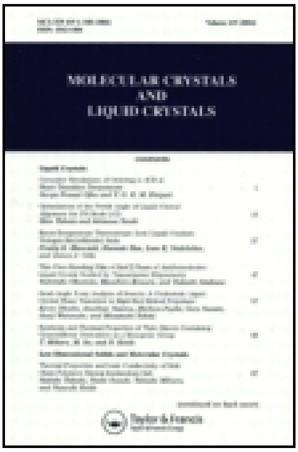

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Sulfur-Bridged Co III Pt II Co III Trinuclear Complex Acting as an S-Donating Complex-Ligand

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Sulfur-Bridged $Co^{III}Pt^{II}Co^{III}$ Trinuclear Complex Acting as an S-Donating Complex-Ligand

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The reaction of *fac(S)*-$[Co(aet)_3]$ (aet = $H_2NCH_2CH_2S^-$) with $[PtCl_2\{Co(aet)_2(en)\}]^+$ gave an S-bridged $Co^{III}Pt^{II}Co^{III}$ trinuclear complex, $[Pt\{Co(aet)_3\}\{Co(aet)_2(en)\}]^{3+}$ ($[\mathbf{1}]^{3+}$). The crystal structure of $[\mathbf{1}]Cl_3$ was determined by X-ray crystallography. In $[\mathbf{1}]^{3+}$, the central Pt^{II} atom is coordinated by four thiolato S atoms from octahedral C_2-*cis(S)*-$[Co(aet)_2(en)]^+$ and *mer(S)*-$[Co(aet)_3]$ units in a square-planar geometry, giving a linear-type S-bridged trinuclear structure with a non-bridging thiolato group. Treatment of $[\mathbf{1}]^{3+}$ with linear Au^I produced an S-bridged $Co^{III}_4Pt^{II}_2Au^I$ heptanuclear complex, $[Au\{Pt[Co(aet)_3][Co(aet)_2(en)]\}_2]^{7+}$ ($[\mathbf{2}]^{7+}$), which indicated that $[\mathbf{1}]^{3+}$ acts as a new class of S-donating trinuclear complex-ligand.

Keywords: polynuclear complexes; cobalt; platinum; gold; S ligands

INTRODUCTION

Recently, we have found that the reactions of *fac(S)*-$[Co(aet)_3]$ (aet = $NH_2CH_2CH_2S^-$) with $[M^{II}Cl_4]^{2-}$ (M = Pd, Pt) give S-bridged $Co^{III}M^{II}Co^{III}$ trinuclear complexes, $[M\{Co(aet)_3\}_2]^{2+}$, in which the central M^{II} ion is coordinated by four thiolato S atoms from two terminal *mer(S)*-[Co(aet)$_3$] units[1,2]. Furthermore, the two non-bridging thiolato S atoms existed in this trinuclear complex were found to bind with Au^{I} or Ag^{I} to construct S-bridged Co$^{III}_4$M$^{II}_2$Au$^{I}_2$ and Co$^{III}_4$M$^{II}_2$Ag$^{I}_2$ octanuclear metallacycles, [(Au or Ag)$_2${M[Co(aet)$_3$]$_2$}$_2$]$^{6+}$. This result indicated that [M{Co(aet)$_3$}$_2$]$^{2+}$ containing two non-bridging thiolato groups can act as a bidentate-*S,S* complex-ligand. Here we report on the preparation and characterization of an S-bridged Co^{III}Pt^{II}Co^{III} trinuclear complex containing one non-bridging thiolato group, [Pt{Co(aet)$_3$}-{Co(aet)$_2$(en)}]$^{3+}$, which could function as a monodentate-*S* complex-ligand. The coordinating ability of the non-bridging thiolato group toward Au^{I} ion, which led to the formation of an S-bridged Co$^{III}_4$Pt$^{II}_2$Au^{I} heptanuclear complex [Au{Pt[Co(aet)$_3$][Co(aet)$_2$(en)]}$_2$]$^{7+}$, is also reported.

EXPERIMENTAL

Preparation

[Pt{Co(aet)$_3$}{Co(aet)$_2$(en)}]$^{3+}$ ([**1**]$^{3+}$)
To a dark-blue suspension of *fac(S)*-[Co(aet)$_3$] [3] (0.10 g, 0.35 mmol) in 20 cm^3 of water was added a solution containing [PtCl$_2${Co(aet)$_2$(en)}]Cl·H$_2$O [4] (0.20 g. 0.34 mmol) in 80 cm^3 of water. The mixture was stirred at room temperature for 1 h, by which time the suspension turned to a dark brown solution. After a small amount of unreacted *fac(S)*-[Co(aet)$_3$] was filtered off, the filtrate was concentrated to a small volume with a rotary evaporator. To the concentrate was added 5 cm^3 of a saturated NaNO$_3$ aqueous solution, followed by storage at 4 °C for 1 day. The resulting red-brown crystals were collected by filtration. Yield: 0.22 g (67%). Anal. Found: C, 14.54; H, 4.36; N, 14.05%. Calcd for [**1**](NO$_3$)$_3$·3H$_2$O: C, 14.50; H, 4.46; N, 14.10%. Single crystals of **1**Cl$_3$·3H$_2$O suitable for X-ray analysis were obtained by slow evaporation of the reaction solution at room temperature, after addition of a saturated NaCl aqueous solution. [Pd{Co(aet)$_3$}{Co(aet)$_2$(en)}](NO$_3$)$_3$·1.5H$_2$O was also obtained by a similar reaction, using [PdCl$_2${Co(aet)$_2$(en)}]Cl·2H$_2$O [5] instead of [PtCl$_2${Co(aet)$_2$(en)}]Cl·H$_2$O. Anal. Found: C, 16.20; H, 4.45; N, 15.79%. Calcd: C, 16.41; H, 4.70; N, 15.95%.

$[Au\{Pt[Co(aet)_3][Co(aet)_2(en)]\}_2]^{7+}$ ($[\mathbf{2}]^{7+}$)

To a solution containing $Na[AuCl_4]$ (0.040 g, 0.10 mmol) in 1 cm^3 of water was added 0.1 cm^3 of 2,2'-thiodiethanol. The resulting colorless solution was added to a solution containing $[\mathbf{1}](NO_3)_3 \cdot 3H_2O$ (0.20 g, 0.20 mmol) in 20 cm^3 of water. The mixture was stirred at room temperature for 30 min, a saturated $NaNO_3$ aqueous solution was added to it, and was allowed to stand at room temperature for several days. The resulting brown powder was collected by filtration. Yield: 0.15 g (66%). Anal. Found: C, 12.54; H, 3.73; N, 12.90%. Calcd for $[\mathbf{2}](NO_3)_7 \cdot 6H_2O$: C, 12.83; H, 3.95; N, 13.09%.

Measurements

The absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer, and the CD spectra with a JASCO J-500C spectropolarimeter at room temperature. The ^{13}C NMR spectra were recorded with a JEOL GSX-500 FT NMR spectrometer at the probe temperature in D_2O. DSS was used as the internal reference. The concentrations of Co, Pt, and Au in the complexes were determined with a SHIMAZU ICPS-1000 III ICP spectrometer.

X-ray Structure Determination of $[\mathbf{1}]Cl_3 \cdot 3H_2O$

X-ray diffraction measurements were made on a Rigaku AFC7S diffractometer using a red-brown crystal of $[\mathbf{1}]Cl_3 \cdot 3H_2O$ (0.48 x 0.23 x 0.12 mm). Crystal data of $[\mathbf{1}]Cl_3 \cdot 3H_2O$ are as follows: $C_{12}H_{44}Cl_3Co_2N_7O_3PtS_5$, orthorhombic, space group *Pbcn* (No. 60), FW = 914.14, a = 19.709(4) Å, b = 13.138(4) Å, c = 27.555(4) Å, V = 7134(4) $Å^3$, Z = 8, ρ_{calc} = 1.70 g cm^{-1}, λ(Mo-Kα) = 0.71069 Å, μ(Mo-Kα) = 53.6 cm^{-1}, T = 293 K, 8926 independent reflections, 3937 observed reflections ($I > 3\sigma(I)$), R = 0.094, R_w = 0.114. The structure was solved by Patterson method and expanded using Fourier techniques. The Cl, Co, Pt, and S atoms were refined anisotropically, and the remaining non-H atoms were refined isotropically by full-matrix least-squares methods. One of en N atoms and a non-bridging aet S atom exhibited positional disorder, which were refined as S atoms with a site occupancy factor of 0.72. All calculations were performed using the teXsan crystallographic software package[6].

RESULTS AND DISCUSSION

Treatment of *fac(S)*-[Co(aet)$_3$] with [PtCl$_2${Co(aet)$_2$(en)}]$^+$ in a 1:1 ratio in water gave a red-brown solution, from which red-brown crystals ([**1**](NO$_3$)$_3$·3H$_2$O) were isolated by adding aqueous NaNO$_3$. The plasma emission analysis indicated that this product contains Co and Pt in a 2:1 ratio and its elemental analytical data are in good agreement with the proposed formula. The molecular structure of [**1**]$^{3+}$ was established by a single-crystal X-ray analysis for the chloride salt. As shown in Figure 1, the central Pt^{II} atom is coordinated by four thiolato S atoms from [Co(aet)$_2$(en)]$^+$ and [Co(aet)$_3$] octahedral units in a square-planer geometry, forming a linear-type S-bridged Co^{III}Pt^{II}Co^{III} trinuclear structure in [Pt{Co(aet)$_3$}{Co(aet)$_2$(en)}]$^{3+}$. In [**1**]$^{3+}$, the [Co(aet)$_3$] unit with a non-bridging thiolato group adopts the *mer(S)* configuration, which is distinct from the *fac(S)* configuration of the parental *fac(S)*-[Co(aet)$_3$], while the [Co(aet)$_2$(en)]$^+$ unit retains the *C*$_2$-*cis(S)* geometry in the course of the reaction. Crystal of [**1**]Cl$_3$ consists of the ΔΔ and ΛΛ isomers which combine to form a racemic compound. This is consistent with the fact that [**1**]$^{3+}$ was optically resolved into the $(+)^{CD}_{530}$ and $(-)^{CD}_{530}$ isomers by the SP-Sephadex C-25 column chromatography (eluent; 0.15 M aqueous Na$_2$[Sb$_2$(*R,R*-tartrato)$_2$]), which show CD spectra enantiomeric to each other. The $(+)^{CD}_{530}$ isomer was assigned to have the ΛΛ configuration by comparing its CD spectrum with that of ΛΛ-[Pd{Co(aet)$_2$(en)}$_2$]$^{4+}$ [5].

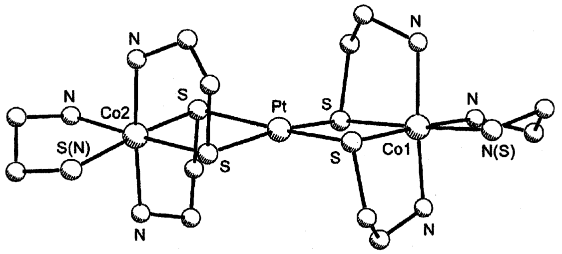

FIGURE 1 A perspective view of the complex cation [**1**]$^{3+}$. Averaged bond distances (Å) and angles (deg): Pt-S = 2.314(8), Co1-S = 2.32(1), Co2-S = 2.24(1), Co1-N = 2.03(3), Co2-N = 1.98(3), S-Pt-S = 90.2(3), S-Co1-S = 85.3(3), S-Co2-S = 88.8(3). One of en nitrogen atoms [N(S)] and a non-bridging aet sulfur atom [S(N)] exhibited positional disorder.

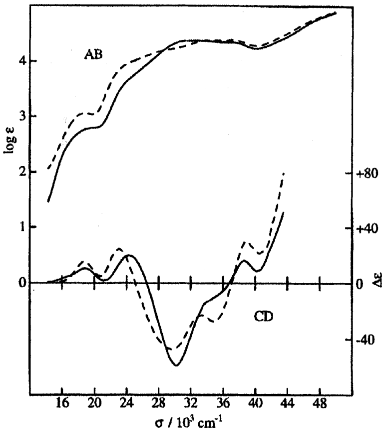

FIGURE 2 Electronic absorption and CD spectra of $[\mathbf{1}]^{3+}$ (—) and $[\mathbf{2}]^{7+} \times 1/2$ (---) in H_2O.

The absorption and CD spectra of ΛΛ-$[\mathbf{1}]^{3+}$ in water (Figure 2) are very similar to those of a 1:1 mixture of ΛΛ-$[Pt\{Co(aet)_3\}_2]^{2+}$ and ΛΛ-$[Pt\{Co(aet)_2(en)\}_2]^{4+}$ [2,4], in parallel with the presence of the *mer(S)*-$[Co(aet)_3]$ and C_2-*cis(S)*-$[Co(aet)_2(en)]^+$ units in $[\mathbf{1}]^{3+}$. Furthermore, the ^{13}C NMR spectral behavior of $[\mathbf{1}]^{3+}$ in D_2O is very similar to that of a 1:1 mixture of $[Pt\{Co(aet)_3\}_2]^{2+}$ and $[Pt\{Co(aet)_2(en)\}_2]^{4+}$ [2,4], giving eight sharp signals, besides one broad signal centered at δ 54.74; the signals at δ 31.37, 35.04, 36.17, 51.56, 54.73, and 56.20 are assignable as arising from the *mer(S)*-$[Co(aet)_3]$ unit, while the signals at δ 35.89, 36.17, 46.42, and 54.73 from the C_2-*cis(S)*-$[Co(aet)_2(en)]^+$ unit. It should be noted that the CH_2S signal at δ 37.39 for $[Pt\{Co(aet)_2(en)\}_2]^{4+}$ splits into two (δ 35.89, 36.17) for $[\mathbf{1}]^{3+}$, because of the lower symmetrical structure in $[\mathbf{1}]^{3+}$. This fact implies that the S-bridged $Co^{III}Pt^{II}Co^{III}$ structure observed in crystal is retained in solution.

When $[\mathbf{1}]^{3+}$ was treated with Au^I in a 2:1 ratio in water, a brown powder ($[\mathbf{2}](NO_3)_7$) was obtained by adding aqueous $NaNO_3$. The plasma emission analysis indicated that this product contains Co, Pt, and Au in a 4:2:1 ratio and its elemental analytical data are in good agreement with the formula for the 2:1 adduct. As shown in Figure 2, the absorption and CD spectral features of $(ΛΛ)_2$-$[\mathbf{2}]^{7+}$, which was prepared from $\Lambda\Lambda$-[**1**]$^{3+}$ and Au$^{\mathrm{I}}$, resemble those of two moles of $\Lambda\Lambda$-[**1**]$^{3+}$. This suggests that [**2**]$^{7+}$ is composed of the two $[\mathrm{Pt\{Co(aet)_3\}\{Co(aet)_2(en)\}}]^{3+}$ units, the structure of which is the same as that of [**1**]$^{3+}$. Consistent with this, the ^{13}C NMR spectrum of [**2**]$^{7+}$ in D_2O gives eight signals (δ 35.26, 36.05, 36.18, 36.34, 37.92, 46.41, 50.09, 56.04), besides one broad signal (δ 54.85), like the ^{13}C NMR spectrum of [**1**]$^{3+}$. However, the CH_2S signal at δ 31.37 for [**1**]$^{3+}$, which is due to the non-bridging thiolato group, shifts to much lower magnetic field (δ 37.92) for [**2**]$^{7+}$, indicating the formation of Au-S bond. A similar NMR shift has been observed when non-bridging thiolato groups in $[\mathrm{Pd\{Co(aet)_3\}_2}]^{2+}$ were bound to Au$^{\mathrm{I}}$ [1]. The formation of Au-S bond in [**2**]$^{7+}$ is also supported by the intense absorption band at *ca.* 34 × 10^3 cm^{-1}, which locates at higher energy than the corresponding band for [**1**]$^{3+}$ [1]. Accordingly, it is confidently assigned that [**2**]$^{7+}$ is an S-bridged $\mathrm{Co^{III}_4Pt^{II}_2Au^{I}}$ heptanuclear complex, $[\mathrm{Au\{Pt[Co(aet)_3][Co(aet)_2(en)]\}_2}]^{7+}$, in which two $[\mathrm{Pt\{Co(aet)_3\}}$- $\mathrm{\{Co(aet)_2(en)\}}]^{3+}$ trinuclear units are linked by a linear Au$^{\mathrm{I}}$ atom through two sulfur bridges.

The analogous $\mathrm{Co^{III}Pd^{II}Co^{III}}$ trinuclear complex, $[\mathrm{Pd\{Co(aet)_3\}}$-$\mathrm{\{Co(aet)_2(en)\}}]^{3+}$, was also prepared from $[\mathrm{PdCl_2\{Co(aet)_2(en)\}}]^{+}$ and *fac(S)*-$[\mathrm{Co(aet)_3}]$, and this complex was found to react with Au$^{\mathrm{I}}$ to afford $[\mathrm{Au\{Pd[Co(aet)_3][Co(aet)_2(en)]\}_2}]^{7+}$. Thus, it is obvious that $[\mathrm{M\{Co(aet)_3\}\{Co(aet)_2(en)\}}]^{3+}$ ($\mathrm{M^{II}} = \mathrm{Pt^{II}}, \mathrm{Pd^{II}}$) having one non-bridging thiolato group can function as a monodentate-*S* trinuclear complex-ligand.

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