Sulfur-Bridged Heterotrimetallic $Co^{III}{}_2Pt^{II}Ag^{I}$ Complexes Consisting of Two Tris(thiolato)-Type Cobalt(III) Octahedra Linked by Pt^{II} and Ag^{I} Ions

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Sulfur-bridged $Co^{III}{}_2Pt^{II}Ag^{I}$ tetranuclear complexes $[Ag\{Pt(NH_3)_2\}\{Co(aet)_3\}_2](NO_3)_3$ (**1**; aet = $NH_2CH_2CH_2S^-$) and $[AgPt\{Co(L)\}_2]Cl_3$ (**2**; L = $N(CH_2NHCH_2CH_2S^-)_3$), in which two *fac*(*S*)-tris(thiolato)-type cobalt(III) units are linked by two different kinds of metal ions, Pt^{II} and Ag^{I}, were newly synthesized by the reaction of *fac*(*S*)-$[Co(aet)_3]$ with a mixture of *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$ and Ag^+ and by the reaction of $[Ag_3\{Co(L)\}_2]^{3+}$ with $[PtCl_4]^{2-}$, respectively. The crystal structures of **1** and **2**, which adopt *racemic* and *meso* forms, respectively, were determined by X-ray crystallography.

It has been recognized that thiolato groups bound to a metal center possess a relatively strong Lewis basicity, which allows them to bind with a second metal center.[1] With the use of this property of thiolato donors, a large number of *S*-bridged polynuclear complexes have been prepared by treatment of isolated mononuclear thiolato complexes with a variety of transition-metal ions.[2,3] In particular, the construction of *S*-bridged polynuclear structures starting from tris(thiolato)-type octahedral complexes has been extensively investigated, because of their intriguing stereochemical, spectrochemical, and redox properties.[2] In the *S*-bridged polynuclear structures of this class, tris(thiolato)-type octahedra have been generally linked by one kind of metal ion(s), leading to the formation of homometallic or heterobimetallic systems. Recently, we have shown that rare examples of *S*-bridged heterotrimetallic complexes, $[M'_2\{M[Co(aet)_3]_2\}_2]^{6+}$ (M = Pd^{II}, Pt^{II} and M′ = Ag^{I}, Au^{I}) and $[Ag\{Pt_2(\mu\text{-}H_2O)(NH_3)_2\}\{Rh(aet)_3\}_2]^{5+}$, are obtained from *fac*(*S*)-$[Co(aet)_3]$ and *fac*(*S*)-$[Rh(aet)_3]$ (aet = $NH_2CH_2CH_2S^-$) by way of $[M\{Co(aet)_3\}_2]^{2+}$ and $[\{Pt(NH_3)_2\}_2\{Rh(aet)_3\}_2]^{4+}$, respectively.[4,5] While each $[Rh(aet)_3]$ unit in the latter $Rh^{III}{}_2Pt^{II}{}_2Ag^{I}$ complex adopts the *fac*(*S*) geometry, as does the starting mononuclear complex, each $[Co(aet)_3]$ unit in the former $Co^{III}{}_4M_2M'_2$ complexes is isomerized to have the *mer*(*S*) geometry. Thus, the linkage of *fac*(*S*)-tris(thiolato)-type cobalt(III) units with two different kinds of metal ions has not been achieved so far. In this paper, we wish to report two synthetic routes to create a novel *S*-bridged $Co^{III}{}_2Pt^{II}Ag^{I}$ heterotrimetallic system that consists of two tris(thiolato)cobalt(III) units having the *fac*(*S*) geometry, *fac*(*S*)-$[Co(aet)_3]$ or *fac*(*S*)-$[Co(L)]$ (L = $N(CH_2NHCH_2CH_2S^-)_3$).

The reaction of *fac*(*S*)-$[Co(aet)_3]$[6] with *trans*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$ (Co:Pt = 2:1), which was freshly prepared from *trans*-$[PtCl_2(NH_3)_2]$ and Ag^+ in water, in the presence of Ag^+ at room temperature gave a dark brown solution, from which almost black crystals ($\mathbf{1}\cdot 3H_2O$) were isolated by adding a $NaNO_3$ aqueous solution. X-ray fluorescence spectroscopy indicated that this product contains Co, Pt, and Ag atoms, and the elemental analytical result was consistent with the formula for a 2:1:1 adduct of $[Co(aet)_3]$, $[Pt(NH_3)_2](NO_3)_2$, and $AgNO_3$. The electronic absorption spectrum of **1**,[7] which is characterized by a visible band at ca. $18 \times 10^3\,cm^{-1}$ and intense near-UV bands at ca. 35×10^3 and $38 \times 10^3\,cm^{-1}$, is similar to that of a *S*-bridged $Co^{III}Ag^{I}{}_3Co^{III}$ complex with two *fac*(*S*)-$[Co(aet)_3]$ units, $[Ag_3\{Co(aet)_3\}_2]^{3+}$,[8] suggesting the presence of $[Co(aet)_3]$ units having the *fac*(*S*) geometry in **1**. The *S*-bridged $Co^{III}{}_2Pt^{II}Ag^{I}$ tetranuclear structure in **1**, which is composed of a discrete complex cation and three nitrate anions, was determined by X-ray analysis.

As shown in Fig. 1, the complex cation of **1** consists of two approximately octahedral $[Co(aet)_3]$ units (av. S–Co–S = 91.8(2)°, N–Co–N = 90.7(5)°), a *trans*-$[Pt(NH_3)_2]^{2+}$ moiety, and a Ag^{I} atom. The two $[Co(aet)_3]$ units are spanned by a *trans*-$[Pt(NH_3)_2]^{2+}$ moiety and a Ag^{I} atom through four of six thiolato S atoms to form a *S*-bridged $Co^{III}{}_2Pt^{II}Ag^{I}$ tetranuclear structure in $[Ag\{Pt(NH_3)_2\}\{Co(aet)_3\}_2]^{3+}$ that possesses two non-bridging thiolato S atoms (S3 and S6). Each $[Co(aet)_3]$ unit has the *fac*(*S*) geometrical configuration, like the parental mononuclear *fac*(*S*)-$[Co(aet)_3]$. This is in contrast to the fact that the linkage of two *fac*(*S*)-$[Co(aet)_3]$ molecules by a square-planar metal ion (M = Pt^{II} and Pd^{II}) has been accompanied by the geometrical isomerization to *mer*(*S*) to form $[M\{Co(aet)_3\}_2]^{2+}$.[4] The coordination geometry about the Pt^{II} atom in **1** is approximately square-planar coordinated by two thiolato S and two ammine N atoms (S–Pt–S = 173.5(1)°, N–Pt–N = 177.2(6)°), while the Ag^{I} atom has a distorted linear geometry coordinated by two thiolato S atoms (169.9(1)°). It is noticed that in **1** the Ag^{I} atom is situated above the Pt atom of a $[PtN_2S_2]$ square-plane with a Ag–Pt distance of 3.052(1) Å. This is suggestive of the presence of a weak bonding interaction between the Ag^{I} and Pt^{II} atoms in **1**.[9] Of the two possible geometrical configurations, *syn* and *anti*, which

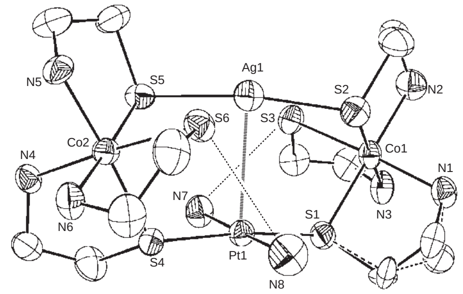

Fig. 1. A perspective view of the complex cation of **1**. The ΛΛ isomer is selected. Hydrogen atoms are omitted for clarity.

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arise from the relative configuration of two non-bridging thiolato groups,[5] **1** adopts the *anti* configuration. The two *fac*(*S*)-[Co(aet)$_3$] units have the same chiral configuration (Δ or Λ) to give the *racemic* form ($\Delta\Delta/\Lambda\Lambda$), and the four bridging S atoms in the $\Delta\Delta$ and $\Lambda\Lambda$ isomers are unified to have the *S* and *R* configurations, respectively. Thus, in **1** an idealized C_2 axis passes through the Ag–Pt line, although there is no crystallographically imposed symmetry. It is worth noting that each of the two NH$_3$ groups is hydrogen bonded with an adjacent non-bridging thiolato group (N7$\cdots$S3 = 3.33(1) Å and N8$\cdots$S6 =3.46(2) Å),[10] which seems to stabilize the *racemic–syn* form in this Co$^{\text{III}}_2$Pt$^{\text{II}}$Ag$^{\text{I}}$ structure. The bond distances around the *fac*(*S*)-[Co(aet)$_3$] units (av. Co–S = 2.257(4) Å, Co–N = 2.00(1) Å) and the Ag$^{\text{I}}$ atom (av. Ag–S = 2.390(4) Å) in **1** resemble those in [Ag$_3${Co(aet)$_3$}$_2$]$^{3+}$ (av. Co–S = 2.248(8) Å, Co–N = 2.03(3) Å, Ag–S = 2.378(8) Å),[8] and the bond distances around the Pt$^{\text{II}}$ atom (av. Pt–S = 2.314(3) Å, Pt–N = 2.05(1) Å) are comparable with those in *anti*-[{Pt(NH$_3$)$_2$}$_2${Rh(aet)$_3$}$_2$]$^{4+}$ (av. Pt–S = 2.323(1) Å, Pt–N = 2.049(5) Å).[5] The ^{13}C NMR of **1** in D$_2$O showed only one set of 6 carbon signals for the 6 aet ligands in the complex. This implies that the *racemic–anti* isomer with an averaged C_2-symmetry found in crystals is retained in solution. Compatible with the *racemic* structure, **1** was successfully optically resolved into a pair of enantiomers by fractional crystallization of its [Sb$_2$(*R*,*R*-tartrato)$_2$]$^{2-}$ diastereomeric salts.[7]

To construct another *S*-bridged Co$^{\text{III}}$Pt$^{\text{II}}$Ag$^{\text{I}}$ structure composed of *fac*(*S*)-tris(thiolato)-type cobalt(III) units, we investigated the possibility of the replacement of two Ag$^{\text{I}}$ atoms in [Ag$_3${Co(aet)$_3$}$_2$]$^{3+}$ by a Pt$^{\text{II}}$ atom. Unfortunately, the reactions of [Ag$_3${Co(aet)$_3$}$_2$]$^{3+}$ with [PtCl$_2$(NH$_3$)$_2$] or [PtCl$_4$]$^{2-}$ gave an unidentified polymeric species, in addition to [Co{Co(aet)$_3$}$_2$]$^{3+}$. On the other hand, the use of [Ag$_3${Co(L)}$_2$]$^{3+}$,[11] in which the terminal N$_3$ face of each [Co$^{\text{III}}$(N)$_3$(S)$_3$] octahedron is aza-capped, instead of [Ag$_3${Co(aet)$_3$}$_2$]$^{3+}$, led to the formation of a desired compound containing Co, Pt, and Ag atoms. That is, treatment of [Ag$_3${Co(L)}$_2$]$^{3+}$ with [PtCl$_4$]$^{2-}$ at 60 °C in the presence of NaBr gave a dark brown solution, from which almost black crystals (**2**$\cdot$11H$_2$O) were isolated by adding a NaCl aqueous solution. The elemental analytical data of **2** are in good agreement with the formula for a 2:1:1 adduct of [Co(L)], PtCl$_2$, and AgCl, and its absorption spectral features resemble those of **1**.[7] The *S*-bridged Co$^{\text{III}}_2$Pt$^{\text{II}}$Ag$^{\text{I}}$ tetranuclear structure in **2**, which is composed of a discrete complex cation and three chloride anions, was established by X-ray analysis.

As shown in Fig. 2, the complex cation of **2** consists of two approximately octahedral [Co(L)] units (av. S–Co–S = 89.17(8)°, N–Co–N = 91.6(3)°) and Pt$^{\text{II}}$ and Ag$^{\text{I}}$ atoms. Two of the three thiolato S atoms in each [Co(L)] unit are bound to a Pt$^{\text{II}}$ atom, and the remaining thiolato S atom is bound to a Ag$^{\text{I}}$ atom to form a *S*-bridged Co$^{\text{III}}_2$Pt$^{\text{II}}$Ag$^{\text{I}}$ tetranuclear structure in [AgPt{Co(L)}$_2$]$^{3+}$. The coordination geometry about the Pt$^{\text{II}}$ atom is approximately square-planar coordinated by four thiolato S donors from two [Co(L)] units (av. *trans* S–Pt–S = 173.50(7)°). On the other hand, the geometry about the Ag$^{\text{I}}$ atom deviates significantly from linearity bound by two thiolato S atoms (S–Ag–S = 148.23(8)°), because of the close contact of one of the three Cl$^-$ anions (Ag–Cl = 2.652(2) Å). Like the Ag$^{\text{I}}$ atom in **1**, the Ag$^{\text{I}}$ atom in **2** is situated above the Pt atom of a [PtS$_4$] plane, but the Pt–Ag distance (2.9012(9) Å) is appreciably shorter than that in **1**. In **2**, the two *fac*(*S*)-[Co(aet)$_3$] units have the opposite chiral configuration to give a *meso* form ($\Delta\Lambda$), and the three bridging S atoms in the Δ- and Λ-[Co(L)] units are fixed to have the *S* and *R* configurations, respectively. Thus, the complex cation of **2** has an averaged C_s symmetry with a mirror plane that involves the Cl, Ag, and Pt atoms. The bond distances about each [Co(L)] unit in [**2**]$^{3+}$ (av. Co–S = 2.250(2) Å, Co–N = 2.003(7) Å) are comparable with those found in the starting [Ag$_3${Co(L)}$_2$]$^{3+}$ (av. Co–S = 2.243(8) Å, Co–N = 2.03(3) Å).[11] However, the Ag–S distances (av. 2.441(2) Å) are longer than those in [Ag$_3${Co(L)}$_2$]$^{3+}$ (av. 2.417(8) Å), which is rationalized by the close contact of the Cl$^-$ anion. The Pt–S distances (av. 2.320(2) Å) are essentially the same as those in [Pt{Co(aet)$_3$}$_2$]$^{2+}$ (av. 2.325(4) Å for the *syn* isomer, 2.321(2) Å for the *anti* isomer),[4b] as expected from the same coordination environment around the Pt$^{\text{II}}$ atom. The ^{13}C NMR spectrum of **2** in D$_2$O shows a single set of 9 signals for 18 carbon atoms in the complex. This implies that the averaged C_s symmetrical structure of **2** found in the crystal is retained in solution.

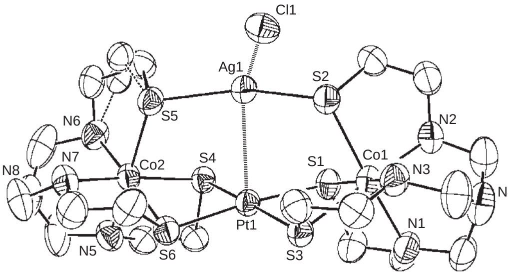

Fig. 2. A perspective view of the complex cation of **2** together with a Cl atom contacted with a Ag atom. Hydrogen atoms are omitted for clarity.

In summary, the formation of a novel heterotrimetallic system consisting of Co$^{\text{III}}$, Pt$^{\text{II}}$, and Ag$^{\text{I}}$ ions was achieved by the direct reaction of *fac*(*S*)-[Co(aet)$_3$] with a mixture of *trans*-[Pt(H$_2$O)$_2$(NH$_3$)$_2$]$^{2+}$ and Ag$^{\text{I}}$, and by the metal replacement reaction of [Ag$_3${Co(L)}$_2$]$^{3+}$ with [PtCl$_4$]$^{2-}$, which produced [Ag{Pt(NH$_3$)$_2$}{Co(aet)$_3$}$_2$]$^{3+}$ (complex cation of **1**) and [AgPt{Co(L)}$_2$]$^{3+}$ (complex cation of **2**), respectively. Complex **1**, in which two *fac*(*S*)-[Co(aet)$_3$] units are connected by linear [Pt(NH$_3$)$_2$]$^{2+}$ and linear Ag$^{\text{I}}$ linkers, gave only the *racemic–anti* isomer.[12,13] This result differs significantly from the previous observation that a related *S*-bridged tetranuclear complex, [{Pt(NH$_3$)$_2$}$_2${Rh(aet)$_3$}$_2$]$^{4+}$, in which two *fac*(*S*)-[Rh(aet)$_3$] units are connected by two *trans*-[Pt(NH$_3$)$_2$]$^{2+}$ linkers, produced the *meso–anti* and *racemic–syn* isomers.[5] In addition, only the *meso* isomer was obtained for **2**,[12] in which two *fac*(*S*)-[Co(L)] units are connected by a square-planar Pt$^{\text{II}}$ and a quasi linear Ag$^{\text{I}}$ linker. Thus, the stereochemical behavior of this class of *S*-bridged polynuclear complexes is drastically changed by the replacement of one of the two linkers that connect two *fac*(*S*)-tris(thiolato)-type octahedrons.

Experimental

Preparation of [Ag{Pt(NH$_3$)$_2$}{Co(aet)$_3$}$_2$](NO$_3$)$_3$ (1). To a stirred light yellow solution containing *trans*-[PtCl$_2$(NH$_3$)$_2$][14]

(0.20 g, 0.67 mmol) in 80 cm^3 of water was added a solution containing $AgNO_3$ (0.27 g, 1.59 mmol) in 5 cm^3 of water. The mixture was stirred at 80 °C for 1 h and then cooled to room temperature. After removing a white-yellow precipitate by filtration through celite, a solid sample of *fac*(*S*)-$[Co(aet)_3]^6$ (0.40 g, 1.39 mmol) was added to the filtrate. The mixture was stirred at room temperature for 1 h, followed by the addition of 10 cm^3 of a saturated $NaNO_3$ aqueous solution. The dark brown reaction solution was allowed to stand at room temperature for 2 days, and the resulting black crystals (**1**$\cdot 3H_2O$) suitable for X-ray analysis were collected by filtration. Yield: 0.26 g (89% based on Ag). Anal. Calcd for $[Ag\{Pt(NH_3)_2\}\{Co(C_6H_{18}N_3S_3)\}_2](NO_3)_3\cdot 3H_2O$: C, 12.51; H, 4.20; N, 13.38%. Found: C, 12.42; H, 3.99; N, 13.26%. ^{13}C NMR (D_2O): δ 34.19, 34.29, and 34.67 for CH_2S and 48.31, 50.39, and 51.25 for CH_2NH_2.

Preparation of $[AgPt\{Co(L)\}_2]Cl_3$ (2). To a stirred dark purple solution of $[Ag_3\{Co(L)\}_2](NO_3)_3\cdot 4H_2O$[11] (0.52 g, 0.40 mmol) in 140 cm^3 of water was successively added $K_2[PtCl_4]$ (0.16 g, 0.40 mmol) suspended in 5 cm^3 of water and NaBr (0.14 g, 1.39 mmol) in 5 cm^3 of water, which immediately gave a dark brown precipitate. The mixture was stirred at 60 °C for 24 h under a nitrogen atmosphere. After removing a dark brown powder by filtration, 5 cm^3 of a saturated NaCl aqueous solution was added to the dark brown filtrate, which was concentrated to ca. 20 cm^3 with a rotary evaporator. The concentrated solution was allowed to stand at room temperature for 1 day. The resulting dark brown microcrystals were collected by filtration and then recrystallized from water by adding a few drops of a saturated NaCl solution to give brown crystals suitable for X-ray analysis. Yield: 0.04 g (8%). Anal. Calcd for $[AgPt\{Co(C_9H_{21}N_4S_3)\}_2]Cl_3\cdot 11H_2O$: C, 16.75; H, 5.01; N, 8.70%. Found: C, 16.75; H, 4.75; N, 8.53%. ^{13}C NMR (D_2O): δ 34.13, 36.51, and 38.26 for CH_2S and 57.78, 58.98, 59.04, 69.93, 70.57, and 71.39 for CH_2N.

Measurements. The electronic absorption spectra were recorded with a 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 JEOL JNM-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.

X-ray Structural Determinations. Single-crystal X-ray diffraction experiments for **1**$\cdot 3H_2O$ and **2**$\cdot 11H_2O$ were performed on Rigaku AFC7S and Rigaku AFC7R four-cycle diffractometers with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), respectively. Unit-cell parameters were determined by a least-squares refinement. The intensity data were collected by the ω-2θ scan mode. The intensities were corrected for Lorentz and polarization, and empirical absorption corrections based on ψ scans were also applied. The structures were solved by direct methods and expanded using Fourier techniques. Hydrogen atoms except those of water molecules were placed at calculated positions but were not refined. For both **1** and **2**, one of six *N*,*S*-chelate rings was disordered. All calculations were performed using the CrystalStructure software package.[15] Crystal data for **1**$\cdot 3H_2O$: fw = 1151.79, monoclinic, $P2_1/n$, $a = 15.455(2)$ Å, $b = 14.115(2)$ Å, $c = 15.914(2)$ Å, $\beta = 92.434(9)°$, $V = 3468.4(7)$ Å^3, $Z = 4$, $D_{calcd} = 2.206$ g cm^{-3}, R (R_w) = 0.070 (0.217). Crystal data for **2**$\cdot 11H_2O$: fw = 1288.30, monoclinic, $C2/c$, $a = 24.975(6)$ Å, $b = 17.982(5)$ Å, $c = 22.480(7)$ Å, $\beta = 112.07(2)°$, $V = 9356(4)$ Å^3, $Z = 8$, $D_{calcd} = 1.829$ g cm^{-3}, R (R_w) = 0.040 (0.135). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition numbers CCDC-297313 and -297314. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information

Experimental procedure of optical resolution of **1** and Fig. S1 in PDF format. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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12 The successful introduction of the *trans*-$[Pt(NH_3)_2]^{2+}$ moiety in **1** can be ascribed in part to the formation of intramolecular NH···S hydrogen bonds.

13 The formation of a single isomer for both **1** and **2** was supported by the cation-exchange column chromatography (SP-Sephadex C-25) of the reaction solutions, although **2** was slowly decomposed in the column.

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