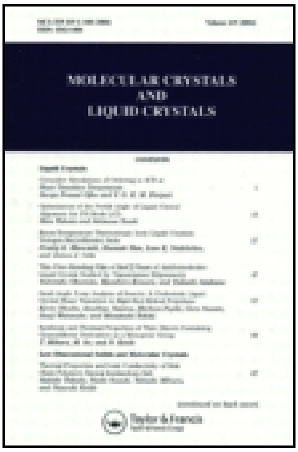

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Linkage of [Cr(aet) 3] or [Cr(D -pen- N , O , S) 2 - Octahedral Units by Forming S-Bridged Structures with AG I or Au I Ions (aet=2-aminoethanethiolate, D -pen= D -penicillaminate)

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Linkage of $[Cr(aet)_3]$ or $[Cr(\text{D-pen-}N,O,S)_2]^-$ Octahedral Units by Forming S-Bridged Structures with Ag^I or Au^I Ions (aet = 2-aminoethanethiolate, D-pen = D-penicillaminate)

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The reaction of $[Cr(aet)_3]$ (aet = 2-aminoethanethiolate) with Ag^I in water gave an S-bridged $Cr^{III}{}_2Ag^I{}_3$ pentanuclear complex $[Ag_3\{Cr(aet)_3\}_2]^{3+}$ ($[\mathbf{1}]^{3+}$). The crystal structure of $[\mathbf{1}](NO_3)_3{\cdot}2H_2O$ was determined by X-ray analysis, which established that two *fac*(*S*)-$[Cr(aet)_3]$ units are linked by three Ag^I ions through S atoms (average Cr-S = 2.387(5), Ag-S = 2.403(5) Å). The three Ag^I ions in $[\mathbf{1}]^{3+}$ were replaced by Au^I ions to form the corresponding $Cr^{III}{}_2Au^I{}_3$ pentanuclear complex $[Au_3\{Cr(aet)_3\}_2]^{3+}$ ($[\mathbf{2}]^{3+}$). Treatment of $[Cr(\text{D-pen-}N,O,S)_2]^-$ (D-pen = D-penicillaminate) with Ag^I in water produced an S-bridged $Cr^{III}{}_3Ag^I{}_3$ hexanuclear complex $[Ag_3\{Cr(\text{D-pen-}N,O,S)_2\}_3]$ ($[\mathbf{3}]$), which has a cyclic structure composed of three *trans*(*O*)-$[Cr(\text{D-pen-}N,O,S)_2]^-$ units. Variable-temperature magnetic susceptibility data indicated the weak antiferromagnetic interaction for $[\mathbf{1}]^{3+}$ ($J = -0.84\ cm^{-1}$) while the very weak ferromagnetic interaction for $[\mathbf{3}]$ ($J = 0.05\ cm^{-1}$).

Keywords: chromium(III); silver(I); gold(I); S-bridge

INTRODUCTION

It has been recognized that coordinated thiolato S atoms in *fac*(*S*)-$[Co(aet)_3]$ tend to make bridges with a variety metal ions to form

S-bridged polynuclear structures, retaining the *fac*(*S*) coordination geometry[1]. For example, the reaction of *fac*(*S*)-[Co(aet)$_3$] with Ag^I has been found to give an S-bridged Co$^{III}_2$Ag$^I_3$ pentanuclear complex, [Ag$^I_3${Co(aet)$_3$}$_2$]$^{3+}$, in which two *fac*(*S*)-[Co(aet)$_3$] units are linked by three Ag^I ions[1c]. On the other hand, recent our studies have shown that the reactions of *trans*(*N*)-[Co(D-pen-*N,O,S*)$_2$]$^-$ with Ag^I or Au^I are accompanied by the geometrical isomerization of [Co(D-pen-*N,O,S*)$_2$]$^-$ to afford S-bridged Co$^{III}_3$M$^I_3$ hexanuclear complexes, [M$^I_3${Co(D-pen-*N,O,S*)$_2$}$_3$] (M = Ag^I, Au^I), in which three *trans*(*O*)-[Co(D-pen-*N,O,S*)$_2$]$^-$ units are linked by three M^I ions in a cyclic form[2]. In order to better understand the stereochemical properties characteristic of S-bridged polynuclear complexes based on tris(thiolato)- or bis(thiolato)-type octahedral units, it is necessary to investigate the reactions with Ag^I or Au^I by using [M(aet)$_3$] and [M(D-pen-*N,O,S*)$_2$]$^-$ as the starting complexes, other than M = Co^{III}. In this paper, we report that [Cr(aet)$_3$] and [Cr(D-pen-*N,O,S*)$_2$]$^-$ also react with Ag^I or Au^I to form S-bridged polynuclear complexes, [Ag$_3${Cr(aet)$_3$}$_2$]$^{3+}$ ([**1**]$^{3+}$), [Au$_3${Co(aet)$_3$}$_2$]$^{3+}$ ([**2**]$^{3+}$), and [Ag$_3${Cr(D-pen-*N,O,S*)$_2$}$_3$] ([**3**]), the structures of which correspond well with those of the analogous cobalt(III) complexes. The difference in magnetic property between [**1**]$^{3+}$ and [**3**] is also reported.

EXPERIMENTAL

Preparation

K[Cr(D-pen-*N,O,S*)$_2$]

This complex was prepared by a modified method employed for K[Cr(L-cysteinato-*N,O,S*)$_2$] [3], using D-penicillamine instead of L-cysteine. Anal. Calcd for K[Cr(D-pen)$_2$]·2H$_2$O: C, 28.49; H, 5.26; N, 6.65%. Found: C, 28.34; H, 5.11; N, 6.57%.

[Ag$_3${Cr(aet)$_3$}$_2$]X$_3$ ([**1**]X$_3$; X = NO$_3$, BF$_4$)

To a suspension containing 0.20 g (0.71 mmol) of [Cr(aet)$_3$] [4] in 20 cm^3 of water was added 0.18 g (1.1 mmol) of AgNO$_3$ in 10 cm^3 of water. The mixture was stirred at room temperature for 1 h, during which time the solution color turned to purple. After filtration, to the filtrate was added 0.27 g of NaNO$_3$ in 5 cm^3 of water, followed by cooling in a refrigerator overnight. The resulting purple powder was collected by filtration. Yield: 0.33 g (82%). Anal. Calcd for [Ag$_3${Cr(aet)$_3$}$_2$](NO$_3$)$_3$·3.5H$_2$O: C, 12.72; H, 3.82; N, 11.12; Cr, 9.17; Ag, 28.55%. Found: C, 12.73; H, 3.83; N, 11.24; Cr, 8.58; Ag, 28.95%.

Visible-UV spectrum in H_2O [σ_{max}, 10^3 cm^{-1} (log ε, $mol^{-1}dm^3cm^{-1}$)]: 18.16 (2.62), 23.46 (2.59), 31.51 (3.68 sh), 40.78 (4.54 sh).

The BF_4^- salt of $[\mathbf{1}]^{3+}$ was prepared in a manner analogous to that for the NO_3^- salt with the use of $AgBF_4$ and $NaBF_4$. Yield: 81%. Anal. Calcd for $[Ag_3\{Cr(aet)_3\}_2](BF_4)_3{\cdot}2.5H_2O$: C, 12.11; H, 3.47; N, 7.06; Cr, 8.74; Ag, 27.20%. Found: C, 12.31; H, 3.50; N, 7.10; Cr, 8.46; Ag, 27.50%.

$[Au_3\{Cr(aet)_3\}_2]Cl(NO_3)_2$ ($[\mathbf{2}]Cl(NO_3)_2$)

To a solution containing 0.11 g (0.28 mmol) of $Na[AuCl_4]{\cdot}2H_2O$ in 15 cm^3 of water was added several drops of 2,2'-thiodiethanol. The resulting colorless solution was added to a solution containing 0.10 g (0.09 mmol) of $[\mathbf{1}](NO_3)_3{\cdot}3.5H_2O$ in 50 cm^3 of water. The mixture was stirred at room temperature for 2 h. After the filtration through Celite, to the red-pink filtrate was added a 1 mol dm^{-3} aqueous solution of $NaNO_3$ (0.5 cm^3), followed by standing in a draft chamber for 2 days. The resulting red-pink powder was collected by filtration. Yield: 0.06 g (49%). Anal. Calcd for $[Au_3\{Cr(aet)_3\}_2]Cl(NO_3)_2{\cdot}4H_2O$: C, 10.42; H, 3.21; N, 8.10; Cr, 7.52; Au, 42.72%. Found: C, 10.50; H, 3.21; N, 8.13; Cr, 6.84; Au 42.72%. Visible-UV spectrum in H_2O [σ_{max}, 10^3 cm^{-1} (log ε, $mol^{-1}dm^3cm^{-1}$)]: 18.58 (2.70), 23.96 (2.64), 30.12 (3.40 sh), 34.36 (4.01 sh), 39.65 (4.44 sh).

$[Ag_3\{Cr(\text{D-pen-}N,O,S)_2\}_3]$ ($[\mathbf{3}]$)

To a solution containing 0.05 g (0.12 mmol) of $K[Cr(\text{D-pen-}N,O,S)_2]{\cdot}2H_2O$ in 50 cm^3 of water was added 0.025 g (0.12 mmol) of $AgClO_4$ in 15 cm^3 of water. The mixture was stood at room temperature for 1 day and the resulting pale brown powder was collected by filtration, followed by washing with water. Yield; 0.04 g (66%). Anal. Calcd for $[Ag_3\{Cr(\text{D-pen})_2\}_3]{\cdot}10H_2O$: C, 23.35; H, 4.83; N, 5.45%. Found: C, 23.53; H, 4.86; N, 5.43%.

Measurements

The electronic absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer, and the CD spectra with a JASCO J-700 spectropolarimeter. The concentrations of Cr, Ag, and Au in the complexes were determined with a SHIMADZU ICPS-1000III ICP spectrometer. The molar conductivities of the complexes were measured with a Horiba DS-12 conductivity meter in water. The IR spectra were measured with a JASCO FT/IR-5000 infrared spectrophotometer. Magnetic susceptibility data in the 2—300 K temperature range were collected using a Quantum Design MPMS-5S SQUID magnetometer.

X-ray Structure Determination

X-ray diffraction measurements were made on a Rigaku AFC7S diffractometer using a purple prismatic crystal of [**1**]$(NO_3)_3 \cdot 2H_2O$ (0.12 × 0.08 × 0.27 mm), which was obtained by recrystallizing the purple powder of [**1**]$(NO_3)_3 \cdot 3.5H_2O$. Crystal data of [**1**]$(NO_3)_3 \cdot 2H_2O$ are as follows: $C_{12}H_{40}Ag_3Cr_2N_9O_{11}S_6$, monoclinic, space group $P2_1/n$, FW = 1106.49, a = 11.915(4) Å, b = 11.638(4) Å, c = 24.912(3) Å, β = 95.55(1)°, V = 3438(1) Å^3, Z = 4, ρ_{calc} = 2.137 g cm^{-3}, λ(Mo-Kα) = 0.71069 Å, μ(Mo-Kα) = 2.709 mm^{-1}, T = 293 K, 6060 independent reflections, 3117 observed reflections ($I > 2\sigma(I)$), R = 0.064, R_w = 0.069. The structure was solved by direct methods and expanded using Fourier techniques. The non-H atoms of the complex cation and one nitrate anion were refined anisotropically, and the remaining non-H atoms were refined isotropically by full-matrix least-squares techniques using the teXsan crystallographic software package[5]. Two C atoms in aet ligands were disordered and refined with an occupancy factor of 0.5.

RESULTS AND DISCUSSION

The reaction of [Cr(aet)$_3$] with 1.5 molar equiv of $AgNO_3$ in water gave a purple solution, from which purple crystals ([**1**]$(NO_3)_3$) were isolated in a high yield. The plasma emission analysis indicated that [**1**]$(NO_3)_3$ contains Cr and Ag in a 2:3 ratio, and its elemental analytical data are in agreement with the formula of $[Cr(aet)_3]_2[AgNO_3]_3 \cdot 3.5H_2O$. As shown in Figure 1, the absorption spectral behavior of [**1**]$^{3+}$ is similar to that of $[Ag_3\{Co(aet)_3\}_2]^{3+}$ over the whole region[1c]. Furthermore, the molar conductivity of [**1**]$(NO_3)_3$ in water gave the value expected for the 1:3 electrolyte (352.1 Ω^{-1}cm^{2}mol^{-1}). These results indicate that [**1**]$^{3+}$ is the S-bridged $Cr^{III}_2Ag^I_3$ pentanuclear complex $[Ag_3\{Cr(aet)_3\}_2]^{3+}$.

The crystal structure of [**1**]$(NO_3)_3$ was determined by a single-crystal X-ray analysis. As shown in Figure 2, in [**1**]$^{3+}$ two octahedral *fac*(*S*)-[Cr(aet)$_3$] units are linked by three Ag^I atoms to form an S-bridged $Cr^{III}_2Ag^I_3$ pentanuclear structure, where five metal atoms form a trigonal-bipyramid (Ag···Ag = 3.108(2) – 3.296(2) Å, Cr···Cr = 6.772(3) Å). The overall structure of [**1**]$^{3+}$ is very similar to that of $[Ag_3\{Co(aet)_3\}_2]^{3+}$ [1c], except the considerably longer Cr-S bonds (average 2.387(5) Å) compared with the Co-S bonds (average 2.248(8) Å). The averaged Ag-S distance (2.403(5) Å) in [**1**]$^{3+}$ is slightly larger than that in $[Ag_3\{Co(aet)_3\}_2]^{3+}$ (2.378(8) Å), which suggests that the S-donating ability of the *fac*(*S*)-[Cr(aet)$_3$] unit is somewhat weaker than that of *fac*(*S*)-$[Co(aet)_3]$.

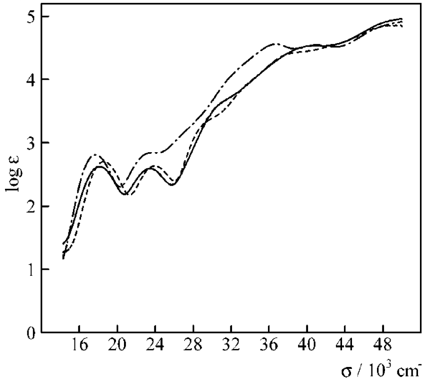

FIGURE 1 Electronic absorption spectra of $[\mathbf{1}]^{3+}$ (—), $[\mathbf{2}]^{3+}$ (---), and $[Ag_3\{Co(aet)_3\}_2]^{3+}$ (–·–) in H_2O.

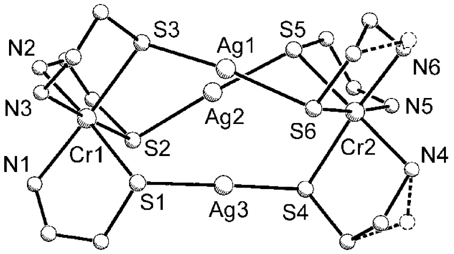

FIGURE 2 Perspective view of the complex cation $[\mathbf{1}]^{3+}$. Averaged bond distances (Å) and angles (°): Cr1-S = 2.386(5), Cr2-S = 2.388(5), Cr1-N = 2.10(1), Cr2-N = 2.10(1), S-Cr1-S = 94.2(2), S-Cr2-S = 93.6(2), N-Cr1-N = 91.1(6), N-Cr2-N = 91.0(6).

When an aqueous solution of $[Ag_3\{Co(aet)_3\}_2](NO_3)_3$ ($[\mathbf{1}](NO_3)_3$) was treated with 3 molar equiv of Au^{I}, which was generated from $Na[AuCl_4]$ and 2,2'-thiodiethanol, a red-pink powder ($[\mathbf{2}]Cl(NO_3)_2$) containing Cr and Au in a 2:3 ratio was isolated in a satisfactory yield. The absorption spectral feature of $[\mathbf{2}]^{3+}$ coincides well with that of $[\mathbf{1}]^{3+}$ over the whole region (Figure 1), and furthermore, the molar conductivity of $[\mathbf{2}]Cl(NO_3)_2$ in water (363.1 $\Omega^{-1}cm^2mol^{-1}$) is consistent with that of $[\mathbf{1}](NO_3)_3$. These results imply that three Ag^{I} ions in $[\mathbf{1}]^{3+}$ were replaced by Au^{I} ions to form the corresponding $Cr^{III}_2Au^{I}_3$ pentanuclear structure in $[Au_3\{Cr(aet)_3\}_2]^{3+}$. It was found that **[2]**$^{3+}$ is also formed by the direct reaction of [Cr(aet)$_3$] with 1.5 molar equiv of Au$^{\mathrm{I}}$ in water.

Treatment of [Cr(D-pen-*N,O,S*)$_2$]$^-$ with equimolar AgClO$_4$ in water produced a pale brown powder ([**3**]), which is insoluble in water. The elemental analysis of [**3**] is consistent with the formula expected for [Ag$_3${Cr(D-pen)$_2$}$_3$], and its absorption and CD spectra in solid state coincide well with those of [Ag$_3${Co(D-pen-*N,O,S*)$_2$}$_3$] [2]. Furthermore, the IR spectrum of [**3**] is very similar to that of [Ag$_3${Co(D-pen-*N,O,S*)$_2$}$_3$], rather than K[Cr(D-pen-*N,O,S*)$_2$]. Accordingly, it is considered that [**3**] has the same S-bridged polynuclear structure as that of [Ag$_3${Co(D-pen-*N,O,S*)$_2$}$_3$] [2]. That is, in [**3**] three *trans*(*O*)-[Cr(D-pen-*N,O,S*)$_2$]$^-$ units are linked by three linear Ag$^{\mathrm{I}}$ ions in a cyclic form.

Magnetic susceptibility data were collected in the range of 2—300 K for [**1**](BF$_4$)$_3$ and [**3**], in which Cr$^{\mathrm{III}}$ ions are connected by Cr-S-Ag-S-Cr linkages. The effective magnetic moment for [**1**](BF$_4$)$_3$ gradually decreases from 5.78 μ_{B} at 290 K to 5.36 μ_{B} at 20 K and finally to 2.48 μ_{B} at 2 K, while that for [**3**] slightly increases from 6.93 μ_{B} at 290 K to 7.22 μ_{B} at 4 K. These data indicate the antiferromagnetic interaction between two Cr$^{\mathrm{III}}$ ions in [**1**]$^{3+}$ and the ferromagnetic interaction among three Cr$^{\mathrm{III}}$ ions in [**3**]. The least-squares fit of the magnetic data gave the parameters of $J = -0.84$ cm^{-1} and $g = 2.13$ for [**1**](BF$_4$)$_3$, while $J = 0.05$ cm^{-1} and $g = 2.07$ for [**3**]. The small J values for these complexes can be ascribed to the large separation of Cr$^{\mathrm{III}}$ ions in the S-bridged polynuclear structures. A small J value (-0.17 cm^{-1}) has also been observed for [Zn$_4$O{Cr(aet)$_3$}$_4$]$^{6+}$ having large Cr$^{\mathrm{III}}\cdots$Cr$^{\mathrm{III}}$ separations (average 6.755(4) Å)[4]. In order to understand the correlation between the magnetic property and the S-bridged structure, other heterometallic polynuclear complexes consisting of thiolato chromium(III) units are under investigation.

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