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Preparation and Properties of S-Bridged $Co^{III}Ag^{I}_3Co^{III}$ Pentanuclear Complexes Having a Triple Helical Chirality. Crystal Structure of $[Ag_3\{Co(aet)_3\}_2](BF_4)_3$ (aet = 2-Aminoethanethiolate)

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Novel S-bridged $Co^{III}Ag^{I}_3Co^{III}$ pentanuclear complexes, $[Ag_3\{Co(aet)_3\}_2]^{3+}$ (**1**) and $[Ag_3\{Co(\text{L-cys-}N,S)_3\}_2]^{3-}$ (**2**), were prepared by reacting *fac*(*S*)-[Co(aet)$_3$] (aet = 2-aminoethanethiolate) or Δ_{LLL}-*fac*(*S*)-$[Co(\text{L-cys-}N,S)_3]^{3-}$ (L-cys = L-cysteinate) with Ag^+ in a ratio of 2 : 3. The crystal structure of **1**$(BF_4)_3$ was determined by X-ray crystallography. **1**$(BF_4)_3\cdot H_2O$, chemical formula $C_{12}H_{38}B_3N_6OF_{12}S_6Co_2Ag_3$, crystallizes in the orthorhombic space group *Pnma* with $a = 16.397(2)$, $b = 13.239(2)$, $c = 15.803(4)$ Å, $V = 3430.5(9)$ Å^3, $Z = 4$, and $R = 0.066$. In **1** the two thiolato S atoms from two octahedral *fac*(*S*)-[Co(aet)$_3$] units coordinate to each of three Ag atoms, such that the three S–Ag–S linkages form a triple helical structure. **1** gave only racemic isomer, $\Delta\Delta$ and $\Lambda\Lambda$, which were optically resolved by cation-exchange column chromatography, while the $\Delta_{LLL}\Delta_{LLL}$ isomer was selectively formed for **2** with a retention of the absolute configuration of the starting Δ_{LLL}-*fac*(*S*)-$[Co(\text{L-cys-}N,S)_3]^{3-}$. **1** was converted to the S-bridged tricobalt(III) complex $[Co\{Co(aet)_3\}_2]^{3+}$ by a reaction with I^- in the presence of Co^{2+}, accompanied by an intermolecular exchange and racemization of the Δ/Λ-*fac*(*S*)-[Co(aet)$_3$] units. The electronic absorption and CD spectral properties of **1** and **2** are also reported.

The aggregation of octahedral *fac*(*S*)-[M(aet)$_3$] or *fac*(*S*)-$[M(\text{L-cys-}N,S)_3]^{3-}$ (M = Co^{III}, Rh^{III}, Ir^{III}; aet = 2-aminoethanethiolate; L-cys = L-cysteinate) assisted by metal ions has been shown to form a variety of S-bridged polynuclear complexes containing several chiral centers.[1—14] It has been noted that the structures of these polynuclear complexes are highly dependent on the coordination geometry of metal ions incorporated with *fac*(S)-$[M(\text{aet or L-cys-}N,S)_3]^{0\text{ or }3-}$. For example, the reactions of *fac*(*S*)-[M(aet)$_3$] or *fac*(*S*)-$[M(\text{L-cys-}N,S)_3]^{3-}$ with octahedral Co^{III} gave linear-type S-bridged trinuclear complexes $[Co\{M(\text{aet or L-cys-}N,S)_3\}_2]^{3+\text{ or }3-}$,[1,3—5] while the reactions with tetrahedral Zn^{II} produced T-cage-type S-bridged octanuclear complexes $[Zn_4O\{M(\text{aet or L-cys-}N,S)_3\}_4]^{6+\text{ or }6-}$.[6—8] Quite recently, we have reported that the reaction of *fac*(*S*)-[Rh(aet)$_3$] with diagonal Ag^I gives a trigonal-bipyramid-type S-bridged pentanuclear complex $[Ag_3\{Rh(aet)_3\}_2]^{3+}$, which is interconvertible with an S-bridged nonanuclear complex $[Ag_5\{Rh(aet)_3\}_4]^{5+}$.[14] In this $Rh^{III}Ag^{I}_3Rh^{III}$ pentanuclear structure, the two *fac*(*S*)-[Rh(aet)$_3$] units are regulated to have the same absolute configuration, forming only the $\Delta\Delta$ and $\Lambda\Lambda$ isomers. This is in contrast to the fact that the linear-type trinuclear complexes $[Co\{M(aet)_3\}_2]^{3+}$ gave all three possible isomers: $\Delta\Delta$, $\Lambda\Lambda$, and $\Delta\Lambda$.[1,4,5] Furthermore, a triple helical structure due to three S–Ag–S linkages exists in $[Ag_3\{Rh(aet)_3\}_2]^{3+}$, which has not been found in $[Co\{M(\text{aet or L-cys-}N,S)_3\}_2]^{3+\text{ or }3-}$ and $[Zn_4O\{M(\text{aet or L-cys-}N,S)_3\}_4]^{6+\text{ or }6-}$.[1,3—8] In order to better understand the properties characteristic of the S-bridged pentanuclear structure of this type, it is necessary to investigate analogous S-bridged pentanuclear complexes composed of *fac*(*S*)-$[M(\text{aet or L-cys-}N,S)_3]^{0\text{ or }3-}$ units other than *fac*(*S*)-[Rh(aet)$_3$]. In this paper we report on the synthesis, structure, and chemical characterization of the $Co^{III}Ag^{I}_3Co^{III}$ pentanuclear complexes $[Ag_3\{Co(aet)_3\}_2]^{3+}$ (**1**) and $[Ag_3\{Co(\text{L-cys-}N,S)_3\}_2]^{3-}$ (**2**), along with the conversion of the S-bridged pentanuclear structure in **1** to the trinuclear structure in $[Co\{Co(aet)_3\}_2]^{3+}$. The absorption and CD spectra of these complexes are discussed in comparison with those of the related cobalt(III) complexes.

Experimental

Preparation and Optical Resolution of $[Ag_3\{Co(aet)_3\}_2]$-$(BF_4)_3$ (1$(BF_4)_3$). To a stirred dark-blue suspension of *fac*(S)-[Co(aet)$_3$][1a)] (0.10 g, 0.35 mmol) in 16 cm^3 of water was dropwise added a solution of $AgBF_4$ (0.10 g, 0.51 mmol) in 4 cm^3 of water at room temperature. The mixture was stirred at room temperature for 1 h, which gave a clear dark-purple solution. To the dark-purple solution was added 0.6 g of $NaBF_4$ dissolved in 10 cm^3 of water, followed by cooling in a refrigerator for 3 d. The resulting dark-purple crystals, one of the which was used for an X-ray analysis, were collected by filtration. Yield: 0.17 g (84%). Anal. Calcd for $[Co_2Ag_3(C_{12}H_{36}N_6S_6)](BF_4)_3\cdot H_2O$: C, 12.25; H, 3.26; N, 7.14; Co, 10.02; Ag, 27.50%. Found: C, 12.35; H, 3.24; N, 7.11; Co, 10.10; Ag, 27.95%.

An aqueous solution of **1**$(BF_4)_3\cdot H_2O$ (0.6 g) was chromatographed on an SP-Sephadex C-25 column (Na^+ form, 4.6 cm×90 cm) using a 0.15 mol dm^{-3} aqueous solution of $Na_2[Sb_2(R,R\text{-tartrato})_2]\cdot 5H_2O$ as an eluent. When the developed band was completely separated into two bands in the column, the eluent was changed to a 0.3 mol dm^{-3} aqueous solution of $NaNO_3$. Each eluate of the two bands was concentrated to a small volume with a rotary evaporator; the resulting dark-purple microcrystals were collected by filtration. It was found from absorption and CD spectral measurements that the earlier and the later moving bands in the column contained $(-)^{CD}_{600}$-**1** and $(+)^{CD}_{600}$-**1**, respectively. Anal. Calcd for $[Co_2Ag_3(C_{12}H_{36}N_6S_6)](NO_3)_3\cdot 2H_2O$: C, 12.86; H, 3.60; N, 11.25%. Found for the $(-)^{CD}_{600}$ isomer: C, 12.80; H, 3.55; N, 11.30%. Found for the $(+)^{CD}_{600}$ isomer: C, 12.88; H, 3.54; N, 11.30%.

Preparation of $\Delta_{LLL}\Delta_{LLL}$-$K_3[Ag_3\{Co(L\text{-}cys\text{-}N,S)_3\}_2]$ ($\Delta_{LLL}\Delta_{LLL}$-$K_3$2). To a solution of Δ_{LLL}-*fac*(*S*)-$K_3[Co(L\text{-}cys\text{-}N,S)_3]\cdot 9H_2O\cdot 0.5KCl$[3a] (0.20 g, 0.27 mmol) in 5 cm^3 of water was added $AgNO_3$ (0.07 g, 0.41 mmol) dissolved in a small amount of water. After the mixture had been stirred at room temperature for 1 h, 20 cm^3 of methanol was added to the reaction solution in an ice bath. The resulting dark-purple powder was collected by filtration, and then recrystallized from water by adding methanol in an ice bath. Yield: 0.14 g (70%). Anal. Calcd for $K_3[Co_2Ag_3(C_{18}H_{30}N_6O_{12}S_6)]\cdot 10H_2O$: C, 14.87; H, 3.47; N, 5.78; Co, 8.11; Ag, 22.26%. Found: C, 14.69; H, 3.45; N, 5.54; Co, 8.43; Ag, 22.27%.

Conversion of $[Ag_3\{Co(aet)_3\}_2]^{3+}$ to $[Co\{Co(aet)_3\}_2]^{3+}$. To a stirred solution containing **1**$(BF_4)_3\cdot H_2O$ (0.10 g, 0.085 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (0.25 g, 0.86 mmol) in 20 cm^3 of water was added NaI (0.04 g, 0.27 mmol) dissolved in a small amount of water, which gave a dark-green precipitate immediately. After the mixture had been stirred at 60 °C for 1 h, the reaction mixture was filtered to remove any insoluble materials. The dark-brown filtrate was poured onto an SP-Sephadex C-25 column (Na^+ form, 2.4 cm×30 cm) and the adsorbed band was eluted with a 0.3 mol dm^{-3} aqueous solution of NaCl. Three bands (A-1 (pink), A-2 (dark brown), and A-3 (greenish brown)) were eluted in this order. It was found from the absorption spectral measurements that the A-1, A-2, and A-3 eluates contained Co^{2+}, $\Delta\Lambda$-$[Co\{Co(aet)_3\}_2]^{3+}$, and $\Delta\Delta/\Lambda\Lambda$-$[Co\{Co(aet)_3\}_2]^{3+}$, respectively.[1,3d] The formation ratio of $\Delta\Lambda$ (*meso*) : $\Delta\Delta/\Lambda\Lambda$ (*racemic*) was evaluated to be 4.9 : 5.1, based on the absorption spectral data of the A-2 and A-3 eluates.

The same reaction using $\Delta\Lambda$-**1**$(NO_3)_3\cdot 2H_2O$ instead of **1**$(BF_4)_3\cdot H_2O$ also gave a dark-brown reaction solution. When the dark-brown solution was chromatographed on an SP-Sephadex C-25 column (Na^+ form, 2.4 cm×30 cm), three bands (B-1 (pink), B-2 (dark brown), and B-3 (greenish brown)) were eluted with a 0.3 mol dm^{-3} aqueous solution of NaCl. It was found from absorption and CD spectral measurements that the B-1, B-2, and B-3 eluates contained Co^{2+}, $\Delta\Lambda$-$[Co\{Co(aet)_3\}_2]^{3+}$, and a mixture of $\Delta\Delta$- and $\Lambda\Lambda$-$[Co\{Co(aet)_3\}_2]^{3+}$, respectively. The formation ratio of $\Delta\Delta$: $\Delta\Lambda$: $\Lambda\Lambda$ was evaluated to be 5.3 : 3.9 : 0.8, based on the absorption and CD spectral data of the B-2 and B-3 eluates.

Measurements. The electronic absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer, and the CD spectra with a JASCO J-600 spectropolarimeter at room temperature. The ^{13}C NMR spectra were recorded with a Bruker AM-500 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 elemental analyses (C, H, N) were performed by the Analysis Center of the University of Tsukuba. The concentrations of Co and Ag in the complexes were determined with a Nippon Jarrel-Ash ICPA-575 ICP spectrophotometer.

X-Ray Structure Determination. A black crystal of **1**$(BF_4)_3\cdot H_2O$ was used for data collection on an Enraf–Nonius CAD4 diffractometer with a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The unit-cell parameters were determined by a least-squares refinement, using the setting angles of 25 reflections in the range of $15 > 2\theta > 20°$. Crystallographic data are summarized in Table 1. The intensity data were collected by the ω–2θ scan mode up to $2\theta = 50°$ with the scan width $(1.20+0.35 \tan\theta)°$ and the scan rate being varied from 1 to 5° min^{-1} (on ω). The intensities were corrected for Lorentz and polarization factors. An empirical absorption correction based on a series of ψ scans was also applied. The 2234 independent reflections with $I < 3\sigma(I)$ of the measured 3788 reflections were considered to be "observed", and were used for a structure determination.

The positions of Co, Ag, and some S atoms were determined by direct methods, and the remaining non-H atom positions were found by successive difference Fourier techniques.[15] The structure was refined by full-matrix least-squares techniques using the teXsan crystallographic software package.[15] The systematic absences led to the choice of the space group $Pna2_1$ (No. 33) or *Pnma* (No. 62). Since the cell parameters for **1**$(BF_4)_3\cdot H_2O$ were almost the same as those for the corresponding $Rh^{III}Ag^{I}_{3}Rh^{III}$ complex $[Ag_3\{Rh(aet)_3\}_2](BF_4)_3\cdot H_2O$, of which the structure has been determined for the space group *Pnma*,[14] the space group for **1**$(BF_4)_3\cdot H_2O$ was deduced to be *Pnma*, and its structure was solved by the procedure used for the structure determination of $[Ag_3\{Rh(aet)_3\}_2](BF_4)_3\cdot H_2O$. All the non-H atoms, except for B2, were refined anisotropically, and the H atoms were not included in the calculations. Ag1, Co1, Co2, C3, C4, and C7 atoms of the complex cation, B1 and F11 atoms of one BF_4^- anion, and a water oxygen atom O1 were constrained to the special positions of symmetry *m* (x, 0.25, z). The site-occupancy factor of each atom was fixed to 0.5, except for Ag2, C1, C2, C5, C8, B2, F13, F21, F22, F23, and F24. The final difference Fourier map showed a maximum peak with 1.0 e Å^{-3}, which locates in the vicinity of Ag1 atom. The final atomic coordinates for **1** are listed in Table 2.[16]

Results and Discussion

Crystal Structure of 1$(BF_4)_3\cdot H_2O$. An X-ray structural analysis for **1**$(BF_4)_3\cdot H_2O$ revealed the presence of a discrete complex cation, BF_4^- anions, and a water molecule. The number of BF_4^- anions implies that the entire complex cation is trivalent, which is consistent with the elemental analytical

Table 1. Crystallographic Data[a] for **1**$(BF_4)_3\cdot H_2O$

Chem. formula	$C_{12}H_{38}B_3N_6OF_{12}S_6Co_2Ag_3$
Fw	1176.7
Cryst color	Black
Cryst size/mm	0.38 × 0.18 × 0.15
Space group	*Pnma* (No. 62)
a/Å	16.397(2)
b/Å	13.239(2)
c/Å	15.803(4)
V/Å^3	3430.5(9)
Z	4
ρ_{calcd}/g cm^{-3}	2.28
μ/cm^{-1}	30.78
Transm coeff	0.87—1.00
R[b]	0.066
R_w[c,d]	0.072

a) $T = 23$ °C. b) $R = \sum|(|F_o| - |F_c|)|/\sum(|F_o|)$.
c) $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$. d) $S = 3.32$.

Table 2. Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters (B_{eq}/Å^2) for the Complex Cation **1**

Atom	x	y	z	B_{eq}[a)]
Ag1	−0.06571(10)	0.2500	0.92433(10)	4.02(4)
Ag2	0.09078(7)	0.13638(10)	0.88501(7)	4.08(2)
Co1	−0.0021(1)	0.2500	0.6821(1)	2.62(5)
Co2	0.0841(2)	0.2500	1.1089(2)	3.21(6)
S1	−0.0816(4)	0.3162(7)	0.7837(4)	4.5(2)
S2	0.0186(5)	0.1054(6)	0.7560(4)	3.8(2)
S3	0.1112(4)	0.3173(6)	0.7380(4)	3.7(2)
S4	0.0691(6)	0.3949(6)	1.0278(5)	4.4(2)
S5	0.1607(4)	0.1780(6)	1.0118(4)	3.7(2)
S6	−0.0297(4)	0.1850(6)	1.0578(4)	3.6(2)
N1	0.065(1)	0.185(2)	0.586(1)	3.7(5)
N2	−0.105(1)	0.193(2)	0.633(1)	5.0(6)
N3	−0.013(2)	0.376(2)	0.612(1)	5.2(7)
N4	0.104(2)	0.136(2)	1.183(2)	6.2(7)
N5	0.187(1)	0.319(2)	1.159(2)	5.7(7)
N6	0.018(1)	0.327(2)	1.199(1)	4.8(6)
C1	0.066(2)	0.072(2)	0.600(1)	9.3(7)
C2	0.101(2)	0.054(1)	0.680(1)	8.3(6)
C3	−0.179(1)	0.2500	0.751(2)	7.7(9)
C4	−0.179(2)	0.2500	0.666(3)	9(1)
C5	0.182(2)	0.058(2)	1.069(1)	11.9(8)
C6	0.180(3)	0.068(3)	1.149(3)	9(1)
C7	−0.102(2)	0.2500	1.134(1)	5.0(7)
C8	−0.079(2)	0.327(2)	1.171(2)	15(1)

a) B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

result. A perspective drawing of the entire complex cation **1** is given in Fig. 1, and its selected bond distances and angles are listed in Table 3.

The entire complex cation **1** consists of two approximately octahedral *fac*(*S*)-[Co(aet)$_3$] units and three Ag atoms. This is compatible with the plasma emission spectral analysis of **1**(BF$_4$)$_3$·H$_2$O that gave the value of Co : Ag = 2 : 3. The two *fac*(*S*)-[Co(aet)$_3$] units are connected by three Ag atoms to form an S-bridged pentanuclear structure, in which five metals form a trigonal-bipyramid (average Ag–Ag = 3.029(1) Å, Ag–Co = 3.864(3) Å, Ag–Co–Ag = 46.14(5)°, Ag–Ag–Co = 66.93(5)°). Each Ag atom has an approximately linear geometry, coordinated by two thiolato S atoms from the two terminal *fac*(*S*)-[Co(aet)$_3$] units (average Ag–S = 2.378(8) Å, S–Ag–S = 174.6(3)°).

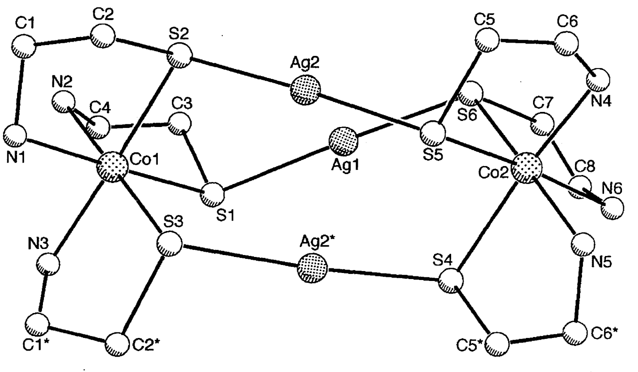

Fig. 1. A perspective view of the complex cation **1** (the ΛΛ isomer) with the atomic labeling scheme. The overlapped ΔΔ isomer is omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**

	Distances		
Ag1–S1	2.402(7)	Co1–N1	2.06(2)
Ag1–S6	2.352(7)	Co1–N2	2.01(2)
Ag2–S2	2.393(7)	Co1–N3	2.01(3)
Ag2–S5	2.372(7)	Co2–S4	2.319(8)
Ag2*–S3	2.426(7)	Co2–S5	2.200(8)
Ag2*–S4	2.321(8)	Co2–S6	2.208(7)
Co1–S1	2.247(8)	Co2–N4	1.94(3)
Co1–S2	2.269(8)	Co2–N5	2.08(3)
Co1–S3	2.242(7)	Co2–N6	2.05(2)
	Angles		
S1–Ag1–S6	171.7(2)	S4–Co2–S6	91.8(3)
S2–Ag2–S5	176.5(3)	S5–Co2–S6	93.3(3)
S3–Ag2–S4	175.6(3)	S4–Co2–N4	174.5(9)
S1–Co1–S2	92.7(3)	S4–Co2–N5	86.3(9)
S1–Co1–S3	92.5(3)	S4–Co2–N6	85.3(8)
S2–Co1–S3	90.5(3)	S5–Co2–N4	89.5(8)
S1–Co1–N1	176.6(7)	S5–Co2–N5	89.5(8)
S1–Co1–N2	86.1(7)	S5–Co2–N6	175.6(8)
S1–Co1–N3	91.3(8)	S6–Co2–N4	93.5(9)
S2–Co1–N1	86.9(7)	S6–Co2–N5	176.6(9)
S2–Co1–N2	90.5(8)	S6–Co2–N6	90.1(7)
S2–Co1–N3	175.7(8)	N4–Co2–N5	88(1)
S3–Co1–N1	90.8(7)	N4–Co2–N6	93(1)
S3–Co1–N2	178.3(8)	N5–Co2–N6	87(1)
S3–Co1–N3	87.8(8)	Ag1–S1–Co1	117.1(4)
N1–Co1–N2	90.5(9)	Ag2–S2–Co1	111.6(3)
N1–Co1–N3	89.2(9)	Ag2*–S3–Co1	111.3(3)
N2–Co1–N3	91(1)	Ag2*–S4–Co2	111.9(3)
S4–Co2–S5	91.9(3)	Ag2–S5–Co2	114.5(3)
		Ag1–S6–Co2	113.4(3)

1(BF$_4$)$_3$·H$_2$O is isostructural with the analogous Rh^{III}Ag$^{I}_3$Rh^{III} complex [Ag$_3${Rh(aet)$_3$}$_2$](BF$_4$)$_3$·H$_2$O (average Ag–Ag = 3.067(2) Å, Ag–Rh = 3.859(2) Å, Ag–Rh–Ag = 46.92(3)°, Ag–Ag–Rh = 66.54(3)°), and the Ag–S distances and the S–Ag–S angles in **1** are quite similar to those observed in [Ag$_3${Rh(aet)$_3$}$_2$]$^{3+}$ (average Ag–S = 2.376(6) Å, S–Ag–S = 176.3(3)°).[14)] However, the Co–S (average 2.248(8) Å) and Co–N (average 2.03(3) Å) distances in **1** are ca. 0.1 Å shorter than the Rh–S (average 2.319(6) Å) and Rh–N (average 2.14(2) Å) ones in [Ag$_3${Rh(aet)$_3$}$_2$]$^{3+}$, respectively, which reflects the difference in covalent radii between the Co and Rh atoms.

Considering the absolute configurations (Δ and Λ) of the two *fac*(*S*)-[Co(aet)$_3$] units, three isomers (ΔΔ, ΛΛ, and ΔΛ) are possible for [Ag$_3${Co(aet)$_3$}$_2$]$^{3+}$. Crystal **1** is a solid solution,[17)] in which the ΔΔ and ΛΛ isomers coexist in a disordered manner in the crystal lattice with a site occupancy of 0.5; the latter isomer is illustrated in Fig. 1. All six bridging sulfur atoms are fixed to the *S* configuration for the ΔΔ isomer and *R* one for the ΛΛ isomer. In addition to the cobalt and sulfur chiral centers, **1** possesses a triple helical chirality due to the three S–Ag–S linkages; the ΔΔ and ΛΛ isomers adopt the left-handed and right-handed helical configurations, respectively. These stereochemical properties are wholly consistent with those observed in $[Ag_3\{Rh(aet)_3\}_2]^{3+}$.[14]

Characterization and Properties. The reaction of *fac*(*S*)-$[Co(aet)_3]$ with Ag^+ in a ratio of 2 : 3 at room temperature gave an S-bridged $Co^{III}Ag^{I}{}_{3}Co^{III}$ pentanuclear complex $[Ag_3\{Co(aet)_3\}_2]^{3+}$ (**1**), the structure of which was determined by X-ray crystallography. When the reaction solution was chromatographed on an SP-Sephadex C-25 column, only one band for $[Ag_3\{Co(aet)_3\}_2]^{3+}$ was eluted with a 0.3 $mol\,dm^{-3}$ $NaNO_3$ aqueous solution. Furthermore, the ^{13}C NMR spectrum of **1** gives only two signals due to two kinds of methylene carbon atoms of the 6 aet ligands in the complex ($\delta = 36.64$ for CH_2S and 51.41 for CH_2N). Thus, only the racemic $\Delta\Delta/\Lambda\Lambda$ isomer with a D_3 symmetrical structure was formed for **1**, taking account of the X-ray analytical result. Molecular model constructions reveal that a significant strain on the bridging sulfur atoms exists in the meso $\Delta\Lambda$ isomer, in which the three S–Ag–S linkages are almost parallel to each other. As shown in Fig. 2 and Table 4, the absorption spectrum of **1** gives two spin-allowed d–d transition bands at ca. 17.7 and 23.5×10^3 cm^{-1} and two intense sulfur-to-cobalt charge transfer (CT) bands at ca. 36.8 and 41.0×10^3 cm^{-1}. The absorption curve of **1** roughly coincides with that of two moles of *fac*(*S*)-$[Co(aet)_3]$ (Fig. 2),[1a,6] indicating that the absorption spectrum of **1** is dominated by the two *fac*(*S*)-$[Co(aet)_3]$ units. However, some notable differences could be observed in more minute detail. That is, each absorption band for **1** shifts slightly to the higher energy side than the corresponding band for *fac*(*S*)-$[Co(aet)_3]$, and one broad sulfur-to-cobalt CT band for *fac*(*S*)-$[Co(aet)_3]$ (ca. 36.5×10^3 cm^{-1}) splits into two bands for **1**.

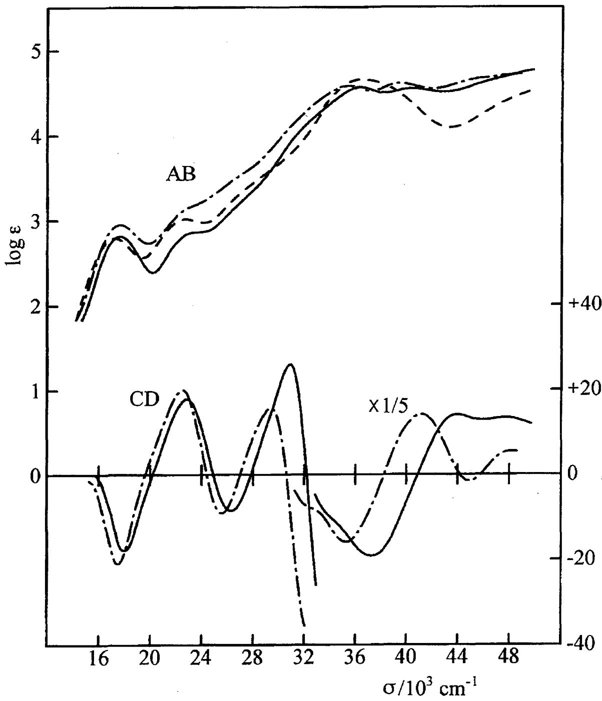

Fig. 2. Electronic absorption and CD spectra of $(-)^{CD}_{600}$-$\Delta\Delta$-**1** (—), $\Delta_{LLL}\Delta_{LLL}$-**2** (–•–), and *fac*(*S*) – $[Co(aet)_3]\times2$ (- - -) in H_2O.

A similar reaction of Δ_{LLL}-*fac*(*S*)-$[Co(L\text{-}cys\text{-}N,S)_3]^{3-}$ with Ag^+ in a ratio of 2 : 3 produced **2**, of which the absorption spectral feature is quite similar to that of **1** over the whole region, giving two d–d absorption bands at ca. 17.7 and $23.2\times10^3 cm^{-1}$ and two sulfur-to-cobalt CT bands at ca. 35.7 and 39.8×10^3 cm^{-1} (Fig. 2 and Table 3). In the d–d absorption band region, **2** exhibits one negative and one positive CD band from lower energy. This CD spectral pattern is the same as that of the starting complex, Δ_{LLL}-*fac*(*S*)-$[Co(L\text{-}cys\text{-}N,S)_3]^{3-}$ [2a,6] Furthermore, the ^{13}C NMR spectrum of **2** gives

Table 4. Absorption and CD Spectral Data of $(-)^{CD}_{600}$-$\Delta\Delta$-$[Ag_3\{Co(aet)_3\}_2]^{3+}$ (**1**) and $\Delta_{LLL}\Delta_{LLL}$-$[Ag_3\{Co(L\text{-}cys\text{-}N,S)_3\}_2]^{3-}$ (**2**) in Water

Absorption maxima $\sigma/10^3$ cm^{-1} ($\log\varepsilon/mol^{-1}$ dm^3 cm^{-1})	CD extrema $\sigma/10^3$ cm^{-1} ($\Delta\varepsilon/mol^{-1}$ dm^3 cm^{-1})
$\Delta\Delta$-$[Ag_3\{Co(aet)_3\}_2]^{3+}$	
17.70 (2.81)	18.01 (−17.8)
23.5 (2.9)^{sh}	22.91 (+17.9)
36.76 (4.56)	26.40 (−8.5)
40.98 (4.55)	30.98 (+26.0)
	37.43 (−95.6)
	44.17 (+70.8)
	47.98 (+67.0)
$\Delta_{LLL}\Delta_{LLL}$-$[Ag_3\{Co(L\text{-}cys\text{-}N,S)_3\}_2]^{3-}$	
17.73 (2.95)	17.67 (−20.9)
23.15 (3.16)	22.83 (+20.1)
35.71 (4.57)	26.04 (−9.08)
39.84 (4.61)	29.94 (+15.8)
	35.97 (−79.6)
	42.37 (+71.0)
	46.30 (−7.8)
	49.50 (+27.6)

The sh label denotes a shoulder.

three signals due to three kinds of carbon atoms of the L-cys ligands (δ = 40.25 for CH_2S, 66.43 for CH_2N, and 178.55 for COO). Taking these facts and the elemental and plasma emission analyses into consideration, **2** can be assigned as a D_3 symmetrical S-bridged $Co^{III}Ag^{I}_3Co^{III}$ complex, $\Delta_{LLL}\Delta_{LLL}$-$[Ag_3\{Co(L\text{-}cys\text{-}N,S)_3\}_2]^{3-}$, in which the two Δ_{LLL}-*fac*(*S*)-$[Co(L\text{-}cys\text{-}N,S)_3]^{3-}$ units are linked by three diagonal Ag^I atoms. That is, *fac*(*S*)-$[Co(L\text{-}cys\text{-}N,S)_3]^{3-}$, having free carboxylate groups, can be incorporated in the trigonal-bipyramid-type pentanuclear structure with a retention of the Δ_{LLL} configuration. The selective formation of the $\Delta_{LLL}\Delta_{LLL}$ isomer for $[Ag_3\{Co(L\text{-}cys\text{-}N,S)_3\}_2]^{3-}$ is supported by the QAE-Sephadex A-25 column chromatography of the reaction solution; only one adsorbed band for $[Ag_3\{Co(L\text{-}cys\text{-}N,S)_3\}_2]^{3-}$ was eluted with a 0.3 mol dm^{-3} $NaNO_3$ aqueous solution.

1 was optically resolved into the $(+)^{CD}_{600}$ and $(-)^{CD}_{600}$ isomers by SP-Sephadex C-25 column chromatography, using $[Sb_2(R,R\text{-}tartrato)_2]^{2-}$ as the resolving agent. As shown in Fig. 2, the CD spectrum of $(-)^{CD}_{600}$-**1** is in good agreement with that of $\Delta_{LLL}\Delta_{LLL}$-$[Ag_3\{Co(L\text{-}cys\text{-}N,S)_3\}_2]^{3-}$ over the whole region, though each CD band for $(-)^{CD}_{600}$-**1** shifts to the higher energy side. Thus, it is assigned that the $(-)^{CD}_{600}$ isomer of **1** has the $\Delta\Delta$ configuration, while the $(+)^{CD}_{600}$ isomer, which shows a CD spectrum enantiomeric to that of the $(-)^{CD}_{600}$ isomer, has the $\Lambda\Lambda$ configuration. $\Delta\Delta$-**1** possesses three kinds of chiralities: a Δ configuration for the two *fac*(*S*)-$[Co(aet)_3]$ unit, an *S* configuration for the six asymmetric sulfur atoms, and a left-handed configuration for the triple helical structure. Figure 3 compares the CD spectrum of $\Delta\Delta$-**1** with that of 0.5 mol of $\Delta\Delta\Delta\Delta$-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$, of which the absorption spectrum is dominated by the *fac*(*S*)-$[Co(aet)_3]$ units, as in the case of the absorption spectrum of **1**.[6] Since $\Delta\Delta\Delta\Delta$-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$ has chiralities due to four Δ configurational *fac*(*S*)-$[Co(aet)_3]$ units and twelve *S* configurational sulfur atoms,[6] it is reasonable to assume that the CD spectral difference between $\Delta\Delta$-**1** and 0.5 mol of $\Delta\Delta\Delta\Delta$-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$ is due to the presence of the left-handed triple helical chirality in $\Delta\Delta$-**1**. In the first d–d absorption band region (ca. 16—20×10^3 cm^{-1}) the CD spectrum of $\Delta\Delta$-**1** resembles that of 0.5 mol of $\Delta\Delta\Delta\Delta$-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$, suggesting that the CD contribution due to the helical chirality is relatively small in this region. On the other hand, in the second d–d and the sulfur-to-cobalt CT bands region (ca. 20—40×10^3 cm^{-1}), the CD intensity of each band for $\Delta\Delta$-**1** is much lower than that for 0.5 mol of $\Delta\Delta\Delta\Delta$-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$, though they show CD spectral patterns similar to each other. This CD spectral deviation suggests that the left-handed triple helical chirality in $\Delta\Delta$-**1** contributes significantly to the CD spectrum in this region and that its CD contribution is opposite in sign to the contribution from a combination of the Δ configurational *fac*(*S*)-$[Co(aet)_3]$ units and the *S* configurational sulfur atoms.

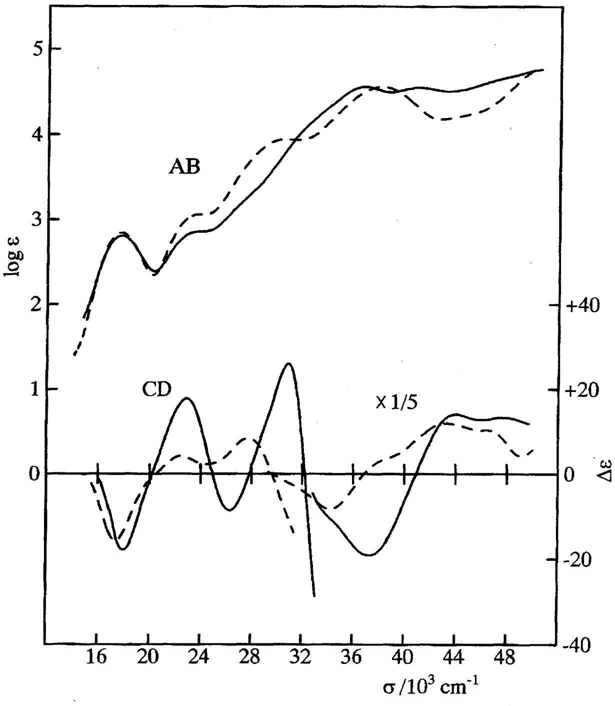

Fig. 3. Electronic absorption and CD spectra of $(-)^{CD}_{600}$-$\Delta\Delta$-**1** (—) and $\Delta\Delta\Delta\Delta$-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$×0.5 (- - -) in H_2O.

No significant absorption or CD spectral changes with time were noticed for $\Delta\Delta$-**1** in water, at least for several hours. Furthermore, the addition of excess $Co(NO_3)_2\cdot6H_2O$ to an aqueous solution of $\Delta\Delta$-**1**, followed by warming at 60 °C for 1 h, caused little absorption and CD spectral changes. The absorption and CD spectral behavior implies that **1** is fairly stable in solution, retaining the S-bridged $Co^{III}Ag^{I}_3Co^{III}$ pentanuclear structure observed in the crystal. However, it was found that **1** is convertible to the linear-type S-bridged tricobalt(III) structure in $[Co\{Co(aet)_3\}_2]^{3+}$ by a reaction with NaI in the presence of excess $Co(NO_3)_2\cdot6H_2O$. Since $[Co\{Co(aet)_3\}_2]^{3+}$ has been produced by a reaction of *fac*(*S*)-$[Co(aet)_3]$ with Co^{2+}, owing to air oxidation,[1a,3d] it is seen that the two-coordinated Ag^I atoms in **1** are reactive toward the I^- ion, which causes a cleavage of the Ag–S bonds in **1**. In this reaction, the meso $\Delta\Lambda$ isomer, besides the racemic $\Delta\Delta/\Lambda\Lambda$ isomer of $[Co\{Co(aet)_3\}_2]^{3+}$, were derived from the racemic $\Delta\Delta/\Lambda\Lambda$-**1** in a ratio of ca. 1 : 1. If the formation of the meso $\Delta\Lambda$ isomer is caused only by the racemization of the Δ/Λ-*fac*(*S*)-$[Co(aet)_3]$ units, $\Delta\Delta$-, $\Lambda\Lambda$-, and $\Delta\Lambda$-$[Co\{Co(aet)_3\}_2]^{3+}$ should be formed in a ratio of ca. 1 : 1 : 2 by using $\Delta\Delta$-**1** as a staring complex. However, a reaction using $\Delta\Delta$-**1** under the same conditions gave $\Delta\Delta$-, $\Lambda\Lambda$-, and $\Delta\Lambda$-$[Co\{Co(aet)_3\}_2]^{3+}$ in a ratio of ca. 5 : 1 : 4. Accordingly, it is considered that not only the racemization of the Δ/Λ-*fac*(*S*)-$[Co(aet)_3]$ units, but also the intermolecular exchange of the Δ/Λ-*fac*(*S*)-$[Co(aet)_3]$ units occur through the conversion reaction of the S-bridged $Co^{III}Ag^{I}_3Co^{III}$ pentanuclear structure in **1** to the $Co^{III}Co^{III}Co^{III}$ trinuclear structure in $[Co\{Co(aet)_3\}_2]^{3+}$. Here, it should be note that the same reaction using NaCl instead of NaI gave a dark-brown crystalline product,[18] which dissolves in water to show an absorption spectrum identical with that of **1**; the formation of $[Co\{Co(aet)_3\}_2]^{3+}$ was not noticed. Considering the elemental analytical data of this dark-brown complex,[18] although the Cl^- ion may be assumed to have an affinity toward the Ag^I atom in **1**, its affinity is not strong enough to break the Ag–S bonds.

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References

1) a) D. H. Busch and D. C. Jicha, *Inorg. Chem.*, **1**, 884 (1962); b) G. R. Brubaker and B. E. Douglas, *Inorg. Chem.*, **6**, 1562 (1967); c) M. J. Heeg, E. L. Blinn, and E. Deutsch, *Inorg. Chem.*, **24**, 1118 (1985).

2) a) R. E. DeSimone, T. Ontko, L. Wardman, and E. L. Blinn, *Inorg. Chem.*, **14**, 1313 (1975); b) J. Suades, X. Solans, M. F-Altaba, and M. Aguilo, *Inorg. Chim. Acta*, **99**, 1 (1985); c) G. R. Brubaker, M. G. Henk, and D. W. Johnson, *Inorg. Chim. Acta*, **100**, 201 (1985); d) D. W. Johnson and T. R. Brewer, *Inorg. Chim. Acta*, **151**, 221 (1988); e) T. Konno, K. Okamoto, and J. Hidaka, *Acta Crystallogr., Sect. C*, **49**, 222 (1993).

3) a) T. Konno, S. Aizawa, K. Okamoto, and J. Hidaka, *Chem. Lett.*, **1985**, 1017; b) K. Okamoto, S. Aizawa, T. Konno, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **59**, 3859 (1986); c) K. Okamoto, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **61**, 1601 (1988); d) T. Konno, S. Aizawa, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **62**, 585 (1989).

4) a) T. Konno, S. Aizawa, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **63**, 792 (1990); b) T. Konno and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **68**, 610 (1995).

5) T. Konno, K. Nakamura, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **66**, 2582 (1993).

6) T. Konno, T. Nagashio, K. Okamoto, and J. Hidaka, *Inorg. Chem.*, **31**, 1160 (1992).

7) T. Konno, K. Okamoto, and J. Hidaka, *Inorg. Chem.*, **33**, 538 (1994).

8) K. Okamoto, T. Konno, and J. Hidaka, *J. Chem. Soc., Dalton Trans.*, **1994**, 533.

9) a) T. Konno, K. Okamoto, and J. Hidaka, *Chem. Lett.*, **1990**, 1043; b) T. Konno, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **67**, 101 (1994).

10) a) T. Konno, Y. Kageyama, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **67**, 1957 (1994); b) Y. Kageyama, T. Konno, K. Okamoto, and J. Hidaka, *Inorg. Chim. Acta*, **239**, 19 (1995).

11) a) K. Okamoto, T. Konno, Y. Kageyama, and J. Hidaka, *Chem. Lett.*, **1992**, 1105; b) K. Okamoto, Y. Kageyama, and T. Konno, *Bull. Chem. Soc. Jpn.*, **68**, 2573 (1995).

12) T. Konno, K. Okamoto, and J. Hidaka, *Inorg. Chem.*, **31**, 3875 (1992).

13) T. Konno, C. Sasaki, and K. Okamoto, *Chem. Lett.*, **1996**, 977.

14) T. Konno and K. Okamoto, *Inorg. Chem.*, **36**, 1403 (1997).

15) "Crystal Structure Analysis Package," Molecular Structure Corporation, 1985 & 1992.

16) List of structure factors, bond distances and angles, and anisotropic thermal parameters for **1**$(BF_4)_3\cdot H_2O$ and a figure of perspective view of disordered complex cation **1** are deposited as Document No. 71023 at the Office of Editor of Bull. Chem. Soc. Jpn.

17) J. Jacques, A. Collet, and S. H. Wilen, "Enantiomers, Racemates and Resolutions," John Wiley & Sons Ltd., New York (1981).

18) Treatment of a solution containing **1**$(BF_4)_3\cdot H_2O$ (0.10 g, 0.085 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (0.25 g, 0.86 mmol) in 20 cm^3 of water with NaCl (0.015 g, 0.26 mmol), followed by stirring at 60 °C for 1 h, gave a dark brown crystalline product, which was collected by filtration. Yield: 0.08 g (86%). Anal. Calcd for $[Co_2Ag_3Cl(C_{12}H_{36}N_6S_6)](NO_3)_2\cdot 2H_2O$: C, 13.18; H, 3.69; N, 10.24%. Found: C, 12.99; H, 3.66; N, 10.21%.