© 2002 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 75, 2185–2193 (2002)

Aggregation of Cobalt(III) Complexes with Single Thiolato or Selenolato Group Assisted by Ag^I Ion: Crystal Structures of Spontaneously Resolved 1D Coordination Polymers $[Ag\{Co(aet\ or\ aese)(en)_2\}](NO_3)_3$ (aet = 2-Aminoethanethiolate, aese = 2-Aminoethaneselenolate)

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(Received May 10, 2002)

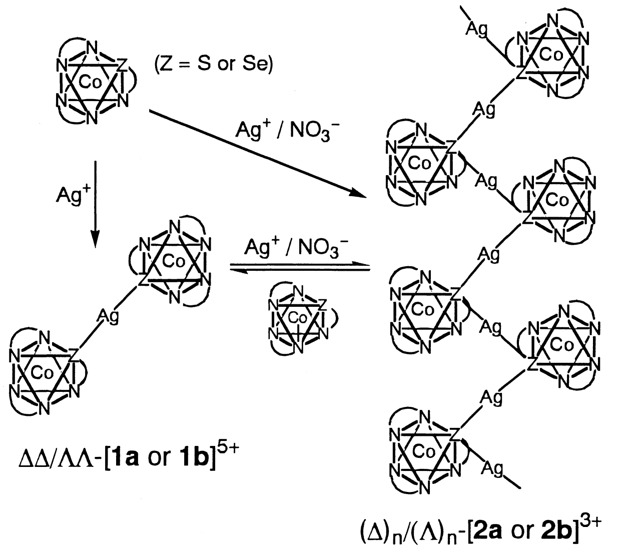
The reactions of $[Co(aet)(en)_2](NO_3)_2$ (aet = 2-aminoethanethiolate) or $[Co(aese)(en)_2](NO_3)_2$ (aese = 2-aminoethaneselenolate) with $AgNO_3$ in a 2:1 ratio in water gave S- or Se-bridged $Co^{III}Ag^{I}Co^{III}$ trinuclear complexes: $[Ag\{Co(aet)(en)_2\}_2](NO_3)_5$ ($[\mathbf{1a}](NO_3)_5$) and $[Ag\{Co(aese)(en)_2\}_2](NO_3)_5$ ($[\mathbf{1b}](NO_3)_5$), while the corresponding 1:1 reactions produced S- or Se-bridged $(Co^{III}Ag^{I})_n$ chain complex-polymers: $[Ag\{Co(aet)(en)_2\}](NO_3)_3$ ($[\mathbf{2a}](NO_3)_3$) and $[Ag\{Co(aese)(en)_2\}](NO_3)_3$ ($[\mathbf{2b}](NO_3)_3$). While the mononuclear $[Co(aet\ or\ aese)(en)_2](NO_3)_2$ and the trinuclear $[\mathbf{1a}$ or $\mathbf{1b}](NO_3)_5$ were racemates, the polymeric $[\mathbf{2a}$ or $\mathbf{2b}](NO_3)_3$ crystallized as a conglomerate to give optically active crystals of Δ and Λ isomers. The crystal structures of Λ-$[\mathbf{2a}](NO_3)_3 \cdot H_2O$ and Λ-$[\mathbf{2b}](NO_3)_3 \cdot H_2O$ were determined by X-ray crystallography. In Λ-$[\mathbf{2a}]^{3+}$ or Λ-$[\mathbf{2b}]^{3+}$, the S or Se atom in each octahedral Λ-$[Co(aet\ or\ aese)(en)_2]^{2+}$ unit is bound to two Ag^I atoms to form a one-dimensional $(Co^{III}Ag^{I})_n$ zigzag chain. Each Ag^I atom in Λ-$[\mathbf{2a}]^{3+}$ or Λ-$[\mathbf{2b}]^{3+}$ is closely contacted with NO_3^- anions, which stabilizes the chiral chain structure. The crystal structure of $[\mathbf{1a}]^{5+}$ was also determined by X-ray crystallography for its ClO_4^- salt ($[\mathbf{1a}](ClO_4)_5 \cdot 2H_2O$), which established that $[\mathbf{1a}]^{5+}$ exists as a racemic compound containing both the ΔΔ and the ΛΛ isomers in the crystal. The optically active S- or Se-bridged complexes, ΛΛ-$[\mathbf{1a}$ or $\mathbf{1b}]^{5+}$ and Λ-$[\mathbf{2a}$ or $\mathbf{2b}]^{3+}$, were obtained by the use of Λ-$[Co(aet\ or\ aese)(en)_2]^{2+}$ as the starting complex, indicating that the reactions with Ag^+ proceed with retention of the absolute configuration of the Co^{III} chiral center.

A thiolato atom coordinated to one Co^{III} center retains some of its nucleophilicity, which allows a mononuclear Co^{III} complex with thiolato groups to function as an S-donating complex-ligand toward a certain metal ion. To date, a number of S-bridged polynuclear complexes aggregating tris(thiolato)-type Co^{III} octahedral units have been prepared by using *fac(S)*-$[Co(aet)_3]$ or *fac(S)*-$[Co(L\text{-}cys\text{-}N,S)_3]^{3-}$ as an S-donating tridentate complex-ligand (aet = 2-aminoethanethiolate ($NH_2CH_2CH_2S^-$); L-cys = L-cysteinate ($NH_2CH(COO^-)CH_2S^-$)), and their unique stereochemical and spectroscopic properties have been recorded and interpreted.[1–12] On the other hand, the chemistry of S-bridged polynuclear complexes aggregating mono(thiolato)-type Co^{III} units has largely been unexplored, although it has been pointed out that Co^{III} complexes with a single thiolato donor atom possess an ability to bind with soft metal ions such as Ag^I, Hg^{II}, and Pt^{II}.[13–15]

In 1979 Heeg et al. reported that the mono(thiolato)-type Co^{III} complexes, $[Co(aet)(en)_2]^{2+}$ and $[Co(tga)(en)_2]^+$ (tga = mercaptoacetate ($^-SCH_2COO^-$)), readily form 1:1 and 2:1 adducts with Ag^I or Hg^{II} in water.[14] Only the 2:1 adducts with Ag^I that were isolated as solid samples have been characterized to have an S-bridged $Co^{III}Ag^{I}Co^{III}$ trinuclear structure in $[Ag\{Co(aet\ or\ tga)(en)_2\}_2]^{5+\ or\ 3+}$.[14,15] No further reports concerning these adducts have appeared to date, despite intensive interest concerning the structures and chiral properties of S-bridged polynuclear complexes constructed by the aggregation of thiolato metal complexes. In this context, it is worthwhile to examine this fundamental system in detail, in order to find key factors to control the aggregation of thiolato complexes assisted by metal ions. A preliminary report concerning the 2:1 and 1:1 S-bridged adducts of $[Co(aet)(en)_2]^{2+}$ with Ag^I, $[Ag\{Co(aet)(en)_2\}_2]^{5+}$ ($[\mathbf{1a}]^{5+}$) and $[Ag\{Co(aet)(en)_2\}]^{3+}$ ($[\mathbf{2a}]^{3+}$), has been presented.[16] In this paper, we report on the complete description of syntheses and chemical and structural characterizations of $[\mathbf{1a}]^{5+}$ and $[\mathbf{2a}]^{3+}$, along with those of the corresponding Se-bridged adducts, $[Ag\{Co(aese)(en)_2\}_2]^{5+}$ ($[\mathbf{1b}]^{5+}$) and $[Ag\{Co(aet)(en)_2\}]^{3+}$ ($[\mathbf{2b}]^{3+}$), which were prepared by the 2:1 and 1:1 reactions of $[Co(aese)(en)_2]^{2+}$ (aese = 2-aminoethaneselenolate ($NH_2CH_2CH_2Se^-$)) with Ag^I (Scheme 1). To our knowledge, $[\mathbf{1b}]^{5+}$ and $[\mathbf{2b}]^{3+}$ are the first examples of Se-bridged aggregates composed of mono(selenolato)-type Co^{III} octahedrons.

Experimental

Preparation of Complexes. **$[Ag\{Co(aet)(en)_2\}_2](NO_3)_5$ ($[\mathbf{1a}](NO_3)_5$).** To a solution containing 0.50 g (1.32 mmol) of $[Co(aet)(en)_2](NO_3)_2$ [17] in 35 cm^3 of water was added a solution containing 0.11 g (0.65 mmol) of $AgNO_3$ in 5 cm^3 of water. The mixture was stirred at room temperature for 30 min, during which time the color of the solution turned from dark-brown to dark-red.



Scheme 1.

To this dark-red reaction solution was added a solution containing 0.5 g of $NaNO_3$ in 2 cm^3 of water, followed by cooling in a refrigerator for 2 days. The resulting dark-red crystals were collected by filtration. Yield: 0.61 g (93%). Anal. Calcd for [**1a**]$(NO_3)_5\cdot 4H_2O$: C, 14.41; H, 5.24; N, 21.00%. Found: C, 14.49; H, 5.10; N, 21.08%. Molar conductivity in H_2O: 605 Ω^{-1} cm^2 mol^{-1}. ^{13}C NMR (D_2O, ppm from DSS) δ 32.94 (CH_2S), 46.35, 46.69, 47.45, 47.74 (CH_2NH_2 of en), and 52.29 (CH_2NH_2 of aet).

[Ag{Co(aet)(en)$_2$}$_2$](ClO$_4$)$_5$ ([1a](ClO$_4$)$_5$). Method 1. To a solution containing 0.20 g of [**1a**]$(NO_3)_5\cdot 4H_2O$ in 10 cm^3 of water was added a solution containing 2.0 g of $NaClO_4\cdot H_2O$ dissolved in a small amount of water, which gave a crystalline precipitate immediately. After the mixture was allowed to stand at room temperature overnight, the resulting microcrystals were collected by filtration. This complex was recrystallized from water by adding a few drops of a saturated aqueous solution of $NaClO_4$. One of the crystals thus obtained was used for X-ray analysis. Yield: 0.18 g (78%). Anal. Calcd for [**1a**]$(ClO_4)_5\cdot 2H_2O$: C, 12.51; H, 4.20; N, 12.16%. Found: C, 12.44; H, 4.24; N, 12.08%. Molar conductivity in H_2O: 597 Ω^{-1} cm^2 mol^{-1}.

Method 2. To a solution containing 0.50 g (1.32 mmol) of $[Co(aet)(en)_2](NO_3)_2$ [17] in 45 cm^3 of water was added a solution containing 0.22 g (1.30 mmol) of $AgNO_3$ in 5 cm^3 of water. The mixture was stirred at room temperature for 30 min, during which time the color of the solution turned from dark-brown to dark-red. To this dark-red reaction solution was added a solution containing 16 g of $NaClO_4\cdot H_2O$ in 10 cm^3 of water, followed by cooling in a refrigerator for 3 days. The resulting dark-red crystals were collected by filtration. Yield: 0.57 g (75%). Anal. Calcd for [**1a**]$(ClO_4)_5\cdot 2H_2O$: C, 12.51; H, 4.20; N, 12.16%. Found: C, 12.43; H, 4.29; N, 12.07%.

[Ag{Co(aet)(en)$_2$}$_2$](BF$_4$)$_5$ ([1a](BF$_4$)$_5$). To a solution containing 0.50 g (1.32 mmol) of $[Co(aet)(en)_2](NO_3)_2$ in 45 cm^3 of water was added a solution containing 0.22 g (1.30 mmol) of $AgNO_3$ in 5 cm^3 of water. The mixture was stirred at room temperature for 30 min, during which time the color of the solution turned from dark-brown to dark-red. To this dark-red reaction solution was added a solution containing 13 g of $NaBF_4$ in 10 cm^3 of water, followed by cooling in a refrigerator for 3 days. The resulting dark-red crystals were collected by filtration. Yield: 0.40 g (54%). Anal. Calcd for [**1a**]$(BF_4)_5\cdot 4H_2O$: C, 12.82; H, 4.66; N, 12.46%. Found: C, 12.68; H, 4.84; N, 12.22%. Molar conductivity in H_2O: 593 Ω^{-1} cm^2 mol^{-1}.

$(-)^{CD}_{280}$-[Ag{Co(aet)(en)$_2$}$_2$](NO$_3$)$_5$ ($(-)^{CD}_{280}$-[1a](NO$_3$)$_5$). To a solution containing 0.21 g (0.46 mmol) of Λ-$[Co(aet)(en)_2](ClO_4)_2$ [18] in 15 cm^3 of water was added a solution containing 0.04 g (0.24 mmol) of $AgNO_3$ in 5 cm^3 of water. The mixture was stirred at room temperature for 30 min, during which time the color of solution turned from dark-brown to dark-red. To this dark-red reaction solution was added a solution containing 1.0 g of $NaNO_3$ in 2 cm^3 of water. This mixture was allowed to stand at room temperature for 1 day. The resulting pink crystalline powder was collected by filtration and recrystallized from water by adding an aqueous solution of $NaNO_3$. Yield: 0.20 g (86%). Anal. Calcd for [**1a**]$(NO_3)_5\cdot 4H_2O$: C, 14.41; H, 5.24; N, 21.00%. Found: C,14.46; H, 5.03; N, 20.99%.

[Ag{Co(aet)(en)$_2$}](NO$_3$)$_3$ ([2a](NO$_3$)$_3$). Method 1. To a solution containing 0.20 g (0.20 mmol) of [**1a**]$(NO_3)_5\cdot 4H_2O$ in 15 cm^3 of water was added a solution containing 0.04 g (0.24 mmol) of $AgNO_3$ in 2 cm^3 of water. The mixture was stirred at room temperature for 30 min. To the dark-red reaction solution were added a few drops of a saturated aqueous solution of $NaNO_3$, followed by cooling in a refrigerator for 2 days. The resulting pink powder was collected by filtration. Yield: 0.18 g (79%). Anal. Calcd for [**2a**]$(NO_3)_3\cdot H_2O$: C, 12.71; H, 4.27; N, 19.76%. Found: C, 12.71; H, 4.30; N, 19.68%. Molar conductivity in H_2O: 365 Ω^{-1} cm^2 mol^{-1}. ^{13}C NMR (D_2O, ppm from DSS): δ 33.43 (CH_2S), 46.40, 46.69, 47.44, 47.71 (CH_2NH_2 of en), and 52.38 (CH_2NH_2 of aet).

Single crystals of [**2a**]$(NO_3)_3\cdot H_2O$ suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution of the pink powder at room temperature.

Method 2. To a solution containing 0.50 g (1.32 mmol) of $[Co(aet)(en)_2](NO_3)_2$ in 45 cm^3 of water was added a solution containing 0.23 g (1.35 mmol) of $AgNO_3$ in 5 cm^3 of water. The mixture was stirred at room temperature for 30 min, during which time the color of solution turned from dark-brown to dark-red. To this dark-red reaction solution was added a solution containing 0.5 g of $NaNO_3$ in 1 cm^3 of water. This mixture was allowed to stand at room temperature for 3 days. The resulting pink powder was collected by filtration. Yield: 0.63 g (84%). Anal. Calcd for [**2a**]$(NO_3)_3\cdot H_2O$: C, 12.71; H, 4.27; N, 19.76%. Found: C, 12.83; H, 4.43; N, 19.73%.

$(-)^{CD}_{280}$-[Ag{Co(aet)(en)$_2$}](NO$_3$)$_3$ ($(-)^{CD}_{280}$-[2a](NO$_3$)$_3$). To a solution containing 0.21 g (0.46 mmol) of Λ-$[Co(aet)(en)_2](ClO_4)_2$ in 25 cm^3 of water was added a solution containing 0.08 g (0.47 mmol) of $AgNO_3$ in 5 cm^3 of water. The mixture was stirred at room temperature for 30 min, during which time the color of solution turned from dark-brown to dark-red. To this dark-red reaction solution was added a solution containing 1.0 g of $NaNO_3$ in 2 cm^3 of water. This mixture was allowed to stand at room temperature for 1 day. The resulting crystalline powder was collected by filtration and recrystallized from water by adding an aqueous solution of $NaNO_3$. Yield: 0.23 g (88%). Anal. Calcd for [**2a**]$(NO_3)_3\cdot H_2O$: C, 12.71; H, 4.27; N, 19.76%. Found: C, 12.82; H, 4.30; N, 19.77%.

Conversion of [2a](NO$_3$)$_3$ to [1a](NO$_3$)$_5$. To a solution containing 0.28 g (0.49 mmol) of [**2a**]$(NO_3)_3\cdot H_2O$ in 30 cm^3 of water was added a solution containing 0.19 g (0.50 mmol) of $[Co(aet)(en)_2](NO_3)_2$ in 15 cm^3 of water, and the mixture was stirred at room temperature for 30 min. After a few drops of a saturated aqueous solution of $NaNO_3$ were added, the dark-red reaction solution was stored in a refrigerator for 5 days. The resulting dark-red crystals were collected by filtration. Yield: 0.38 g (77%). Anal. Calcd for [**1a**]$(NO_3)_5\cdot 4H_2O$: C, 14.41; H, 5.24; N, 21.00%. Found: C, 14.55; H, 5.20; N, 21.10%.

[Ag{Co(aese)(en)$_2$}$_2$](NO$_3$)$_5$ ([1b](NO$_3$)$_5$). To a solution containing 0.30 g (0.68 mmol) of $[Co(aese)(en)_2](NO_3)_2\cdot H_2O$ [18,19] in 80 cm^3 of water was added a solution containing 0.06 g (0.35 mmol) of $AgNO_3$ in 20 cm^3 of water. The mixture was stirred at room temperature for 30 min, during which time the color of the solution turned from dark-brown to dark-red. To this dark-red reaction solution was added a solution containing 0.5 g of $NaNO_3$ in 2 cm^3 of water, followed by cooling in a refrigerator for 4 days. The resulting dark-red crystals were collected by filtration. Yield: 0.27 g (72%). Anal. Calcd for [**1b**]$(NO_3)_5\cdot 4.5H_2O$: C, 13.06; H, 4.84; N, 19.04%. Found: C, 12.84; H, 4.56; N, 18.86%. ^{13}C NMR (D_2O, ppm from DSS) δ 22.43 (CH_2Se), 46.04, 47.03, 47.86, 48.66 (CH_2NH_2 of en), and 53.22 (CH_2NH_2 of aese). Molar conductivity in H_2O: 624 Ω^{-1} cm^2 mol^{-1}.

$(-)^{CD}_{300}$-[Ag{Co(aese)(en)$_2$}$_2$](NO$_3$)$_5$ ($(-)^{CD}_{300}$-[1b](NO$_3$)$_5$). To a solution containing 0.020 g (0.040 mmol) of Λ-$[Co(aese)(en)_2](ClO_4)_2$ [18] in 15 cm^3 of water was added a solution containing 0.004 g (0.024 mmol) of $AgNO_3$ in 2 cm^3 of water. The mixture was stirred at room temperature for 30 min, during which time the color of solution turned from dark-brown to dark-red. To this dark-red reaction solution was added a few drops of saturated aqueous solution of $NaNO_3$. This mixture was allowed to stand at room temperature for 1 day. The resulting dark-red crystals were collected by filtration. Yield: 0.014 g.

The concentration of an aqueous solution of $(-)^{CD}_{300}$-[**1b**]$(NO_3)_5$ used for CD spectral measurements was evaluated on the basis of the absorption spectral datum of its racemate.

[Ag{Co(aese)(en)$_2$}](NO$_3$)$_3$ ([2b](NO$_3$)$_3$). To a solution containing 0.20 g (0.45 mmol) of $[Co(aese)(en)_2](NO_3)_2\cdot H_2O$ in 25 cm^3 of water was added a solution containing 0.08 g (0.47 mmol) of $AgNO_3$ in 5 cm^3 of water. The mixture was stirred at room temperature for 30 min, during which time the color of solution turned from dark-brown to dark-red. To this dark-red reaction solution was added a solution containing 0.5 g of $NaNO_3$ in 1 cm^3 of water. This mixture was allowed to stand at room temperature for 4 days. The resulting dark-red powder was collected by filtration. Yield: 0.25 g (79%). Anal. Calcd for [**2b**]$(NO_3)_3\cdot 2H_2O$: C, 11.40; H, 4.15; N, 17.73%. Found: C, 11.54; H, 4.02; N, 17.81%. ^{13}C NMR (D_2O, ppm from DSS) δ 23.01 (CH_2Se), 46.12, 47.02, 47.84, 48.63 (CH_2NH_2 of en), and 53.38 (CH_2NH_2 of aese). Molar conductivity in H_2O: 366 Ω^{-1} cm^2 mol^{-1}. Single crystals of [**2b**]$(NO_3)_3\cdot H_2O$ suitable for X-ray analysis were obtained by slow evaporation of an aqueous solution of the dark-red powder at room temperature.

$(-)^{CD}_{300}$-[Ag{Co(aese)(en)$_2$}](NO$_3$)$_3$ ($(-)^{CD}_{300}$-[2b](NO$_3$)$_3$). To a solution containing 0.020 g (0.040 mmol) of Λ-$[Co(aese)(en)_2](ClO_4)_2$ in 25 cm^3 of water was added a solution containing 0.007 g (0.041 mmol) of $AgNO_3$ in 4 cm^3 of water. The mixture was stirred at room temperature for 30 min, during which time the color of solution turned from brown to dark-red. To this dark-red reaction solution was added a solution containing 0.5 g of $NaNO_3$ in 1 cm^3 of water. This mixture was allowed to stand at room temperature for 1 day. The resulting crystalline powder was collected by filtration and recrystallized from water by adding an aqueous solution of $NaNO_3$. Yield: 0.014 g.

The concentration of an aqueous solution of $((-)^{CD}_{300}$-[**2b**]$(NO_3)_5$ used for CD spectral measurements was evaluated on the basis of the absorption spectral datum of its racemate.

Caution! *Perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities.*

Measurements. The electronic absorption spectra were recorded with a JASCO Ubest-55 spectrometer, and the CD spectra with a JASCO J-700 spectropolarimeter at room temperature. The ^{13}C NMR spectra were recorded in D_2O with a JOEL JNM-A500 NMR spectrometer at probe temperature. 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 SHIMADZU ICPS-1000III ICP spectrophotometer. The molar conductivities were measured with a Horiba DS-12 conductivity meter in water.

X-ray Structure Determination. Single crystals of [**1a**]$(ClO_4)_5\cdot 2H_2O$, [**2a**]$(NO_3)_3\cdot H_2O$, and [**2b**]$(NO_3)_3\cdot H_2O$ were used for data collection on a Rigaku AFC-7S four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Crystallographic data are summarized in Table 1. Unit cell parameters were determined by a least-squares refinement, using the setting angles of 25 reflections in the ranges of $29.6° < 2\theta < 30.0°$, $26.0° < 2\theta < 29.8°$, and $23.92° < 2\theta < 29.47°$ for [**1a**]$(ClO_4)_5\cdot 2H_2O$, [**2a**]$(NO_3)_3\cdot H_2O$, and [**2b**]$(NO_3)_3\cdot H_2O$, respectively. The intensity

Table 1. Crystallographic Data[a)] for [**1a**]$(ClO_4)_5\cdot 2H_2O$, [**2a**]$(NO_3)_3\cdot H_2O$, and [**2b**]$(NO_3)_3\cdot H_2O$

	[**1a**]$(ClO_4)_5\cdot 2H_2O$	[**2a**]$(NO_3)_3\cdot H_2O$	[**2b**]$(NO_3)_3\cdot H_2O$
Empirical formula	$C_{12}H_{48}AgCl_5Co_2N_{10}O_{22}S_2$	$C_6H_{24}AgCoN_8O_{10}S$	$C_6H_{24}AgCoN_8O_{10}Se$
Fw	1151.7	567.2	614.1
Space group	$C2/c$ (no. 15)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a/Å	15.820(3)	13.852(2)	13.966(1)
b/Å	8.943(3)	15.746(1)	15.638(1)
c/Å	27.592(3)	8.135(2)	8.290(2)
β/deg	97.16(1)		
V/Å^3	3873(1)	1774.3(4)	1810.5(4)
Z	4	4	4
ρ_{calcd}/g cm^{-3}	1.975	2.123	2.253
μ/cm^{-1}	18.89	22.22	40.73
R[b)]	0.051	0.033	0.033
R_w[c)]	0.053	0.033	0.034

a) $T = 23$ °C; λ(Mo $K\alpha$) = 0.71073 Å. b) $R = \Sigma|(|F_o| - |F_c|)|/\Sigma(|F_o|)$.
c) $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$.

data were collected by the ω-2θ scan mode up to $2\theta = 55°$. The intensities were corrected for Lorentz and polarization. Empirical absorption corrections based on a series of ψ scans were also applied. The 3230, 1902, and 2055 independent reflections with $I > 2\sigma(I)$ of the measured 4747, 2349, and 2369 reflections were considered as 'observed' and were used for structure determinations of [**1a**]$(ClO_4)_5 \cdot 2H_2O$, [**2a**]$(NO_3)_3 \cdot H_2O$, and [**2b**]$(NO_3)_3 \cdot H_2O$, respectively.

The structures were solved by the Patterson method and were expanded using Fourier techniques. H atoms, except for water H atoms, were located and added to calculations but not refined. For [**1a**]$(ClO_4)_5 \cdot 2H_2O$ one of two en chelate rings was disordered with C atoms in two alternative positions, corresponding to the disorder of one of the ClO_4^- anions. The disordered atoms, C6a, C6b, and O33, were refined with a site occupancy factor of 0.5. Ag1, Cl3, and O32 were constrained to the special positions of symmetry *2* (0, *y*, 0.25) with a site occupancy factor of 0.5. H atoms attached to the disordered en chelate ring besides water H atoms were not included in the calculation. All of the calculations were performed using the teXsan crystallographic software package.[20]

Lists of final atomic coordinates and thermal factors and of bond distances and angles are deposited as Document No. 75040 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 184954–184956.

Results and Discussion

Crystal Structure of [Ag{Co(aet)(en)$_2$}$_2$](ClO$_4$)$_5$ ([1a]-(ClO$_4$)$_5$). X-ray structural analysis of [**1a**]$(ClO_4)_5 \cdot 2H_2O$ showed the presence of a discrete complex cation, perchlorate anions, and water molecules. The total number of ClO_4^- anions implies that the entire complex cation is heptavalent. A perspective drawing of the complex cation [**1a**]$^{5+}$ is shown in Fig. 1, and its selected bond distances and angles are listed in Table 2.

The complex cation [**1a**]$^{5+}$ consists of two approximately octahedral $[Co(aet)(en)_2]^+$ units that are linked by one Ag^I atom, forming an S-bridged Co^{III}Ag^{I}Co^{III} trinuclear structure in $[Ag\{Co(aet)(en)_2\}_2]^{5+}$. This trinuclear structure is the same as that reported by Heeg et al.,[14] which has been poorly determined ($R > 0.17$). The S–Ag–S angle (164.50(8)°) in [**1a**]$^{5+}$ deviats from 180°. This is ascribed to weak interactions between the central Ag^I atom and ClO_4^- anions (Ag···O = 2.884(9) Å, 2.884(9) Å, and 3.01(1) Å) (Fig. 1). The Co–S (2.259(2) Å) and Ag–S (2.400(1) Å) bond distances in [**1a**]$^{5+}$ are similar to those observed for the related Co^{III}Ag^{I}Co^{III} trinuclear structures in $[Ag\{Co(tga)(en)_2\}_2]^{3+}$ (Co–S = 2.247(1) Å, Ag–S = 2.370(1) Å) and $\Lambda_L\Lambda_L$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{3+}$ (average Co–S = 2.257(5) Å, Ag–S = 2.383(5) Å).[15,21] If one considers the chiral configurations (Δ and Λ) of the two $[Co(aet)(en)_2]^{2+}$ units, three isomers (ΔΔ, ΛΛ, and ΔΛ) are possible for [**1a**]$^{5+}$. Crystal [**1a**]$(ClO_4)_5$ consists of the ΔΔ and ΛΛ isomers, which combine to form a racemic compound; the latter isomer is illustrated in Fig. 1. The two bridging S atoms adopt the *S* configuration for the ΔΔ isomer and the *R* configuration for the ΛΛ isomer. The same stereochemical behavior has been found in $[Ag\{Co(tga)(en)_2\}_2]^{3+}$.[15]

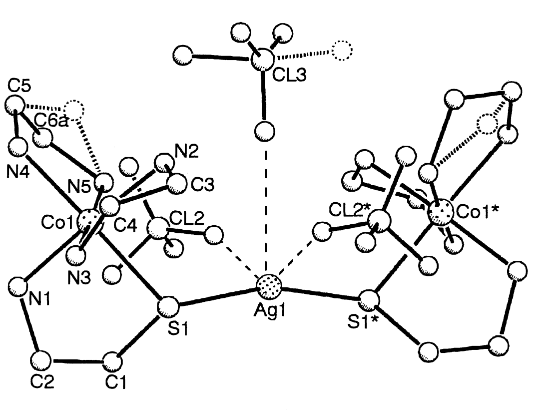


Fig. 1. A perspective view of [**1a**]$(ClO_4)_5$; the ΛΛ isomer is selected. Perchlorate anions, which do not contact with Ag^I atom, besides H atoms, are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Ag\{Co(aet)(en)_2\}_2]^{5+}$ ([**1a**]$^{5+}$)

Distances			
Ag1–S1	2.400(1)	Co1–S1	2.259(2)
Co1–N1	1.978(5)	Co1–N2	1.977(5)
Co1–N3	1.957(5)	Co1–N4	2.011(5)
Co1–N5	1.971(5)		
Angles			
S1–Ag1–S1*	164.50(8)	S1–Co1–N1	87.6(2)
S1–Co1–N4	176.5(2)	N1–Co1–N2	174.8(2)
N2–Co1–N3	85.0(2)	N3–Co1–N5	176.4(2)
N4–Co1–N5	85.1(2)	Ag1–S1–Co1	121.52(7)

Crystal Structure of [Ag{Co(aet)(en)$_2$}](NO$_3$)$_3$ ([2a]-(NO$_3$)$_3$). X-ray analysis of [**2a**]$(NO_3)_3 \cdot H_2O$ revealed the presence of an asymmetric unit consisting of one approximately octahedral $[Co(aet)(en)_2]^{2+}$ unit and one Ag^I atom (Fig. 2a), besides three nitrate anions and a water molecule. The selected bond distances and angles of the complex cation [**2a**]$^{3+}$ are listed in Table 3.

An inspection of the extended structure of [**2a**]$^{3+}$ indicated that the thiolato S atom of each $[Co(aet)(en)_2]^{2+}$ unit is bound to two Ag^I atoms to form a μ_3-thiolato mode and that each Ag^I atom is coordinated by two S atoms from two different $[Co(aet)(en)_2]^{2+}$ units (S–Ag–S = 173.14(6)°. As a result, the $[Co(aet)(en)_2]^{2+}$ octahedrons are alternately linked by Ag^I atoms to form a one-dimensional zigzag chain in the direction parallel to the *c* axis, as illustrated in Fig. 2b. In [**2a**]$^{3+}$, the Ag-S bonds (2.546(2) Å and 2.532(2) Å) are considerably longer than the Ag–S bond (2.400(1) Å) in [**1a**]$^{5+}$. One may assume that this is due to the μ_3-thiolato bridging mode in [**2a**]$^{3+}$, which is distinct from the μ_2-thiolato mode in [**1a**]$^{5+}$. However, it has been shown that, in the S-bridged Rh$^{III}_4$Ag$^I_5$ nonanuclear structure of $[Ag_5\{Rh(aet)_3\}_4]^{5+}$, there is no significant differences between Ag-S(μ_3) and Ag–S(μ_2) bond distances, while the averaged Ag–S bond distance for three-coordinated Ag^I (2.506(8) Å) is ca. 0.15 Å longer than that for two-coordinated Ag^I (2.361(6) Å).[22] Thus, the much longer Ag–S bonds in [**2a**]$^{3+}$ are ascribed mainly to the bonding interaction of each Ag^I atom with three NO_3^- anions (Ag···O = 2.657(6)

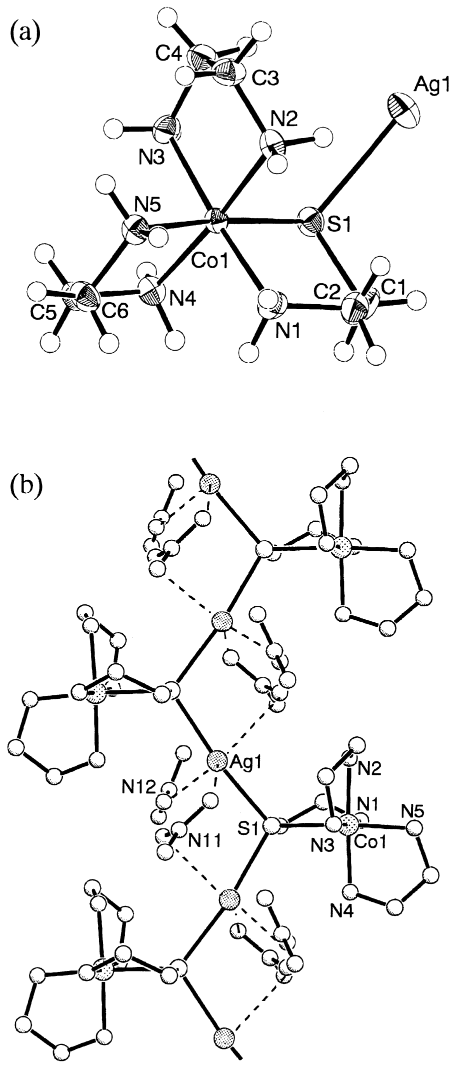


Fig. 2. (a) An ORTEP plot of the complex cation Λ-[**2a**]$^{3+}$ (asymmetric unit). (b) A perspective view of Λ-[**2a**]$(\mathrm{NO_3})_3$. Nitrate anions, which do not contact with Ag$^{\mathrm{I}}$ atom, besides H atoms, are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [Ag{Co(aet)(en)$_2$}]$^{3+}$ ([**2a**]$^{3+}$)

	Distances		
Ag1–S1	2.546(2)	Ag1–S1*	2.532(2)
Co1–S1	2.287(2)	Co1–N1	1.968(5)
Co1–N2	1.955(6)	Co1–N3	1.985(5)
Co1–N4	1.969(6)	Co1–N5	1.974(5)
	Angles		
S1–Ag1–S1*	173.14(6)	S1–Co1–N1	87.7(2)
S1–Co1–N5	174.7(2)	N1–Co1–N3	175.7(3)
N2–Co1–N3	85.0(3)	N2–Co1–N4	174.7(2)
N4–Co1–N5	85.1(2)	Ag1–S1–Ag1*	106.77(5)
Ag1–S1–Co1	122.30(8)	Ag1*–S1–Co1	115.01(8)

Å, 2.725(7) Å, and 2.924(7) Å) (Fig. 2b), which could diminish the electrophilicity of Ag$^{\mathrm{I}}$ atom toward the S atom in [Co(aet)(en)$_2$]$^{2+}$. The similarity of the Co–S bond distances in

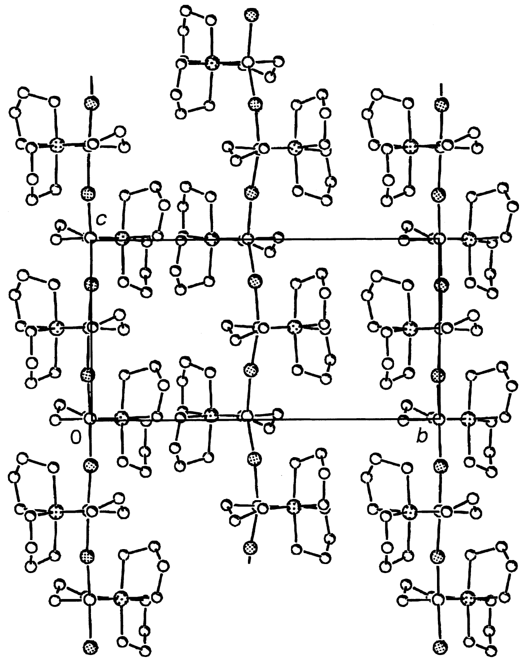


Fig. 3. A perspective view of Λ-[**2a**]$^{3+}$ along the *a* direction, showing the packing of the $(\mathrm{Co^{III}Ag^{I}})_n$ chain units in the crystal. H atoms are omitted for clarity.

[**2a**]$^{3+}$ (2.287(2) Å) and [**1a**]$^{5+}$ (2.259(2) Å) seems to support this assumption.

In [**2a**]$^{3+}$, the [Co(aet)(en)$_2$]$^{2+}$ units are unified so as to have the same absolute configuration to form a chiral $(\mathrm{Co^{III}Ag^{I}})_n$ chain (Fig. 2b). Furthermore, crystal [**2a**]$(\mathrm{NO_3})_3$ is composed of the same configurational $(\mathrm{Co^{III}Ag^{I}})_n$ chains (Fig. 3), as evidenced by the chiral space group $P2_12_12_1$ (Table 1). For the crystal used for X-ray analysis, which showed a negative CD value at 280 nm, the absolute configuration for the [Co(aet)(en)$_2$]$^{2+}$ unit was determined to be Λ from the Flack parameter (0.07(6)).[23] This assignment is compatible with the fact that the same $(-)^{\mathrm{CD}}_{280}$-[**2a**]$^{3+}$ isomer was obtained by using the Λ isomer of [Co(aet)(en)$_2$]$^{2+}$ as the starting complex.

Crystal Structure of [Ag{Co(aese)(en)$_2$}](NO$_3$)$_3$ ([2b]-(NO$_3$)$_3$). X-ray analysis for [**2b**]$(\mathrm{NO_3})_3\cdot\mathrm{H_2O}$ indicated that [**2b**]$^{3+}$ also has a one-dimensional zigzag chain structure consisting of asymmetric [Ag{Co(aese)(en)$_2$}]$^{3+}$ units (Fig. 4a). The selected bond distances and angles of the complex cation [**2b**]$^{3+}$ are listed in Table 4.

In the extended structure of [**2b**]$^{3+}$, the Se atom of each octahedral [Co(aese)(en)$_2$]$^{2+}$ unit is bound to two Ag$^{\mathrm{I}}$ atoms to form an infinite $(\mathrm{Co^{III}Ag^{I}})_n$ chain (Fig. 4b). This Se-bridged chain structure is essentially the same as the S-bridged structure found in [**2a**]$^{3+}$, although the Se-Ag-Se angle (169.70(4)°) in [**2b**]$^{3+}$ is somewhat smaller than the S–Ag–S angle (173.14(6)°) in [**2a**]$^{3+}$, because of the slightly different bonding interaction of $\mathrm{NO_3}^-$ anions with Ag$^{\mathrm{I}}$ atom (Ag···O = 2.661(7) Å, 2.740(9) Å, and 3.059(7) Å). The Co-Se bond (2.386(1) Å) in [**2b**]$^{3+}$ is ca. 0.10 Å longer than the Co-S bond (2.287(2) Å) in [**2a**]$^{3+}$, which is ascribed to the difference in covalent radius between Se and S.[24] On the other hand, the Ag–Se bonds in [**2b**]$^{3+}$ (average 2.580(1) Å) is only ca. 0.04 Å longer than the Ag–S bonds in [**2a**]$^{3+}$ (average 2.539(2) Å).

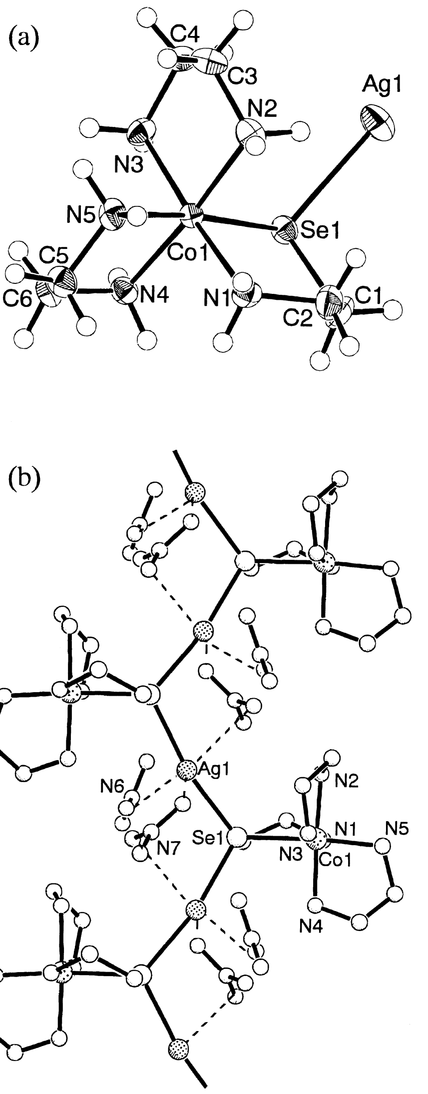


Fig. 4. (a) An ORTEP plot of the complex cation Λ-[**2b**]$^{3+}$ (asymmetric unit). (b) A perspective view of Λ-[**2b**]$(NO_3)_3$. Nitrate anions, which do not contact with Ag^{I} atom, besides H atoms, are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [Ag{Co(aese)$(en)_2$}]$^{3+}$ ([**2b**]$^{3+}$)

Distances			
Ag1–Se1	2.573(1)	Co1–Se1	2.386(1)
Ag1–Se1*	2.5864(9)	Co1–N1	1.977(5)
Co1–N2	1.964(7)	Co1–N3	1.974(6)
Co1–N4	1.967(6)	Co1–N5	1.987(6)
Angles			
Se1–Ag1–Se1*	169.70(4)	Se1–Co1–N1	92.6(2)
Se1–Co1–N5	174.4(2)	N1–Co1–N3	176.3(3)
N2–Co1–N3	85.5(3)	N2–Co1–N4	175.0(2)
N4–Co1–N5	84.8(3)	Ag1–Se1–Ag1*	107.62(2)
Ag1–Se1–Co1	113.68(4)	Ag1*–Se1–Co1	123.24(4)

This suggests that the Se atom in [Co(aese)$(en)_2$]$^{2+}$ coordinates to Ag^{I} atoms more tightly than does the S atom in [Co(aet)$(en)_2$]$^{2+}$. Here it should be noted that the Co–Se bond distance in [**2b**]$^{3+}$ is in agreement with that found in the mononuclear [Co(aese)$(en)_2$]$^{2+}$ (2.378(1) Å).[19] On the other hand, the Co–S bond in [**2a**]$^{3+}$ is ca. 0.04 Å longer than that in the mononuclear [Co(aet)$(en)_2$]$^{2+}$ (2.2494(8) Å),[25] indicating that the Co–S bond is weakened by the coordination to two Ag^{I} atoms to form a μ_3-thiolato structure. Accordingly, we assume that the selenolato group in [Co(aese)$(en)_2$]$^{2+}$ can bind with two Ag^{I} atoms, retaining the strength of the Co–Se bond.

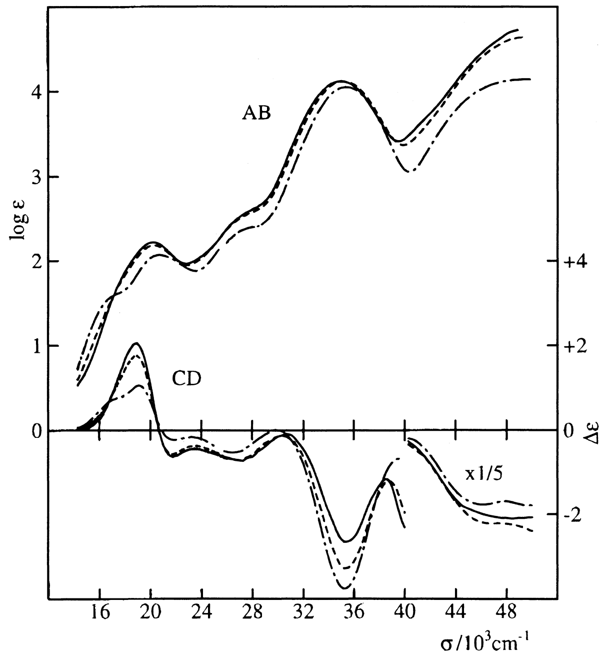


Fig. 5. Electronic absorption and CD spectra of Λ-[Co(aet)$(en)_2$]$(NO_3)_2$ (—•—), $(-)^{\mathrm{CD}}_{280}$-ΛΛ-[**1a**]$(NO_3)_5$ × 0.5 (- - -), and $(-)^{\mathrm{CD}}_{280}$-Λ-[**2a**]$(NO_3)_3$ (—) in H_2O (per [Co(aet)$(en)_2$]$^{2+}$ unit).

Crystal [**2b**]$(NO_3)_3$·H_2O is isostructural with [**2a**]$(NO_3)_3$·H_2O (Table 1); the same configurational [Co(aese)$(en)_2$]$^{2+}$ units are linked by Ag^{I} ions to give a chiral Se-bridged $(Co^{III}Ag^{I})_n$ chain (Fig. 4b), and furthermore the same configurational $(Co^{III}Ag^{I})_n$ chains are aggregated in one crystal. For the spontaneously resolved crystal used for X-ray analysis, which showed a negative CD value at 300 nm, the absolute configuration for each [Co(aese)$(en)_2$]$^{2+}$ unit was determined to be Λ from the Flack parameter (0.0009(8)), together with the fact that the same $(-)^{\mathrm{CD}}_{280}$-[**2b**]$^{3+}$ isomer was obtained by using the Λ isomer of [Co(aese)$(en)_2$]$^{2+}$ as the starting complex.

Synthesis and Properties of the S-Bridged Complexes. The reaction of a dark-brown aqueous solution of [Co(aet)$(en)_2$]$(NO_3)_2$ with $AgNO_3$ in a 2:1 ratio gave a dark-red solution, from which a red crystalline powder ([**1a**]$(NO_3)_5$·$4H_2O$) was isolated by adding an aqueous solution of $NaNO_3$. The elemental and plasma emission analyses (Co/Ag = 1.95) of this red product are in good agreement with the formula for an S-bridged $Co^{III}Ag^{I}Co^{III}$ trinuclear complex, [Ag{Co(aet)$(en)_2$}$_2$]$(NO_3)_5$, and its trinuclear structure was confirmed by X-ray analysis for the ClO_4^- salt. As shown in Fig. 5, the electronic absorption spectrum of 0.5 mol of [**1a**]$^{5+}$ in water resembles that of [Co(aet)$(en)_2$]$^{2+}$,[17,18] giving a first d-d band at ca. 20 ×

10^3 cm^{-1} and an S-to-Co charge-transfer (CT) band at ca. 35×10^3 cm^{-1}. However, $[\mathbf{1a}]^{5+}$ shows no distinct shoulder at the lower energy side of the first d-d band, which is characteristically observed for $[\mathrm{Co(aet)(en)_2}]^{2+}$, suggesting that the thiolato group of the $[\mathrm{Co(aet)(en)_2}]^{2+}$ unit in $[\mathbf{1a}]^{5+}$ is still bound with a $\mathrm{Ag^I}$ atom to form an S-bridged trinuclear structure in water.[26] This is supported by the fact that the absorption spectrum of $[\mathbf{1a}]^{5+}$ in the solid state (Nujol paste) is essentially the same as that in water. The molar conductivities of $[\mathbf{1a}]\mathrm{X_5}$ ($\mathrm{X = NO_3, ClO_4, BF_4}$) in water, which are comparable to that of the 1:5 electrolyte, $[\mathrm{Zn_3(OH)\{Rh(aet)_3\}_4}]\mathrm{Br_5}$ (641 Ω^{-1} cm^2 mol^{-1}),[27] also support this suggestion. The CD spectrum of 0.5 mol of $(-)^{\mathrm{CD}}_{280}$-$[\mathbf{1a}](\mathrm{NO_3})_5$, which was prepared by using the Λ isomer of $[\mathrm{Co(aet)(en)_2}]^{2+}$ instead of its racemate, is similar to that of Λ-$[\mathrm{Co(aet)(en)_2}]^{2+}$ over the whole region (Fig. 5 and Table 5). This spectral comparison indicates that $(-)^{\mathrm{CD}}_{280}$-$[\mathbf{1a}]^{5+}$ is composed of the two Λ configurational $[\mathrm{Co(aet)(en)_2}]^{2+}$ units and that the reaction of $[\mathrm{Co(aet)(en)_2}]^{2+}$ with $\mathrm{Ag^+}$ proceeds with retention of the absolute configuration of the $\mathrm{Co^{III}}$ chiral center. Previously, we have pointed out that the chirality due to asymmetric sulfur atom coordinated to $\mathrm{Co^{III}}$ center contributes significantly to the CD spectrum especially in the S-to-Co CT band region.[28] If the trinuclear structure of $[\mathrm{Ag\{Co(aet)(en)_2\}_2}]^{5+}$ found in crystal is retained in solution, the CD spectral feature of 0.5 mol of $\Lambda\Lambda$-$[\mathbf{1a}]^{5+}$, which possesses an additional chirality due to two *R* configurational S atoms, would be different from that of Λ-$[\mathrm{Co(aet)(en)_2}]^{2+}$. Thus, it is reasonable to assume that the chiral configuration of the bridging S atoms in $[\mathbf{1a}]^{5+}$ is not fixed in solution, presumably because of the intramolecular and/or intermolecular exchange of the two $[\mathrm{Co(aet)(en)_2}]^{2+}$ units. The appearance of a single set of six signals in the ^{13}C NMR spectrum of $[\mathbf{1a}]^{5+}$ in $\mathrm{D_2O}$ would be due to the facile exchange of the $[\mathrm{Co(aet)(en)_2}]^{2+}$ units, which is fast on the NMR time scale, rather than to the existence of a single racemic isomer ($\Delta_S\Delta_S/\Lambda_R\Lambda_R$) found in the crystal.

Table 5. Electronic Absorption and CD Spectral Data

Absorption max: $\sigma/10^3$ cm^{-1} (log ε/mol^{-1} dm^3 cm^{-1})	CD extrema: $\sigma/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
$\Lambda\Lambda$-$[\mathrm{Ag\{Co(aet)(en)_2\}_2}]^{5+}$ ($(-)^{\mathrm{CD}}_{280}$-$[\mathbf{1a}]^{5+}$)	
20.33 (2.48)	18.82 (+3.51)
27.46 (2.8)$^{\mathrm{sh}}$	21.60 (−1.12)
35.19 (4.42)	26.41 (−1.42)
	35.31 (−6.55)
Λ-$[\mathrm{Ag\{Co(aet)(en)_2\}}]^{3+}$ ($(-)^{\mathrm{CD}}_{280}$-$[\mathbf{2a}]^{3+}$)	
20.24 (2.22)	18.82 (+2.05)
27.73 (2.6)$^{\mathrm{sh}}$	21.59 (−0.62)
35.01 (4.13)	27.13 (−0.74)
	35.38 (−2.64)
$\Lambda\Lambda$-$[\mathrm{Ag\{Co(aese)(en)_2\}_2}]^{5+}$ ($(-)^{\mathrm{CD}}_{300}$-$[\mathbf{1b}]^{5+}$)	
19.64 (2.45)	18.64 (+3.26)
33.13 (4.41)	21.19 (−0.79)$^{\mathrm{sh}}$
40.23 (3.96)$^{\mathrm{sh}}$	24.36 (−1.42)
	33.44 (−5.72)
Λ-$[\mathrm{Ag\{Co(aese)(en)_2\}}]^{3+}$ ($(-)^{\mathrm{CD}}_{300}$-$[\mathbf{2b}]^{3+}$)	
19.58 (2.47)	18.66 (+2.88)
33.16 (4.42)$^{\mathrm{sh}}$	21.10 (−0.62)$^{\mathrm{sh}}$
40.13 (3.94)$^{\mathrm{sh}}$	24.36 (−1.24)
	33.56 (−4.90)

The sh label denotes a shoulder.

When an aqueous solution of $[\mathbf{1a}](\mathrm{NO_3})_5$ was treated with ca. 1 molar equiv of $\mathrm{AgNO_3}$ at room temperature, the first d-d absorption band at 20.33×10^3 cm^{-1} for $[\mathbf{1a}]^{5+}$ shifted slightly to the lower energy side. A pink powder ($[\mathbf{2a}](\mathrm{NO_3})_3\cdot\mathrm{H_2O}$) was isolated from this mixture on adding an aqueous solution of $\mathrm{NaNO_3}$. Complex $[\mathbf{2a}](\mathrm{NO_3})_3$ was also obtained directly from the 1:1 reaction of $[\mathrm{Co(aet)(en)_2}](\mathrm{NO_3})_2$ with $\mathrm{AgNO_3}$ in water. The plasma emission analysis (Co/Ag = 1.03) indicated that $[\mathbf{2a}]^{3+}$ contains Co and Ag atoms in a 1:1 ratio, and its elemental analysis is consistent with the 1:1 stoichiometry of $[\mathrm{Co(aet)(en)_2}]$ $(\mathrm{NO_3})_2\cdot\mathrm{AgNO_3}$. X-ray analysis demonstrated that $[\mathbf{2a}]^{3+}$ is not a discrete S-bridged $\mathrm{Co^{III}Ag^I}$ dinuclear complex, but a novel one-dimensional $(\mathrm{Co^{III}Ag^I})_n$ chain complex-polymer. Complex $[\mathbf{2a}](\mathrm{NO_3})_3$ is soluble in water, and its molar conductivity (365 Ω^{-1} cm^2 mol^{-1}) is within the range found in the S-bridged polynuclear complexes of 1:3 electrolytes.[11,29] Furthermore, treatment of an aqueous solution of $[\mathbf{2a}](\mathrm{NO_3})_3$ with ca. 1 molar equiv of $[\mathrm{Co(aet)(en)_2}](\mathrm{NO_3})_2$ led to the isolation of $[\mathbf{1a}](\mathrm{NO_3})_5$ in a high yield. These results imply that the chain structure in $[\mathbf{2a}]^{3+}$ is not retained in an aqueous solution, being converted at least in part into the trivalent $\mathrm{Co^{III}Ag^I}$ dinuclear species such as $[\mathrm{Ag\{Co(aet)(en)_2\}(H_2O)}]^{3+}$, which reacts readily with $[\mathrm{Co(aet)(en)_2}]^{2+}$ to form $[\mathrm{Ag\{Co(aet)(en)_2\}_2}]^{5+}$ ($[\mathbf{1a}]^{5+}$).

The absorption spectrum of $[\mathbf{2a}](\mathrm{NO_3})_3$ in water is very similar to that of 0.5 mol of $[\mathbf{1a}]^{5+}$, but each band for $[\mathbf{2a}]^{3+}$ locates at somewhat lower energy than the corresponding band for $[\mathbf{1a}]^{5+}$ (Fig. 5 and Table 5). This tendency is more clearly observed in the solid state absorption spectra; $[\mathbf{2a}](\mathrm{NO_3})_3$ exhibits the first d–d absorption band at 20.08×10^3 cm^{-1}, while the corresponding band for $[\mathbf{1a}](\mathrm{NO_3})_5$ appears at 20.28×10^3 cm^{-1}. The optically active $(-)^{\mathrm{CD}}_{280}$ isomer of $[\mathbf{2a}]^{3+}$, which was prepared by using the Λ isomer of $[\mathrm{Co(aet)(en)_2}]^{2+}$ instead of its racemate, exhibits a CD spectrum essentially the same as that of 0.5 mol of $(-)^{\mathrm{CD}}_{280}$-$\Lambda\Lambda$-$[\mathbf{1a}]^{5+}$ (Fig. 5). This spectral behavior clearly indicates that the $(-)^{\mathrm{CD}}_{280}$ isomer of $[\mathbf{2a}]^{3+}$ is composed of the Λ configurational $[\mathrm{Co(aet)(en)_2}]^{2+}$ unit.

Synthesis and Properties of the Se-Bridged Complexes. Similar 2:1 and 1:1 reactions of $[\mathrm{Co(aese)(en)_2}](\mathrm{NO_3})_2$ with $\mathrm{AgNO_3}$ gave dark-red solutions, from which $[\mathbf{1b}](\mathrm{NO_3})_5$ and $[\mathbf{2b}](\mathrm{NO_3})_3$ were isolated as dark-red solids by adding an aqueous solution of $\mathrm{NaNO_3}$. The plasma emission analyses imply that $[\mathbf{1b}](\mathrm{NO_3})_5$ (Co/Ag = 2.05) and $[\mathbf{2b}](\mathrm{NO_3})_3$ (Co/Ag = 1.02) contain Co and Ag atoms in 2:1 and 1:1 ratios, respectively. Furthermore, the elemental analytical results of $[\mathbf{1b}](\mathrm{NO_3})_5$ and $[\mathbf{2b}](\mathrm{NO_3})_3$ are consistent with the 2:1 and 1:1 stoichiometries, $\{[\mathrm{Co(aese)(en)_2}](\mathrm{NO_3})_2\}_2\cdot\mathrm{AgNO_3}$ and $[\mathrm{Co(aese)(en)_2}](\mathrm{NO_3})_2\cdot\mathrm{AgNO_3}$, respectively. The structure of $[\mathbf{2b}](\mathrm{NO_3})_3$ was established by X-ray crystallography, which demonstrated that $[\mathbf{2b}]^{3+}$ is a one-dimensional Se-bridged $(\mathrm{Co^{III}Ag^I})_n$ coordination-polymer, $[\mathrm{Ag\{Co(aese)(en)_2\}}](\mathrm{NO_3})_3$. As illustrated in Fig. 6, the absorption spectrum of 0.5 mol of $[\mathbf{1b}](\mathrm{NO_3})_5$ in water coincides well with that of $[\mathbf{2b}](\mathrm{NO_3})_3$ over the whole region. The disappearance of a distinct shoulder at the lower energy side of the first d–d band (ca. 20×10^3

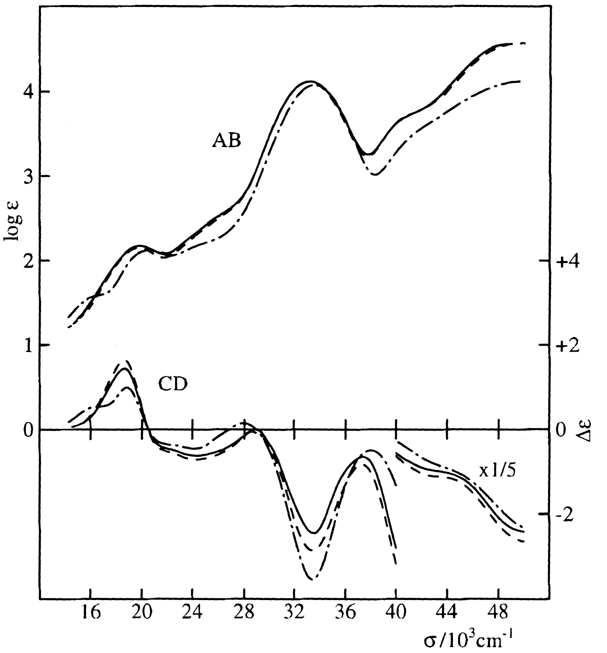


Fig. 6. Electronic absorption and CD spectra of Λ-[Co(aese)(en)$_2$](NO$_3$)$_2$ (— • —), $(-)^{\mathrm{CD}}_{300}$-ΛΛ-[**1b**](NO$_3$)$_5$ × 0.5 (- - -), and $(-)^{\mathrm{CD}}_{300}$-Λ-[**2b**](NO$_3$)$_3$ (—) in H$_2$O (per [Co(aese)(en)$_2$]$^{2+}$ unit).

cm^{-1}), which is observed for [Co(aese)(en)$_2$]$^{2+}$,[18,19] is indicative of the coordination of the selenolato group to Ag^{I} atom. In the solid state, the first d–d absorption band for [**1b**](NO$_3$)$_5$ locates at 19.84 × 10^3 cm^{-1}, which is a higher energy value than the corresponding band for [**2b**](NO$_3$)$_3$ (19.65 × 10^3 cm^{-1}). From these results, we conclude that [**1b**]$^{5+}$ is an Se-bridged Co^{III}Ag^{I}Co^{III} trinuclear complex with μ_2-selenolato donors, [Ag{Co(aese)(en)$_2$}$_2$]$^{5+}$, the structure of which corresponds with the S-bridged Co^{III}Ag^{I}Co^{III} trinuclear structure in [**1a**]$^{5+}$.

The overall absorption spectral behavior of [**1b**](NO$_3$)$_5$ and [**2b**](NO$_3$)$_3$ in water is quite similar to that of [**1a**](NO$_3$)$_5$ and [**2a**](NO$_3$)$_3$, although the first d–d and the chalcogen-to-Co CT bands for the former complexes locate at lower energy than the corresponding bands for the latter complexes (Figs. 5 and 6 and Table 5). This spectral correlation is the same as that between [Co(aese)(en)$_2$]$^{2+}$ and [Co(aet)(en)$_2$]$^{2+}$, reflecting the order of the ligand field strength (S > Se).[18] When the Λ isomer of [Co(aese)(en)$_2$]$^{2+}$ was reacted with AgNO$_3$ in 2:1 and 1:1 ratios, $(-)^{\mathrm{CD}}_{300}$-[**1b**](NO$_3$)$_5$ and $(-)^{\mathrm{CD}}_{300}$-[**2b**](NO$_3$)$_3$ were obtained. The CD spectral behavior of these complexes is very similar to that of Λ-[Co(aese)(en)$_2$]$^{2+}$ over the whole region (Fig. 6),[18] indicating that the reactions of Λ-[Co(aese)(en)$_2$]$^{2+}$ with Ag^{+} also proceed with retention of the Λ configuration of the Co^{III} chiral center to produce ΛΛ-[**1b**]$^{5+}$ and Λ-[**2b**]$^{3+}$, like the reactions of Λ-[Co(aet)(en)$_2$]$^{2+}$ with Ag^{+}.

Formation and Characteristics of the (Co^{III}Ag^{I})$_n$ Chain Structure. In contrast to the 1:1 reaction of [Co(aet)(en)$_2$](NO$_3$)$_2$ with AgNO$_3$ in water, the corresponding 1:1 reaction with AgClO$_4$ or AgBF$_4$, followed by the addition of NaClO$_4$ or NaBF$_4$, did not produce the S-bridged (Co^{III}Ag^{I})$_n$ chain complex, [Ag{Co(aet)(en)$_2$}]$^{3+}$ ([**2a**]$^{3+}$); only the S-bridged trinuclear complex, [Ag{Co(aet)(en)$_2$}$_2$](X)$_5$ ([**1a**](X)$_5$; X = ClO$_4$, BF$_4$), was precipitated from the dark-red reaction solution. This was also the case for the 1:1 reaction of [Co(aese)(en)$_2$](NO$_3$)$_2$ with AgClO$_4$/NaClO$_4$ in water, which afforded only the Se-bridged trinuclear complex, [Ag{Co(aese)(en)$_2$}$_2$](ClO$_4$)$_5$ ([**1b**](ClO$_4$)$_5$). It is considered that neither ClO$_4^-$ nor BF$_4^-$ anion contacts with Ag^{I} atom as closely as does the NO$_3^-$ anion, because of their non-planar geometry and lower nucleophilic character. Thus, the chain structure in [**2a**]$^{3+}$ or [**2b**]$^{3+}$ seems to be stabilized by the close contact of NO$_3^-$ anions with Ag^{I} atom, which weakens the electrophilicity of Ag^{I} atom, so as to permit the thiolato or selenolato group in [Co(aet or aese)(en)$_2$]$^{2+}$ to bind with two Ag^{I} atoms. Although [**2a**]$^{3+}$ or [**2b**]$^{3+}$ is no other than the aggregate of the mononuclear [Co(aet or aese)(en)$_2$]$^{2+}$, the chain structure in [**2a**]$^{3+}$ or [**2b**]$^{3+}$ can be regarded as resulting from the aggregation of the Co^{III}Ag^{I}Co^{III} trinuclear structure in [**1a**]$^{5+}$ or [**1b**]$^{5+}$ (Scheme 1). Since this aggregation is achieved by the linkage of additional Ag^{I} atom with each μ_2-thiolato or μ_2-selenolato group in [**1a**]$^{5+}$ or [**1b**]$^{5+}$, a variety of aggregates based on S- or Se-bridged polynuclear complexes could be constructed if the nucleophilicity of μ_2-thiolato or μ_2-selenolato group is increased and/or the electrophilicity of bridging metal ion is decreased, so as to form μ_3-thiolato or μ_3-selenolato bridging structures.

Interestingly, it was found that not only the S-bridged structure in [**2a**]$^{3+}$ but also the Se-bridged structure in [**2b**]$^{3+}$ was found to discriminate the chiral configurations (Δ and Λ) of [Co(aet or aese)(en)$_2$]$^{2+}$ to exclusively give a pair of enantiomeric chains, (Δ-Co^{III}Ag^{I})$_n$ and (Λ-Co^{III}Ag^{I})$_n$. Furthermore, the enantiomeric chains for each [**2a**]$^{3+}$ and [**2b**]$^{3+}$ were found to separate spontaneously from one another as homochiral crystals; each crystal that was picked up from the bulk showed a positive or negative CD sign at 280 nm for [**2a**]$^{3+}$ and at 300 nm for [**2b**]$^{3+}$. It should be noted that none of the mononuclear complexes, Δ/Λ-[Co(aet)(en)$_2$](NO$_3$)$_2$ and Δ/Λ-[Co(aese)(en)$_2$](NO$_3$)$_2$, and the trinuclear complexes, ΔΔ/ΛΛ-[**1a**](NO$_3$)$_5$ and ΔΔ/ΛΛ-[**1b**](NO$_3$)$_5$, are spontaneously resolved. Accordingly, it is considered that the high organization of the [Co(aet)(en)$_2$]$^{2+}$ or [Co(aese)(en)$_2$]$^{2+}$ octahedrons in a one-dimensional chalcogen-bridged array leads to spontaneous resolution, which is relatively rare for the aggregates composed of chiral complex-molecules.[30] This result would provide an important insight into the design and construction of polynuclear systems that are subject to spontaneous resolution.

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