Rh(aet)_3\}_4](NO_3)_5\cdot 2H_2O$ [2b] (0.20 g, 0.11 mmol) in 280 cm^3 of water was added $Na[AuCl_4]\cdot 2H_2O$ (0.16 g, 0.40 mmol), and the mixture was stirred at 50 °C for 1 h. After addition of a saturated aqueous solution of $NaNO_3$ (8 cm^3), the reaction solution was allowed to stand at room temperature for 3 d. The resulting light-yellow needle crystals, which show a negative CD value at 375 nm, were collected by filtration. Yield: 0.11 g (54% based on Au). Anal. Found: C, 9.40; H, 2.84; N, 8.18%. The absorption spectrum of this complex was identical with that of **1**$(NO_3)_3\cdot 4H_2O$. Visible-UV spectrum in H_2O [σ_{max}, 10^3 cm^{-1} (log ε, $mol^{-1}dm^3cm^{-1}$)]: 27.39 (3.30), 35.3 (4.0 sh), 38.3 (4.4 sh), 44.5 (4.8 sh), 47.66 (4.97). The sh label denotes a shoulder. CD spectrum in H_2O [σ_{extr}, 10^3 cm^{-1} ($\Delta\varepsilon$, $mol^{-1}dm^3cm^{-1}$)]: 26.66 (−22.94), 29.62 (+9.07), 38.02 (−126.1), 45.24 (+155.4), 47.50 (+158.0).

Measurements

The absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer, and the CD spectra with a JASCO J-700 spectropolarimeter at room temperature. The ^{13}C NMR spectra were recorded with a JOEL JAM-A500 NMR spectrometer at the probe temperature in D_2O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. The molar conductivities of the complexes were measured with a Holiba DS-12 conductivity meter in water.

X-ray Structure Determination of 1

X-ray diffraction measurements were made on a Rigaku AFC7S diffractometer using a yellow prismatic crystal of **1** (0.33 × 0.13 × 0.10 mm). Crystal data of **1** are as follows: $C_{12}H_{44}Au_3N_9O_{13}Rh_2S_6$, tetragonal, space group $P4_2/nnm$, FW = 1511.64, a = 16.694(4) Å, c = 26.188(9) Å; V = 7297(4) Å^3, Z = 8, ρ_{calc} = 2.75 g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, μ(Mo-Kα) = 13.35 mm^{-1}, T = 298 K, 3238 independent reflections, 1070 observed reflections ($I > 2\sigma(I)$), R = 0.060, R_w = 0.062. The structure was solved by direct methods and expanded using Fourier techniques. The Au, Rh, and S atoms were refined anisotropically, and remaining non-H atoms were refined isotropically by full-matrix least-squares techniques using the teXsan crystallographic software package.[5]

RESULTS AND DISCUSSION

Treatment of an aqueous yellow suspension of *fac*(*S*)-$[Rh(aet)_3]$ with $Na[AuCl_4]$ in a molar ratio of 1:0.9 gave a clear solution, from which a light-yellow powder ($\mathbf{1}(NO_3)_3\cdot 4H_2O$) was isolated in a high yield by adding aqueous $NaNO_3$. The plasma emission analysis indicated that $\mathbf{1}(NO_3)_3\cdot 4H_2O$ contains Rh and Au in a ratio of 2:3, and its elemental analytical data are in agreement with the formula of $[Rh(aet)_3]_2$-$[AuNO_3]_3\cdot 4H_2O$. The electronic absorption spectrum of **1** is very similar to that of $[Ag_3\{Rh(aet)_3\}_2]^{3+}$ over the whole region.[3a] In the ^{13}C NMR spectrum **1** exhibits only two sharp signals at δ 38.53 and 50.55. This NMR spectral behavior corresponds well with that observed for $[Ag_3\{Rh(aet)_3\}_2]^{3+}$ (δ 35.66 for CH_2S and 52.54 for CH_2N),[3a] rather than that for $[Pd\{Pd(aet)\}\{Rh(aet)_2\}\{Rh(aet)_3\}_2]^{4+}$.[4] From these results, it is assigned that **1** has an S-bridged $Rh^{III}{}_2Au^I{}_3$ pentanuclear structure in $[Au_3\{Rh(aet)_3\}_2]^{3+}$. This assignment is supported by the molar conductivity of $\mathbf{1}(NO_3)_3\cdot 4H_2O$ in water (345 Ω^{-1} cm^2 mol^{-1}), which is consistent with that of the 1:3 electrolyte $[Ag_3\{Rh(aet)_3\}_3](BF_4)_3\cdot H_2O$ (359 Ω^{-1} cm^2 mol^{-1}).[3a]

The structure of $\mathbf{1}(NO_3)_3\cdot 4H_2O$ was established by a single-crystal

X-ray analysis. As shown in Figure 1, two octahedral *fac*(*S*)-[Rh(aet)$_3$] units are linked by three Au^{I} atoms to form an S-bridged Rh$^{III}_2$Au$^{I}_3$ pentanuclear structure, where five metals form a trigonal-bipyramid. The intramolecular Au-Au distances are in the range 3.044(5)–3.162(5) Å, which suggests that bonding interactions exist between three Au^{I} atoms in **1**. Each Au^{I} atom has an almost linear geometry, coordinated by two S atoms from the two *fac*(*S*)-[Rh(aet)$_3$] units (average Au-S = 2.28(3) Å, S-Au-S = 177(1)°). The overall structure of **1** is very similar to that of the corresponding Rh$^{III}_2$Ag$^{I}_3$ pentanuclear complex [Ag$_3${Rh(aet)$_3$}$_3$]$^{3+}$.[3a] However, it should be noted that the two Rh$^{III}_2$Au$^{I}_3$ complex-cations are connected through a weak Au-Au interaction (3.311(3) Å), which forms a dimer of the Rh$^{III}_2$Au$^{I}_3$ pentanuclear structure. This is in contrast to the fact that [Ag$_3${Rh(aet)$_3$}$_3$]$^{3+}$ crystallizes as a monomer in the BF$_4^-$ salt. Considering the chiral configurations (Δ, Λ) of the two *fac*(*S*)-[Rh(aet)$_3$] units, three isomers (ΔΔ, ΛΛ, ΔΛ) are possible for [Au$_3${Rh(aet)$_3$}$_2$]$^{3+}$. Crystal **1** is a solid solution, in which the ΔΔ and ΛΛ isomers coexist in a disordered manner; the latter isomer is illustrated in Figure 1. The helical structure due to three S-Au-S linkages is left-handed for the ΔΔ isomer and right-handed for the ΛΛ isomer. These stereochemical properties are the same as those found in [Ag$_3${Rh(aet)$_3$}$_3$]$^{3+}$ having a D_3 symmetry.[3a]

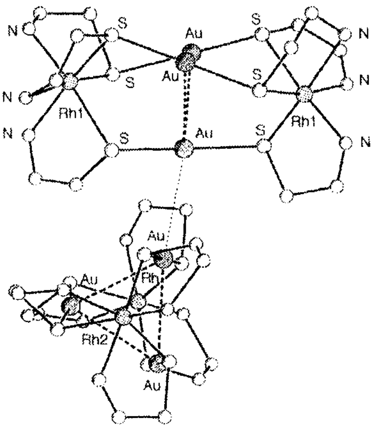

FIGURE 1 Perspective view of the complex cation **1**. Averaged bond distances (Å) and angles (°): Rh1-S = 2.28(2), Rh2-S = 2.27(3), Rh1-N = 2.17(8), Rh2-N = 2.06(10), S-Rh1-S = 94.1(10), S-Rh2-S = 93.2(10), N-Rh2-N = 91(2), N-Rh2-N = 88(3).

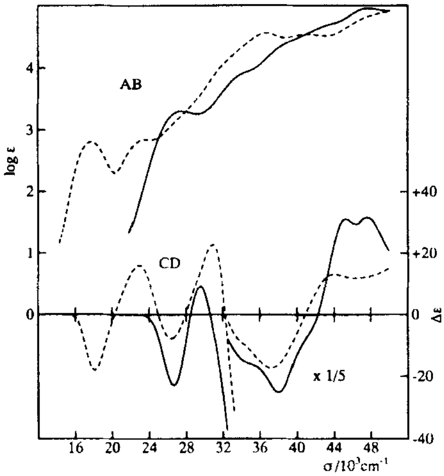

FIGURE 2 Electronic absorption and CD spectra of $(-)^{CD}_{375}$-ΔΔ-**1** (—) and ΔΔ-$[Ag_3\{Co(aet)_3\}_2]^{3+}$ (---) in H_2O.

Attempts to resolve **1** by the SP-Sephadex column chromatography were unsuccessful because of complete adsorption on the top of the column. While **1** was partially resolved by the fractional crystallization with use of *R*,*R*-tartrate, the pure ΔΔ isomer was derived from ΔΔΔΔ-$[Zn_3(HO)\{Rh(aet)_3\}_4]^{5+}$.[2b] That is, the 1:3.6 reaction of ΔΔΔΔ-$[Zn_3(HO)\{Rh(aet)_3\}_4](NO_3)_5$ with $Na[AuCl_4]$ in water, followed by addition of aqueous $NaNO_3$, gave light-yellow crystals of $(-)^{CD}_{375}$-**1**$(NO_3)_3\cdot 4H_2O$. As shown in Figure 2, the CD spectrum of $(-)^{CD}_{375}$-**1** exhibits a negative and a positive CD bands from lower energy in the first d-d absorption band region (ca. 24–31 × 10^3 cm^{-1}). This CD spectral behavior agrees well with that of the related pentanuclear complex ΔΔ-$[Ag_3\{Co(aet)_3\}]^{3+}$,[3b] considering that each absorption band for **1** shifts to higher energy than that for $[Ag_3\{Co(aet)_3\}]^{3+}$. Thus, it is assigned that the $(-)^{CD}_{375}$ isomer of **1** has the ΔΔ configuration.

In the present work, it was found that the reaction of *fac*(*S*)-$[Rh(aet)_3]$ with $[Au^{III}Cl_4]^-$ gives the S-bridged $Rh^{III}{}_2Au^{I}{}_3$ pentanuclear complex $[Au^{I}{}_3\{Rh(aet)_3\}_2]^{3+}$ (**1**). This result obviously implies that square-planar Au^{III} is spontaneously reduced to linear Au^{I} by reacting with *fac(S)*-$[Rh(aet)_3]$; no reducing agents such as free thiols were employed for this reaction. Furthermore, the spontaneous reduction of Au^{III} to Au^{I} also occurred through the reaction of $[Zn_3(HO)\{Rh(aet)_3\}_4]^{5+}$

with $[Au^{III}Cl_4]^-$, which produced **1** with retention of the chiral configuration of the *fac*(*S*)-$[Rh(aet)_3]$ units. Although **1** contains *fac(S)*-$[Rh(aet)_3]$ units and Au^I ions in a ratio of 2:3, the 2:3 reaction of *fac(S)*-$[Rh(aet)_3]$ with $[Au^{III}Cl_4]^-$ gave **1** in a low yield (28%); **1** was obtained in an excellent yield (99%) when the molar ratio *fac(S)*-$[M(aet)_3]$:$[Au^{III}Cl_4]^-$ is about 1:0.9. Quite recently, it has been shown that *fac*(*S*)-$[M(aet)_3]$ (M = Rh^{III}, Ir^{III}) could be oxidized to give dinuclear complexes $[M_2(aet)_4(cysta)]^{2+}$ (cysta = $NH_2CH_2CH_2SSCH_2CH_2NH_2$), in which two octahedral units are linked by a coordinated disulfide bond.[6] Accordingly, it is reasonable to assume that *fac*(*S*)-$[Rh(aet)_3]$ acts not only as a building block of the S-bridged pentanuclear structure, but also as a reducing agent for Au^{III}. The corresponding reaction of *fac*(*S*)-$[Co(aet)_3]$ with $[Au^{III}Cl_4]^-$ was found to produce an S-bridged $Co^{III}_2Au^I_3$ pentanuclear complex $[Au^I_3\{Co(aet)_3\}_2]^{3+}$, also accompanied by the reduction of Au^{III} to Au^I.

Acknowledgments

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