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Synthesis, Characterization, and Chiral Properties of $Co^{III}_2Ag^I_3$ Pentanuclear, $Co^{III}_4Zn^{II}_4$ Octanuclear, and Co^{III} Mononuclear Complexes with Aza-Capped Hexadentate-N_3S_3 Thiolate Ligands: Crystal Structures of $[Ag_3\{Co(L)\}_2][PF_6]_3$ and $[Zn_4O\{Co(L)\}_4][PF_6]_6$ (L = $N(CH_2NHCH_2CH_2S^-)_3$)

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The reaction of an S-bridged $Co^{III}_2Ag^I_3$ pentanuclear complex, $[Ag_3\{Co(aet)_3\}_2][BF_4]_3$ (aet = $NH_2CH_2CH_2S^-$), with paraformaldehyde in basic acetonitrile, followed by adding aqueous ammonia, produced an aza-capped $Co^{III}_2Ag^I_3$ complex, $[Ag_3\{Co(L)\}_2]^{3+}$ ($[\mathbf{1}]^{3+}$) (L = $N(CH_2NHCH_2CH_2S^-)_3$). The crystal structure of $[\mathbf{1}]^{3+}$ was determined by X-ray crystallography. $[\mathbf{1}][PF_6]_3\cdot H_2O$, empirical formula $C_{18}H_{44}Ag_3Co_2F_{18}N_8OP_3S_6$, crystallizes in the tetragonal space group $I\bar{4}2m$ with $a = 13.012(1)$ Å, $c = 24.707(2)$ Å, and $Z = 4$. In $[\mathbf{1}]^{3+}$ the two aza-capped [Co(L)] units are linked by three Ag^I atoms, such that the two Co^{III} atoms are encapsulated in a macrobicyclic metallocage, $[Ag^I_3(L)_2]^{3-}$. $[\mathbf{1}]^{3+}$ was converted to an aza-capped $Co^{III}_4Zn^{II}_4$ octanuclear complex, $[Zn_4O\{Co(L)\}_4]^{6+}$ ($[\mathbf{2}]^{6+}$), by reaction with I^- in the presence of Zn^{2+} and ZnO in water. The crystal structure of $[\mathbf{2}]^{6+}$ was also determined by X-ray crystallography. $[\mathbf{2}][PF_6]_6\cdot 8H_2O$, empirical formula $C_{36}H_{100}Co_4F_{36}N_{16}O_9P_6S_{12}Zn_4$, crystallizes in the monoclinic space group $P2_1/n$ with $a = 14.33(7)$ Å, $b = 25.67(10)$ Å, $c = 24.83(6)$ Å, $\beta = 101.3(3)°$, and $Z = 4$. In $[\mathbf{2}]^{6+}$ each of four [Co(L)] units is bound to each trigonal Zn^{II}_3 face of the tetrahedral $[Zn^{II}_4O]^{6+}$ core, such that each Co^{III} atom is encapsulated in a macrobicyclic $[Zn^{II}_4O(L)]$ fragment. Treatment of $[\mathbf{2}]^{6+}$ with a basic aqueous solution resulted in a cleavage of the Zn−S bonds to produce an aza-capped Co^{III} mononuclear complex, [Co(L)] ([**3**]), from which $[\mathbf{1}]^{3+}$ is readily reproduced by the reaction with Ag^+ in water. All the reactions were found to proceed with retention of the absolute configuration (Δ or Λ) of the Co^{III} chiral centers; ΔΔ-$[\mathbf{1}]^{3+}$, ΔΔΔΔ-$[\mathbf{2}]^{6+}$, and Δ-[**3**] were derived from ΔΔ-$[Ag_3\{Co(aet)_3\}_2]^{3+}$. The contributions to circular dichroism (CD) from the triple helicity in $[\mathbf{1}]^{3+}$, besides from the asymmetric N and S donor atoms and the Co^{III} chiral centers in $[\mathbf{1}]^{3+}$ and $[\mathbf{2}]^{6+}$, were estimated by comparing the CD spectra of ΔΔ-$[\mathbf{1}]^{3+}$, ΔΔΔΔ-$[\mathbf{2}]^{6+}$, and Δ-[**3**].

Introduction

Coordinated thiolato S atoms in mononuclear Co^{III} complexes tend to bind with other metal ions to form S-bridged polynuclear structures.[2−30] In fact, a number of S-bridged polynuclear complexes composed of *fac*-[Co(thiolato-*S*)$_3$(amine-*N*)$_3$]-type units have been prepared by the reactions of *fac*-$[Co(aet)_3]$ or *fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ (aet = 2-aminoethanethiolate; L-cys = L-cysteinate) with a variety of metal ions.[9−24] It has been pointed out that the structures of these polynuclear complexes are highly dependent on the properties of metal ions incorporated with *fac*-[Co(aet or L-cys-*N*,*S*)$_3$]$^{0\text{ or }3-}$. For example, the reaction

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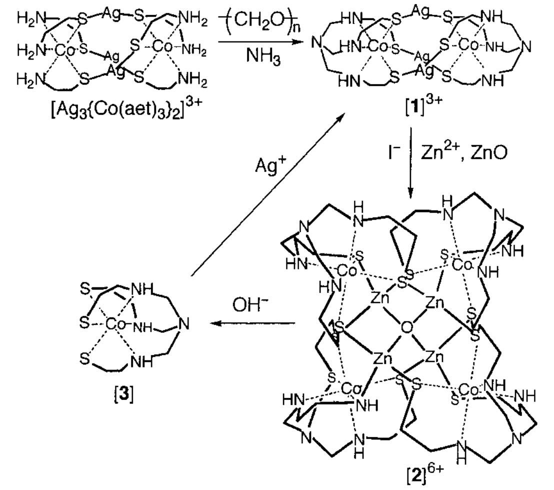
of *fac*-[Co(aet)$_3$] with Zn^{2+} gave an S-bridged Co$^{III}_4$Zn$^{II}_4$ octanuclear complex, [Zn$_4$O{Co(aet)$_3$}$_4$]$^{6+}$,[16] while the reaction with Ag$^+$ produced an S-bridged Co$^{III}_2$Ag$^{I}_3$ pentanuclear complex, [Ag$_3${Co(aet)$_3$}$_2$]$^{3+}$.[19] On the other hand, it has been shown that the reactions of *fac*-[Co(aet)$_3$] with reducing metal ions such as Cr^{2+} and Fe^{2+} or oxidizing metal ions such as Ce^{4+} and V^{4+} cause the rearrangement of the aet ligand to form the stable end product of an S-bridged Co$^{III}_3$ trinuclear complex, [Co{Co(aet)$_3$}$_2$]$^{3+}$,[12,13] which is generally prepared by reacting *fac*-[Co(aet)$_3$] with Co^{2+} or [CoX(NH$_3$)$_5$]$^{2+}$ (X = Cl, Br).[9,23] This fact indicates that the potential utility of *fac*-[Co(aet or L-cys-*N*,*S*)$_3$]$^{0 \text{ or } 3-}$ as a building block of the S-bridged polynuclear structures is limited. In this context, it is desirable to employ more robust *fac*-[Co(thiolato-*S*)$_3$(amine-*N*)$_3$] as a building block, to develop the chemistry of the S-bridged polynuclear complexes of this class.

One way to do this is to construct a cap on the trigonal N$_3$ face of the three primary amine groups in *fac*-[Co(aet)$_3$]. Since it has been established that each trigonal N$_3$ face in [Co(en)$_3$]$^{3+}$ (en = NH$_2$CH$_2$CH$_2$NH$_2$), [Co(sen)]$^{3+}$ (sen = CH$_3$C(CH$_2$NHCH$_2$CH$_2$NH$_2$)$_3$), and [Co(ten)] (ten = CH$_3$C(CH$_2$SCH$_2$CH$_2$NH$_2$)$_3$) is capped with a N(CH$_2$)$_3$ group by facile condensation reactions with formaldehyde and aqueous ammonia to give aza-capped macrobicyclic cage molecules [Co(sep)]$^{3+}$, [Co(azamesar)]$^{3+}$, and [Co(azacapten)]$^{3+}$,[31−33] we expected that a similar aza-capping reaction is applicable for *fac*-[Co(aet)$_3$]. However, attempts to construct a cap on the trigonal N$_3$ face of the mononuclear *fac*-[Co(aet)$_3$] were unsuccessful, because of its poor solubility in any solvent and unstability in solution. Instead, we found that the two terminal N$_3$ faces in the S-bridged Co$^{III}_2$Ag$^{I}_3$ pentanuclear complex [Ag$_3${Co(aet)$_3$}$_2$]$^{3+}$ are capped with N(CH$_2$)$_3$ groups by a modified condensation reaction with paraformaldehyde and aqueous ammonia to produce a macrobicyclic Co$^{III}_2$Ag$^{I}_3$ cage complex, [Ag$_3${Co(L)}$_2$]$^{3+}$ (L = N(CH$_2$NHCH$_2$CH$_2$S$^-$)$_3$) ([**1**]$^{3+}$).[34] Furthermore, [**1**]$^{3+}$ was found to be convertible to an aza-capped Co$^{III}_4$Zn$^{II}_4$ octanuclear complex, [Zn$_4$O{Co(L)}$_4$]$^{6+}$ ([**2**]$^{6+}$), from which the desired aza-capped mononuclear complex [Co^{III}(L)] ([**3**]) was easily isolated (Scheme 1). A partial report of the preparation and crystal structure of [**1**]$^{3+}$ has been published as a preliminary communication.[34] In this paper we report on the complete description of the synthesis, optical resolution, and spectroscopic properties of the optically active isomers for [**1**]$^{3+}$, [**2**]$^{6+}$, and [**3**], along with the crystal structures of [**1**]$^{3+}$ and [**2**]$^{6+}$. Quite recently, it has been reported that a related aza-capped Co$^{III}_3$ trinuclear complex, [Co{Co(L)}$_2$]$^{3+}$, is prepared by a condensation reaction of [Co{Co(aet)$_3$}$_2$]$^{3+}$ with paraformaldehyde and gaseous ammonia, by way of a hexaimine intermediate, [Co{Co(CH$_2$=NCH$_2$CH$_2$S)$_3$}$_2$]$^{3+}$.[35]

Experimental Section

Preparation and Optical Resolution of Complexes. [Ag$_3${Co(L)}$_2$][NO$_3$]$_3$ ([1][NO$_3$]$_3$). To a dark purple solution of [Ag$_3${Co(aet)$_3$}$_2$](BF$_4$)$_3$·H$_2$O[19] (1.0 g, 0.82 mmol) in 50 cm^3 of acetonitrile were added paraformaldehyde (1.0 g) and triethylamine (0.37 g). The mixture was stirred at room temperature for 3 h, during which time the solution color turned from dark purple to dark red. To the dark red solution was added 50 cm^3 of an 8% aqueous ammonia, followed by stirring at room temperature for 1 h. The resulting dark purple reaction solution was concentrated to dryness with a rotary evaporator, and then the residue was dissolved in 0.02 mol dm^{-3} HNO$_3$. To this solution was added 25 cm^3 of a saturated aqueous solution of NaNO$_3$ to precipitate a dark purple powder ([1][NO$_3$]$_3$·4H$_2$O), which was collected by filtration after being stored in a refrigerator overnight. Yield: 0.94 g (88%). Anal. Calcd for [Ag$_3$(CoC$_9$H$_{21}$N$_4$S$_3$)$_2$][NO$_3$]$_3$·4H$_2$O: C, 17.12; H, 3.99; N, 12.20; Co, 9.34; Ag, 25.63. Found: C, 17.05; H, 3.78; N, 12.25; Co, 9.28; Ag, 25.63. Molar conductivity: 349 Ω cm^2 mol^{-1}.

Scheme 1



Single crystals of [**1**][PF$_6$]$_3$·H$_2$O suitable for X-ray analysis were obtained by adding a saturated aqueous solution of NaPF$_6$ to an aqueous solution of [**1**][NO$_3$]$_3$, followed by storing in a refrigerator for several days. Anal. Calcd for [Ag$_3$(CoC$_9$H$_{21}$N$_4$S$_3$)$_2$][PF$_6$]$_3$·H$_2$O: C, 14.83; H, 3.04; N, 7.69. Found: C, 15.13; H, 3.03; N, 7.73.

An aqueous solution of [**1**][NO$_3$]$_3$·4H$_2$O (0.10 g) was chromatographed on an SP-Sephadex C-25 column (Na$^+$ form, 2 cm × 25 cm), using a 0.15 mol dm^{-3} aqueous solution of Na$_2$[Sb$_2$(*R*,*R*-tartrato)$_2$]·5H$_2$O 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, and the resulting dark purple powder was collected by filtration. It was found from the absorption and circular dichroism (CD) spectral measurements that the earlier and the later moving bands in the column contained $(-)^{\text{CD}}_{580}$-[**1**]$^{3+}$ and $(+)^{\text{CD}}_{580}$-[**1**]$^{3+}$, respectively. Anal. Calcd for [Ag$_3$(CoC$_9$H$_{21}$N$_4$S$_3$)$_2$][NO$_3$]$_3$·3H$_2$O: C, 17.37; H, 3.89; N, 12.38. Found for the $(-)^{\text{CD}}_{580}$ isomer: C, 17.50; H, 3.76; N, 12.48%. Found for the $(+)^{\text{CD}}_{580}$ isomer: C, 17.34; H, 3.67; N, 12.15.

$(-)^{\text{CD}}_{580}$-[**1**][NO$_3$]$_3$·3H$_2$O was also prepared by the same procedure described above, using the ΔΔ isomer[19] instead of the racemic isomer of [Ag$_3${Co(aet)$_3$}$_2$][BF$_4$]$_3$.

[Zn$_4$O{Co(L)}$_4$][ClO$_4$]$_6$ ([2][ClO$_4$]$_6$). To a solution containing [**1**][NO$_3$]$_3$·4H$_2$O (0.50 g, 0.40 mmol) and Zn(NO$_3$)$_2$·6H$_2$O (1.25 g, 4.2 mmol) in 100 cm^3 of water was added ZnO (2.5 g). A solution of NaI (0.20 g, 1.33 mmol) in 5 cm^3 of water was added to it with stirring, which gave a dark green precipitate immediately. After being stirred at room temperature for 1 h, the reaction mixture was filtered to remove insoluble materials. To the dark purple filtrate was added a saturated aqueous solution of NaClO$_4$ (10 cm^3), followed by cooling in a refrigerator overnight. The resulting black powder ([**2**][ClO$_4$]$_6$·7H$_2$O) was collected by filtration. When [**2**][ClO$_4$]$_6$·7H$_2$O was chromatographed on an SP-Sephadex C-25 column, the adsorbed band was separated into two bands, $(+)^{\text{CD}}_{580}$-[**2**]$^{6+}$ and $(-)^{\text{CD}}_{580}$-[**2**]$^{6+}$, by eluting with 0.5 mol dm^{-3} aqueous solution of Na$_2$[Sb$_2$(*R*,*R*-tartrato)$_2$]·5H$_2$O. Yield: 0.21 g (43%). Anal. Calcd for [Zn$_4$O(CoC$_9$H$_{21}$N$_4$S$_3$)$_4$][ClO$_4$]$_6$·7H$_2$O: C, 18.31; H, 4.18; N, 9.49; Co, 9.98; Zn, 11.07. Found: C,

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18.16; H, 4.24; N, 9.76; Co, 10.25; Zn, 11.45. Molar conductivity: 751 Ω cm^2 mol^{-1}.

The same procedure using $\Delta\Delta$-[**1**][NO_3]$_3$·3H_2O or $\Lambda\Lambda$-[**1**][NO_3]$_3$·3H_2O instead of [**1**][NO_3]$_3$·4H_2O gave the optically active isomer $(-)^{CD}_{580}$ -[**2**]$^{6+}$ or $(+)^{CD}_{580}$ -[**2**]$^{6+}$. Anal. Calcd for [$Zn_4O(CoC_{12}H_{21}N_4S_3)_4$][$ClO_4$]$_6$·7$H_2O$: C, 18.31; H, 4.18; N, 9.49. Found for the $(-)^{CD}_{580}$ isomer: C, 18.15; H, 4.15; N, 9.29. Found for the $(+)^{CD}_{580}$ isomer: C, 18.09; H, 4.19; N, 9.34.

The PF_6^- salt of [**2**]$^{6+}$ was obtained by adding a saturated aqueous solution of NH_4PF_6 to an aqueous solution of [**2**][ClO_4]$_6$·7H_2O. The resulting powder was recrystallized from water by adding a few drops of 60% HPF_6 at room temperature, which gave single crystals of [**2**][PF_6]$_6$·8H_2O suitable for X-ray analysis. Anal. Calcd for [$Zn_4O(CoC_{12}H_{21}N_4S_3)_4$][$PF_6$]$_6$·8$H_2O$: C, 16.30; H, 3.80; N, 8.45. Found: C, 16.23; H, 3.90; N, 8.37.

[Co(L)] ([3]). To a stirred solution containing [**2**][ClO_4]$_6$·7H_2O (0.10 g, 0.04 mmol) in 5 cm^3 of water was added NaOH (0.02 g, 0.50 mmol) dissolved in a small amount of water, which gave a dark green-blue powder immediately. After the mixture was stirred at room temperature for a few minutes, the powder was collected by filtration and then dissolved in 50 cm^3 of water. The insoluble white powder was filtered off, and the dark green-blue filtrate was passed through an SP-Sephadex C-25 column (Na^+ form, 2 cm × 10 cm), eluting with water. The eluate was concentrated almost to dryness with a rotary evaporator, and the resulting dark green powder was washed with ethanol. Yield: 0.02 g (43%). Anal. Calcd for [$Co(C_9H_{21}N_4S_3)$]: C, 31.75; H, 6.22; N, 16.46. Found: C, 31.84; H, 6.18; N, 16.15. Molar conductivity: 4.8 Ω cm^2 mol^{-1}.

The same procedure using $\Delta\Delta\Delta\Delta$-[**2**][ClO_4]$_6$·7H_2O or $\Lambda\Lambda\Lambda\Lambda$-[**2**][$ClO_4$]$_6$·7$H_2O$ instead of [**2**][ClO_4]$_6$·7H_2O gave the optically active isomer $(-)^{CD}_{580}$ -[**3**] or $(+)^{CD}_{580}$ -[**3**].

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 with a JEOL JNM-A500 NMR spectrometer at 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, Ag, and Zn in the complexes were determined with a Shimazu ICPS-1000III ICP spectrophotometer. The molar conductivities were measured with a Horiba DS-12 conductivity meter in water. Electrochemical measurements were made with a CV-1B apparatus (Bioanalytical Systems, Inc.), using a glassy-carbon working electrode (Bioanalytical Systems, Inc.; GCE). An aqueous Ag/AgCl/NaCl (3 mol dm^{-3}) electrode (Bioanalytical Systems, Inc.; RE-1) and platinum wire were used as reference and auxiliary electrodes, respectively. Electrochemical experiments were conducted in a 0.2 mol dm^{-3} aqueous solution of $NaNO_3$ as the supporting electrolyte with a complex concentration of 1.0 mmol dm^{-3}.

X-ray Structure Determination. Single crystals of [**1**][PF_6]$_3$·H_2O and [**2**][PF_6]$_6$·8H_2O were used for data collection on a Rigaku RASA-7S four-circle diffractometer with graphite-monochromatized Mo Kα 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 range of $23° < 2\theta < 30°$ for [**1**][PF_6]$_3$·H_2O and $28° < 2\theta < 30°$ for [**2**][PF_6]$_6$·8H_2O. The intensity data were collected by the $\omega - 2\theta$ 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 1025 independent reflections with $I > 1.5\sigma(I)$ of the measured 1413 reflections were considered as "observed" and used for structure determination of [**1**][PF_6]$_3$·H_2O, and the 8382 independent reflections with $I > 2\sigma(I)$ of the measured 21723 reflections were used for [**2**][PF_6]$_6$·8H_2O.

Table 1. Crystallographic Data[a] for [**1**][PF_6]$_3$·H_2O and [**2**][PF_6]$_6$·8H_2O

	[**1**][PF_6]$_3$·H_2O	[**2**][PF_6]$_6$·8H_2O
empirical formula	$C_{18}H_{44}Ag_3Co_2F_{18}N_8OP_3S_6$	$C_{36}H_{100}Co_4F_{36}N_{16}O_9P_6S_{12}Zn_4$
fw	1457.3	2653.05
space group	$I\bar{4}2m$ (no. 121)	$P2_1/n$ (no. 14)
a, Å	13.012(1)	14.33(7)
b, Å	13.012(1)	25.67(10)
c, Å	24.707(2)	24.83(6)
β, deg		101.3(3)
V, Å^3	4182.8(8)	8955(47)
Z	4	4
ρ_{calcd}, g cm^{-3}	2.31	1.968
μ, cm^{-1}	26.81	22.90
R^b	0.053	0.069
$R_w{}^c$	0.057	0.077

[a] $T = 23$ °C; λ(Mo Kα) = 0.710 73 Å. [b] $R = \Sigma|(|F_o| - |F_c|)|/\Sigma(|F_o|)$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$.

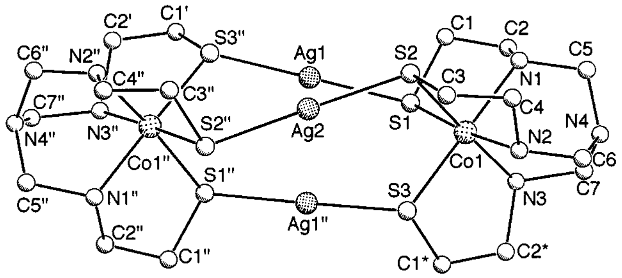

Figure 1. A perspective view of the complex cation [**1**]$^{3+}$ (the $\Delta\Delta$ isomer) with the atomic labeling scheme. The overlapped $\Lambda\Lambda$ isomer is omitted for clarity.

The positions of metal atoms for [**1**][PF_6]$_3$·H_2O and [**2**][PF_6]$_6$·8H_2O were determined by Patterson and direct methods, respectively, and the remaining non-H atom positions were found by successive difference Fourier techniques. The structures were refined by full-matrix least-squares techniques using anisotropic thermal parameters for the non-H atoms, except F21 and F22 of [**1**][PF_6]$_3$·H_2O, which were refined isotropically. H atoms were not included in the calculations. For the atoms of the complex cation [**1**]$^{3+}$, Co1, Ag1, N4, C3, and C4 were constrained to the special positions of symmetry m with a site occupancy factor of 0.5, while Ag2 was constrained to the position of symmetry 2mm with a site occupancy factor of 0.25. The site occupancy factor of other atoms of the complex cation [**1**]$^{3+}$, except C1 and C2, was fixed to 0.5. The symmetry-expansion operation for [**1**][PF_6]$_3$·H_2O showed that a pair of enantiomers coexist in each of four sites in the unit cell, sharing the C atoms of the N,S-chelate rings, besides the Ag, Co, and aza-capped N atoms. All of the calculations were performed using the teXsan crystallographic software package.[36]

Results and Discussion

Crystal Structure of [1][PF$_6$]$_3$·H$_2$O. X-ray structural analysis of [**1**][PF_6]$_3$·H_2O revealed the presence of a discrete complex cation, PF_6^- anions, and a water molecule. The total occupancy factor of the PF_6^- anions implies that the entire complex cation is trivalent, which is consistent with the elemental analytical result. A perspective drawing of the entire complex cation [**1**]$^{3+}$ is given in Figure 1, and its selected bond distances and angles are summarized in Table 2.

The entire complex cation [**1**]$^{3+}$ contains two Co^{III} atoms, each of which is surrounded by an aza-capped hexadentate-N_3S_3 ligand L to form an approximately octahedral [Co^{III}(L)] unit. The two [Co^{III}(L)] units are spanned by three Ag^I atoms, such that the three S−Ag−S linkages form a triple helical structure. As a result, the two Co^{III} atoms are encapsulated in a macrobicyclic metallocage, [$Ag^I_3(L)_2$]$^{3-}$, in which each of three Ag^I atoms is linearly coordinated by two S atoms from two

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[36] Crystal Structure Analysis Package, Molecular Structure Corp., 1985 and 1992.

Table 2. Selected Bond Distances (Å) and Angles (deg) (Averaged) for $[Ag_3\{Co(L)\}_2]^{3+}$ ($[\mathbf{1}]^{3+}$) and $[Ag_3\{Co(aet)_3\}_2]^{3+}$

	$[Ag_3\{Co(L)\}_2]^{3+}$ ($[\mathbf{1}]^{3+}$)	$[Ag_3\{Co(aet)_3\}_2]^{3+}$
	Distances	
Co−S	2.243(8)	2.248(8)
Co−N	2.02(3)	2.03(3)
Ag−S	2.417(8)	2.378(8)
Ag···Ag	2.956(5)	3.029(3)
N_{aet}−C_{cap}	1.49(5)	
N_{cap}-C_{cap}	1.49(5)	
	Angles	
S−Co−S	91.3(3)	92.1(3)
N−Co−N	89(1)	90(1)
S−Ag−S	177.9(4)	174.6(3)
Ag−S−Co	114.9(3)	113.3(4)
C−N_{cap}−C	115(3)	

aza-capped ligands L. Except for the presence of the two terminal aza caps, the overall structure of $[\mathbf{1}]^{3+}$ is similar to that of the parental complex $[Ag_3\{Co(aet)_3\}_2]^{3+}$.[19] In particular, the bond distances and angles around the Co^{III} atoms in $[\mathbf{1}]^{3+}$ are in good agreement with those in $[Ag_3\{Co(aet)_3\}_2]^{3+}$ (Table 2), indicating that introduction of aza caps at the two terminal N_3 faces in $[Ag_3\{Co(aet)_3\}_2]^{3+}$ causes little strain around the Co^{III} atoms. However, it should be noted that the averaged Ag−S distance in $[\mathbf{1}]^{3+}$ (2.417(8) Å) is ca. 0.04 Å longer than that found in $[Ag_3\{Co(aet)_3\}_2]^{3+}$ (2.378(8) Å). Moreover, the S−Ag−S angles (average 177.9(4)°) in $[\mathbf{1}]^{3+}$ are closer to 180° than those in $[Ag_3\{Co(aet)_3\}_2]^{3+}$ (average 174.6(3)°), which permits the slightly shorter Ag···Ag separations in $[\mathbf{1}]^{3+}$ (average 2.956(4) Å), compared with the separations in $[Ag_3\{Co(aet)_3\}_2]^{3+}$ (average 3.029(3) Å).

The two [Co(L)] units in $[\mathbf{1}]^{3+}$ have the same chiral configuration to form the ΔΔ and ΛΛ isomers; the former isomer is illustrated in Figure 1. In the crystal lattice the ΔΔ and ΛΛ isomers coexist in a disordered manner with a site occupancy of 0.5, which indicates that crystal $[\mathbf{1}](PF_6)_3$ is not a racemic compound but a solid solution,[37] as in the case of $[Ag_3\{Co(aet)_3\}_2][BF_4]_3$.[19] All six bridging S atoms have the *S* configuration for the ΔΔ isomer and *R* for the ΛΛ isomer. The helical structure due to three S−Ag−S linkages is left-handed for the ΔΔ isomer and right-handed for the ΛΛ isomer. These stereochemical properties are the same as those in $[Ag_3\{Co(aet)_3\}_2]^{3+}$.[19] All the five-membered N,S-chelate rings in $[\mathbf{1}]^{3+}$ possess the *lel* conformation. This is in contrast with the fact that the *ob* conformation as well as the *lel* one has been found in $[Ag_3\{Co(aet)_3\}_2]^{3+}$. Since all the N,S-chelate rings in $[Co(sep)]^{3+}$ and $[Co(azacapten)]^{3+}$ also adopt the *lel* conformation,[31,33] it is seen that attachment of aza caps to the two terminal N_3 faces in $[Ag_3\{Co(aet)_3\}_2]^{3+}$ results in the fixation of the N,S-chelate rings to be *lel*, which could affect the geometry of flexible Ag^I atoms. In $[\mathbf{1}]^{3+}$ all six N donor atoms are also asymmetric, and their configurations are regulated to *R* for the ΔΔ isomer and *S* for the ΛΛ isomer. Thus, the overall symmetry of $[\mathbf{1}]^{3+}$ having three kinds of chiral centers besides the helical and conformational chiralities is very close to D_3.

Crystal Structure of $[\mathbf{2}][PF_6]_6 \cdot 8H_2O$. The X-ray structural analysis for $[\mathbf{2}][PF_6]_6 \cdot 8H_2O$ revealed the presence of a discrete complex cation, six PF_6^- anions, and water molecules. The number of PF_6^- anions implies that the complex cation $[\mathbf{2}]^{6+}$ is hexavalent. As shown in Figure 2, the complex cation consists of four aza-capped [Co(L)] units, four Zn atoms, and one central μ_4-O atom. This is compatible with the plasma emission spectral analysis of $[\mathbf{2}]^{6+}$ that gave the value of Co:Zn = 4:4. Each of four [Co(L)] units is bound to the tetrahedral $[Zn_4O]^{6+}$ core, such that the trigonal S_3 face of the [Co(L)] unit is capped by the $[Zn_4O]^{6+}$ core. As a result, in $[\mathbf{2}]^{6+}$ each of four Co^{III} atoms is encapsulated in a macrobicyclic $[Zn_4O(L)]$ fragment (Figure 3). Except for the presence of the four aza caps, the overall structure of $[\mathbf{2}]^{6+}$ is essentially the same as that of the S-bridged $Co^{III}_4Zn^{II}_4$ octanuclear complex composed of four *fac*-$[Co(aet)_3]$ units, $[Zn_4O\{Co(aet)_3\}_4]^{6+}$.[16] That is, the bond distances and angles around the Co^{III} and Zn^{II} atoms in $[\mathbf{2}]^{6+}$ are quite similar to those in $[Zn_4O\{Co(aet)_3\}_4]^{6+}$, although the Co−S−Zn bridging angles in $[\mathbf{2}]^{6+}$ (average 118.8(3)°) are slightly larger than those in $[Zn_4O\{Co(aet)_3\}_4]^{6+}$ (average 116.2(1)°) (Table 3).

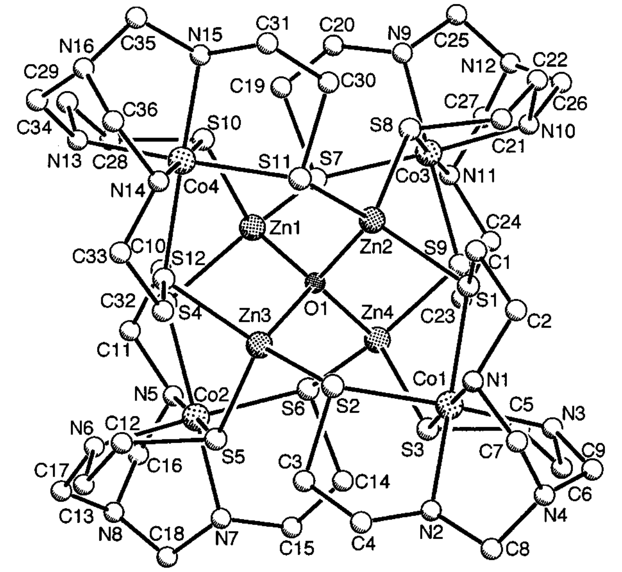

Figure 2. A perspective view of the complex cation $[\mathbf{2}]^{6+}$ (the ΔΔΔΔ isomer) with the atomic labeling scheme.

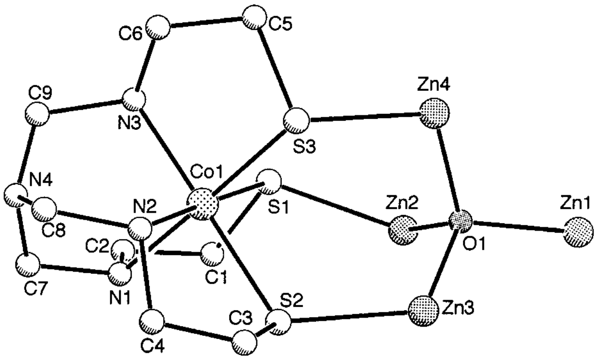

Figure 3. A perspective view of the $[Zn_4O\{Co(L)\}]$ fragment in $[\mathbf{2}]^{6+}$. The three [Co(aet)] units for Co2, Co3, and Co4 are omitted from the ΔΔΔΔ isomer of the complex cation $[\mathbf{2}]^{6+}$.

The four [Co(L)] units in $[\mathbf{2}]^{6+}$ have the same chiral configuration to form the ΔΔΔΔ isomer and its enantio ΛΛΛΛ isomer, which combine to form the racemic compound; the former isomer is illustrated in Figure 2. All 12 bridging S atoms are fixed to the *S* configuration for the ΔΔΔΔ isomer and the *R* configuration for the ΛΛΛΛ isomer. The same stereochemical behavior has been found in the corresponding S-bridged octanuclear structure in $[Zn_4O\{M(aet)_3\}_4]^{6+}$ (M = Co^{III}, Rh^{III}).[16,38,39] The chiral configurations of the 12 N donor atoms

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(37) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates and Resolutions*; John Wiley & Sons Ltd.: New York, 1981.

(38) Konno, T.; Okamoto, K.; Hidaka, J. *Inorg. Chem.* **1991**, *30*, 2253.

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

Table 3. Selected Bond Distances (Å) and Angles (deg) (Averaged) for $[Zn_4O\{Co(L)\}_4]^{6+}$ ($[\mathbf{2}]^{6+}$) and $[Zn_4O\{Co(aet)_3\}_4]^{6+}$

	$[Zn_4O\{Co(L)\}_4]^{6+}$ ($[\mathbf{2}]^{6+}$)	$[Zn_4O\{Co(aet)_3\}_4]^{6+}$
	Distances	
Co−S	2.26(1)	2.266(4)
Co−N	2.03(2)	2.006(11)
Zn−S	2.345(8)	2.343(3)
Zn−O	1.937(10)	1.948(12)
$N_{aet}-C_{cap}$	1.53(2)	
$N_{cap}-C_{cap}$	1.46(3)	
	Angles	
S−Co−S	92.2(2)	93.8(1)
N−Co−N	91.0(6)	90.2(5)
S−Zn−S	111.1(3)	111.7(1)
S−Zn−O	107.8(4)	107.1(3)
Zn−S−Co	118.8(3)	116.2(1)
$C-N_{cap}-C$	114(2)	

in $[\mathbf{2}]^{6+}$ are unified to be *R* for the ΔΔΔΔ isomer and *S* for the ΛΛΛΛ isomer. Thus, only a pair of enantiomers with a *T* symmetry, $(\Delta)_4(S_S)_{12}(R_N)_{12}$ and $(\Lambda)_4(R_S)_{12}(S_N)_{12}$, are selectively formed for $[\mathbf{2}]^{6+}$, which contains a total of 28 chiral centers. In addition, all 12 five-membered N,S-chelate rings in $[\mathbf{2}]^{6+}$ uniformly adopt the *lel* conformation (Figures 2 and 3). This is in contrast with a mixture of *lel* and *ob* conformations of the aet chelate rings found in $[Zn_4O\{M(aet)_3\}_4]^{6+}$.[16,38,39]

Synthesis and Characterization. Treatment of a dark purple acetonitrile solution containing $[Ag_3\{Co(aet)_3\}_2][BF_4]_3$ with paraformaldehyde and triethylamine gave a dark red solution, which turned dark purple in color upon the addition of aqueous ammonia. From the dark purple reaction solution the aza-capped Co$^{III}_2$Ag$^{I}_3$ complex $[Ag_3\{Co(L)_3\}_2]^{3+}$ ($[\mathbf{1}]^{3+}$) was isolated as a nitrate salt in high yield. A related aza-capped Co$^{III}_3$ trinuclear complex, $[Co\{Co(L)\}_2]^{3+}$, has been prepared by reaction of $[Co\{Co(aet)_3\}_2]^{3+}$ with paraformaldehyde and gaseous ammonia in acetonitrile, by way of a hexaimine intermediate $[Co\{Co(CH_2{=}NCH_2CH_2S)_3\}_2]^{3+}$, although none of the complexes have been structurally characterized. These facts indicate that the capping procedure of a trigonal N_3 face of three primary amine groups, which has been established for the mononuclear metal complexes,[31−33] is applicable for the polynuclear metal complexes. Here it should be noted that $[\mathbf{1}]^{3+}$ was little formed by the direct reaction of $[Ag_3\{Co(aet)_3\}_2]^{3+}$ with formaldehyde and ammonia in aqueous solution, while this method has been employed for the preparation of the aza-capped mononuclear complexes $[Co(sep)]^{3+}$, $[Co(azamesar)]^{3+}$, and $[Co(azacapten)]^{3+}$, from the precursory amine complexes $[Co(en)_3]^{3+}$, $[Co(sen)]^{3+}$, and $[Co(ten)]^{3+}$, respectively.[31−33]

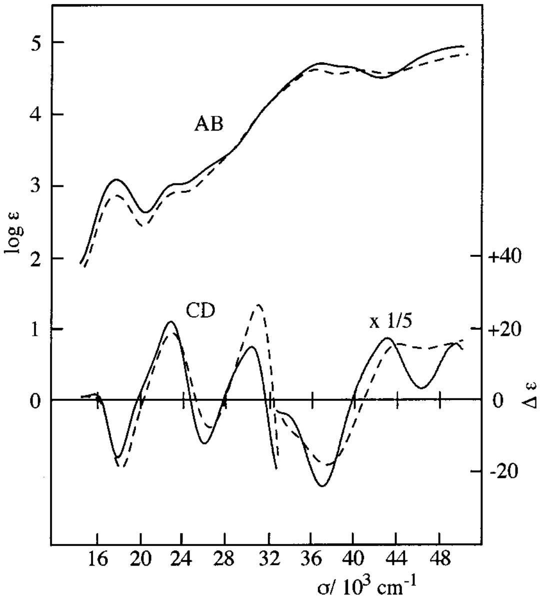

Figure 4. Electronic absorption and CD spectra of $(-)^{\mathrm{CD}}_{580}$-ΔΔ-$[\mathbf{1}]^{3+}$ (—) and ΔΔ-$[Ag_3\{Co(aet)_3\}_2]^{3+}$ (- - -) in H_2O.

Table 4. Electronic Absorption and CD Spectral Data

abs max: $\sigma/10^3\,\mathrm{cm^{-1}}$ (log ϵ/mol^{-1} dm^3 cm^{-1})	CD extrema: $\sigma/10^3\,\mathrm{cm^{-1}}$ ($\Delta\epsilon$/mol^{-1} dm^3 cm^{-1})
ΔΔ-$[Ag_3\{Co(L)\}_2]^{3+}$ ($(-)^{\mathrm{CD}}_{580}$-$[\mathbf{1}]^{3+}$)	
17.66 (3.03)	15.57 (+0.78)
23.35 (3.0) sh[a]	17.77 (−16.88)
36.76 (4.64)	22.78 (+21.05)
38.85 (4.6) sh	25.85 (−13.12)
	30.23 (+13.92)
	36.84 (−125.51)
	42.96 (+81.45)
	49.41 (+73.61)
ΔΔΔΔ-$[\{Co(L)\}_4Zn_4O]^{6+}$ ($(-)^{\mathrm{CD}}_{580}$-$[\mathbf{2}]^{6+}$)	
17.56 (3.30)	17.16 (−18.32)
23.46 (3.40)	21.82 (+8.30)
29.85 (4.31)	26.71 (+11.64)
37.31 (4.91)	34.63 (−105.43)
	39.56 (+112.74)
	43.59 (+134.85)
Δ-[Co(L)] ($(-)^{\mathrm{CD}}_{580}$-[**3**])	
17.28 (2.59)	16.87 (−6.77)
22.61 (2.66)	21.6 (+2.5) sh
37.15 (4.34)	22.70 (+2.64)
	27.95 (+6.00)
	31.27 (−1.92)
	35.24 (+32.93)
	38.76 (−16.76)
	46.5 (−3.5) sh

[a] The sh label denotes a shoulder.

Figure 4 illustrates the electronic absorption spectrum of $[\mathbf{1}]^{3+}$, together with that of the parental complex $[Ag_3\{Co(aet)_3\}_2]^{3+}$; their data are summarized in Table 4. The absorption spectrum of $[\mathbf{1}]^{3+}$ is quite similar to that of $[Ag_3\{Co(aet)_3\}_2]^{3+}$ over the whole region,[19] giving two spin-allowed d−d transition bands at ca. 17.7 × 10^3 and 23.4 × 10^3 cm^{-1} and two intense sulfur-to-cobalt charge-transfer (CT) bands at ca. 36.8 × 10^3 and 38.9 × 10^3 cm^{-1}, although each band for $[\mathbf{1}]^{3+}$ is slightly intensified, compared with the corresponding band for $[Ag_3\{Co(aet)_3\}_2]^{3+}$. This is compatible with the X-ray analytical result, which demonstrates that each Co^{III} atom in $[\mathbf{1}]^{3+}$ is situated in a coordination environment quite similar to that in $[Ag_3\{Co(aet)_3\}_2]^{3+}$. No significant absorption spectral change with time was noticed for $[\mathbf{1}]^{3+}$ at least for 1 day. Furthermore, in the 500 MHz ^{13}C NMR $[\mathbf{1}]^{3+}$ gives only three sharp signals due to three kinds of methylene carbon atoms in the two [Co(L)] units (δ 34.64, CH_2S; δ 61.62, CH_2N; δ 69.76, NCH_2NH). These results suggest that the D_3-symmetrical structure observed in the crystal is retained in solution. $[\mathbf{1}]^{3+}$ was optically resolved into its enantiomers, $(+)^{\mathrm{CD}}_{580}$ and $(-)^{\mathrm{CD}}_{580}$, by SP-Sephadex C-25 column chromatography, using $[Sb_2(R,R\text{-tartrato})_2]^{2-}$ as the resolving agent. As shown in Figure 4, the CD spectrum of $(-)^{\mathrm{CD}}_{580}$-$[\mathbf{1}]^{3+}$ corresponds well with that of the ΔΔ isomer of $[Ag_3\{Co(aet)_3\}_2]^{3+}$ [16] over the whole region. Thus, the $(-)^{\mathrm{CD}}_{580}$ isomer of $[\mathbf{1}]^{3+}$ is assigned to the ΔΔ isomer, while $(+)^{\mathrm{CD}}_{580}$-$[\mathbf{1}]^{3+}$ is the ΛΛ one. This assignment is supported by the fact that only the $(-)^{\mathrm{CD}}_{580}$ isomer of $[\mathbf{1}]^{3+}$ was formed when ΔΔ-$[Ag_3\{Co(aet)_3\}_2]^{3+}$ was used as the starting complex for the condensation reaction.

Attempts to fit the S-bridged Co$^{III}_4$Zn$^{II}_4$ octanuclear $[Zn_4O\{Co(aet)_3\}_4]^{6+}$ with aza caps by a similar condensation reaction

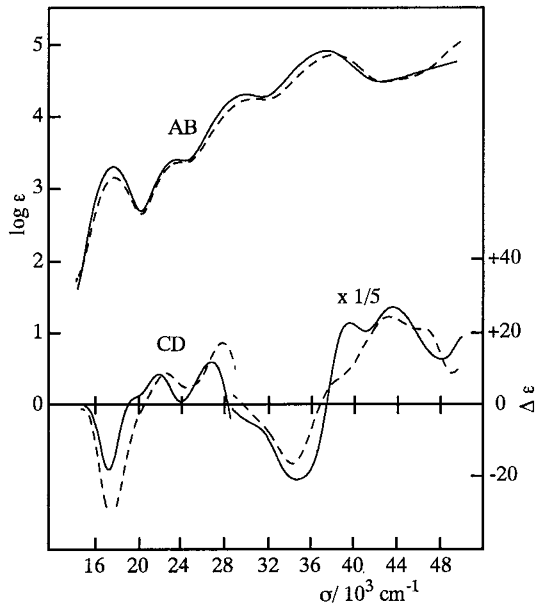

Figure 5. Electronic absorption and CD spectra of $(-)^{CD}_{580}$-ΔΔΔΔ-[**2**]$^{6+}$ (—) and ΔΔΔΔ-[$Zn_4O\{Co(aet)_3\}_4$]$^{6+}$ (- - -) in H_2O.

were unsuccessful, mainly because of the decomposition of [$Zn_4O\{Co(aet)_3\}_4$]$^{6+}$ in basic conditions. However, the corresponding aza-capped complex [$Zn^{II}_4O\{Co^{III}(L)\}_4$]$^{6+}$ ([**2**]$^{6+}$) was successfully derived from [**1**]$^{3+}$ (Scheme 1). That is, treatment of [**1**][NO_3]$_3$ with a stoichiometric amount of NaI in the presence of excess ZnO and $Zn(NO_3)_2$ in water gave a dark blue-purple solution, from which [**2**]$^{6+}$ was isolated as a perchlorate salt in satisfactory yield. As shown in Figure 5 and Table 4, the absorption spectrum of [**2**]$^{6+}$ gives two spin-allowed d−d transition bands at ca. 17.6 × 10^3 and 23.5 × 10^3 cm^{-1} and two intense sulfur-to-cobalt CT bands at ca. 29.9 × 10^3 and 37.3 × 10^3 cm^{-1}. This spectral feature coincides well with that of [$Zn_4O\{Co(aet)_3\}_4$]$^{6+}$,[16] which is compatible with the X-ray analytical result. The ^{13}C NMR spectrum of [**2**]$^{6+}$ exhibits only three sharp signals due to three kinds of methylene carbon atoms in the four [Co(L)] units (δ 32.63, CH_2S; δ 61.15, CH_2N; δ 69.51, NCH_2NH). In the cyclic voltammogram at a grassy-carbon electrode in a 0.2 mol dm^{-3} aqueous $NaNO_3$ solution, [**2**]$^{6+}$ displays four consecutive redox couples ($E°' = -0.43$, −0.55, −0.62, and −0.75 V vs Ag/AgCl) with a peak separation ($E_{pc} - E_{pa}$) of ca. 80 mV at a scan rate of 100 mV s^{-1}. Similar redox behavior has been characteristically observed for [$M_4O\{Co(aet)_3\}_4$]$^{6+}$ (M = Zn^{II}, $E°' = -0.40$, −0.52, −0.65, and −0.83 V; M = Hg^{II}, $E°' = -0.47$, −0.58, −0.72, and −0.90 V) having a *T*-symmetrical S-bridged $Co^{III}_4M_4$ octanuclear structure.[16,17] These results imply that the *T*-symmetrical octanuclear structure observed in the crystal is retained in solution. [**2**]$^{6+}$ was optically resolved into its enantiomers, $(+)^{CD}_{580}$ and $(-)^{CD}_{580}$, by SP-Sephadex C-25 column chromatography. The $(+)^{CD}_{580}$ and $(-)^{CD}_{580}$ isomers of [**2**]$^{6+}$ are assigned the ΛΛΛΛ and ΔΔΔΔ configurations, respectively, by comparing their CD spectra with those of ΛΛΛΛ- and ΔΔΔΔ-[$Zn_4O\{Co(aet)_3\}_4$]$^{6+}$ (Figure 5).[16] When ΔΔ-[**1**]$^{3+}$ was used as the starting complex, instead of the racemate of [**1**]$^{3+}$, only the ΔΔΔΔ isomer of [**2**]$^{6+}$ was formed. This result indicates that the $Co^{III}_2Ag^I_3$ pentanuclear structure in [**1**]$^{3+}$ is converted to the $Co^{III}_4Zn^{II}_4$ octanuclear structure in [**2**]$^{6+}$ with retention of the chiral configuration of the [Co(L)] units.

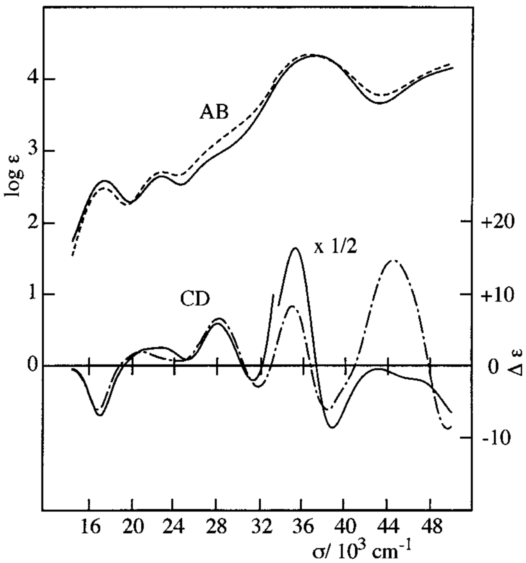

Figure 6. Electronic absorption and CD spectra of $(-)^{CD}_{580}$-Δ-[**3**] (—), *fac*-[$Co(aet)_3$] (- - -), and $Δ_{LLL}$-*fac*-[Co(L-cys-*N,S*)$_3$]$^{3-}$ (— • —) in H_2O.

While [**2**]$^{6+}$ is stable enough to measure its absorption, CD, and NMR spectra in neutral or acidic solution, it readily decomposes in basic solution. In fact, treatment of [**2**][ClO_4]$_6$ with NaOH in aqueous medium produced a dark green-blue powder of [**3**] immediately, which was purified by SP-Sephadex C-25 column chromatography. As shown in Figure 6, the absorption spectrum of [**3**] is quite similar to that of the mononuclear *fac*-[$Co(aet)_3$][9,16] over the whole region, giving two spin-allowed d−d absorption bands at ca. 17.3 × 10^3 and 22.6 × 10^3 cm^{-1} and one broad sulfur-to-cobalt CT band at ca. 37.2 × 10^3 cm^{-1}. Furthermore, the molar conductivity of [**3**] in water (4.8 Ω cm^2 mol^{-1}) suggests that [**3**] is a nonelectrolyte. From these facts and the elemental analysis, it is assigned that [**3**] is the aza-capped mononuclear complex [Co(L)]. This assignment is supported by its electrospray mass spectrum recorded in water at a cone voltage of 50 V, which exhibits a major peak at *m/z* 341 corresponding to [Co(L) + H]$^+$. When ΔΔΔΔ-[**2**]$^{6+}$ was used as the starting complex instead of the racemate of [**2**]$^{6+}$, only the $(-)^{CD}_{580}$ isomer of [**3**] was obtained. The CD spectral behavior of $(-)^{CD}_{580}$-[**3**] coincides well with that of $Δ_{LLL}$-*fac*-[Co(L-cys-*N,S*)$_3$]$^{3-}$ [16,20] in the energy region lower than ca. 40 × 10^3 cm^{-1} (Figure 6). Furthermore, the reaction of $(-)^{CD}_{580}$-[**3**] with $AgNO_3$ in a ratio of 2:3 in water at room temperature produced only the ΔΔ isomer of [$Ag_3\{Co(L)\}_2$]$^{3+}$ ([**1**]$^{3+}$), which was confirmed by SP-Sephadex C-25 column chromatography of the reaction solution. These results indicate that $(-)^{CD}_{580}$-[**3**] is the Δ isomer of [Co(L)] and that the conversion reactions of [**2**]$^{6+}$ to [**3**] and [**3**] to [**1**]$^{3+}$ proceed with retention of the chiral configuration of [Co(L)]. The aqueous solution of [**3**] changes its color from green-blue to brown after several days at room temperature, which implies that [**3**] is not so stable in solution. A similar trend has been noticed for the mononuclear *fac*-[$Co(aet)_3$] and *fac*-[Co(L-cys-*N,S*)$_3$]$^{3-}$.[16,17] However, the absorption spectral change with time for [**3**] was found to be considerably slower than that for *fac*-[$Co(aet)_3$]. That is, the absorption peak of the sulfur-to-cobalt CT band (269 nm) for [**3**] decreased only 1% in intensity for 1 h, while a 19% decrease of the corresponding band (274 nm) was observed for *fac*-[$Co(aet)_3$]. This result clearly indicates that attachment of an aza cap on the trigonal N_3 face in *fac*-[$Co(aet)_3$] stabilizes the tris(thiolato)cobalt(III) mononuclear structure.

CD Spectra. The ΔΔΔΔ isomer of [$Zn_4O\{Co(L)\}_4$]$^{6+}$ ([**2**]$^{6+}$) possesses three kinds of chiralities which would contribute mainly to the CD spectrum: 4 Co^{III} chiral centers with the Δ

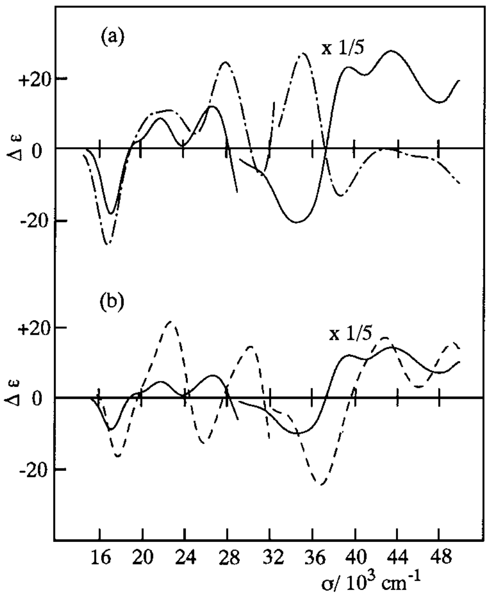

Figure 7. The CD spectral curves of ΔΔΔΔ-[**2**]$^{6+}$ (—) and Δ-[**3**] × 4 (- • -) (a), and the curves of ΔΔ-[**1**]$^{3+}$ (- - -) and ΔΔΔΔ-[**2**]$^{6+}$ × 0.5 (—) (b).

configuration, 12 asymmetric S donor atoms with the *S* configuration, and 12 asymmetric N donor atoms with the *R* configuration. As illustrated in Figure 5, the CD spectrum of ΔΔΔΔ-[**2**]$^{6+}$ resembles that of ΔΔΔΔ-[$Zn_4O\{Co(aet)_3\}_4$]$^{6+}$, which has two kinds of chiralities (4 Co chiral centers with the Δ configuration and 12 asymmetric S donor atoms with the *S* configuration). Thus, it is considered that the CD contribution due to the asymmetric N donor atoms in [**2**]$^{6+}$ is relatively small, assuming that the CD contributions in the S-bridged polynuclear structure are additive.[27] This is also the case for the asymmetric N donor atoms in [$Ag_3\{Co(L)\}_2$]$^{3+}$ ([**1**]$^{3+}$); the CD spectral features for ΔΔ-[**1**]$^{3+}$ and ΔΔ-[$Ag_3\{Co(aet)_3\}_2$]$^{3+}$ agree well with each other over the whole region (Figure 4). Figure 7a compares the CD spectrum of ΔΔΔΔ-[**2**]$^{6+}$ with that of 4 mol of Δ-[Co(L)] (Δ-[**3**]). In the energy region lower than ca. 30 × 10^3 cm^{-1} the two CD spectral curves are similar to each other, showing one negative and two positive CD bands from the lower energy side. This similarity suggests that the CD contribution due to the asymmetric S donor atoms in [**2**]$^{6+}$ is minor in this region. However, in the near-UV region (ca. (32−48) × 10^3 cm^{-1}) the CD spectral curve of ΔΔΔΔ-[**2**]$^{6+}$ differs significantly from that of 4 mol of Δ-[**3**]. In particular, the CD bands of ΔΔΔΔ-[**2**]$^{6+}$ in the sulfur-to-cobalt CT band region (ca. (32−40) × 10^3 cm^{-1}) are reversed in sign, compared with those of 4 mol of Δ-[**3**]. Thus, in the sulfur-to-cobalt CT band region the CD signs of ΔΔΔΔ-[**2**]$^{6+}$ are dominated by the 12 asymmetric S donor atoms with the *S* configuration.

ΔΔ-[$Ag_3\{Co(L)\}_2$]$^{3+}$ (ΔΔ-[**1**]$^{3+}$) has the left-handed triple helical chirality due to three S−Ag−S linkages, besides the three kinds of chiralities (two Co^{III} chiral centers with the Δ configuration, six asymmetric S donor atoms with the *S* configuration, and six asymmetric N donor atoms with the *R* configuration). Since ΔΔΔΔ-[**2**]$^{6+}$ has 4 Δ configurational Co^{III} centers, 12 *S* configurational S donor atoms, and 12 *R* configurational N donor atoms, the CD spectral deviation between ΔΔ-[**1**]$^{3+}$ and 0.5 mol of ΔΔΔΔ-[**2**]$^{6+}$ would be attributed to the CD contribution from the triple helical chirality in ΔΔ-[**1**]$^{3+}$. As compared in Figure 7b, the CD spectral curve of ΔΔ-[**1**]$^{3+}$ is considerably deviated from that of 0.5 mol of ΔΔΔΔ-[**2**]$^{6+}$, although they show CD spectral signs similar to each other in the first d−d band and the sulfur-to-cobalt CT band regions. Accordingly, it is reasonable to assume that the triple helical chirality in the S-bridged $Co^{III}{}_2Ag^{I}{}_3$ pentanuclear structure of [**1**]$^{3+}$ contributes conspicuously to the CD spectrum over the whole region.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of [**1**][PF_6]$_3$•H_2O and [**2**][PF_6]$_6$•$8H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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