Synthesis, Crystal Structures, and Spectroscopic Characterization of Two Pairs of Racemic Isomers of $[\{Co_2(aet)_2\}\{Co(aet)_3\}_2]^{4+}$ (aet = 2-Aminoethanethiolate): A Novel S-Bridged Tetranuclear Cobalt(III) Complex Formed by Ligand Transfer from Nickel(II) to Cobalt(III)

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A novel S-bridged tetracobalt(III) complex, $[\{Co_2(aet)_2\}\{Co(aet)_3\}_2]^{4+}$ (**1**), was prepared by reacting [Ni(aet)$_2$] (aet = 2-aminoethanethiolate) with $[CoCl(NH_3)_5]^{2+}$ or $[CoCl_2(en)_2]^{+}$ (en = ethylenediamine) in water. **1** formed two pairs of racemic isomers, **1a** and **1b**, which were separated by fractional crystallization and/or cation-exchange column chromatography. The crystal structures of **1a** and **1b** were determined by X-ray crystallography. **1a**(NO$_3$)$_4$·2H$_2$O, empirical formula $C_{16}H_{52}N_{12}O_{14}S_8Co_4$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 13.585(3)$ Å, $b = 15.132(3)$ Å, $c = 10.699(2)$ Å, $\alpha = 101.46(1)°$, $\beta = 104.78(1)°$, $\gamma = 95.89(1)°$, and $Z = 2$. **1b**(NO$_3$)$_4$·2H$_2$O crystallizes in the monoclinic space group *Cc* with $a = 26.633(6)$ Å, $b = 10.204(1)$ Å, $c = 15.907(4)$ Å, $\beta = 110.33(1)°$, and $Z = 4$. Each of **1a** and **1b** contains four cobalt atoms which are linked by one double and two triple sulfur bridges in a boat-type metal array. The two outer cobalt atoms have a *fac*-Co(N)$_3$(S)$_3$ chromophore, while the two inner cobalt atoms have a Co(N)(S)$_5$ chromophore. The isomers possible for **1** are discriminated by a combination of the Δ or Λ configuration for the outer cobalt centers and the *C* or *A* configuration for the inner cobalt centers, and X-ray analyses indicated that **1a** and **1b** have the $\Delta AA\Delta/\Lambda CC\Lambda$ and $\Delta CC\Delta/\Lambda AA\Lambda$ configurations, respectively. Each of **1a** and **1b** was optically resolved, and their electronic absorption, circular dichroism (CD), and NMR spectral properties are also reported. The additivity on CD was considered to assign the absolute configuration for the optically resolved isomers of **1a** and **1b**.

Introduction

It has been recognized that [Ni(thiolato-*S*)$_2$(amine-*N*)$_2$]-type mononuclear complexes react with a variety of metal ions to form S-bridged polynuclear complexes.[1−8] For the most part, the isolated polynuclear complexes are composed of *cis(S)*-[Ni(thiolato-*S*)$_2$(amine-*N*)$_2$] units, which act as chelating or bridging bidentate-*S,S* metalloligands.[1−7] For example, the reaction of [Ni(aet)$_2$] (aet = $NH_2CH_2CH_2S^-$) with Ni^{2+} gave a linear-type S-bridged trinuclear complex $[Ni\{Ni(aet)_2\}_2]^{2+}$, in which each of two *cis(S)*-[Ni(aet)$_2$] units chelates to the central Ni^{II} atom,[1a,c] while the reaction with Pd^{2+} produced a pinwheel-type S-bridged hexanuclear complex $[Pd_2\{Ni(aet)_2\}_4]^{4+}$, in which each of four *cis(S)*-[Ni(aet)$_2$] units bridges two Pd^{II} atoms.[1d] On the other hand, we have recently reported that the reaction product of [Ni(aet)$_2$] and $[CoCl_2(en)_2]^{+}$ (en = $NH_2CH_2CH_2NH_2$) does not contain *cis(S)*-[Ni(aet)$_2$] units but *cis(S)*-$[Co(aet)_2(en)]^{+}$ ones which chelate to the central Ni^{II} atom to form an S-bridged Co^{III}Ni^{II}Co^{III} trinuclear structure in $[Ni\{Co(aet)_2(en)\}_2]^{4+}$.[8] From this result, it was proved that the bidentate-*N,S* ligand aet in [Ni(aet)$_2$] transfers to the octahedral Co^{III} coordination sphere.

In order to explore the possibility that a similar S-bridged Co^{III}Ni^{II}Co^{III} trinuclear structure is formed by using another cobalt(III) complex, we examined the reaction of [Ni(aet)$_2$] with $[CoCl(NH_3)_5]^{2+}$. However, this reaction was found to produce a novel S-bridged tetracobalt(III) complex $[\{Co_2(aet)_2\}\{Co(aet)_3\}_2]^{4+}$ (**1**), which forms two pairs of racemic isomers. A preliminary result concerning the crystal structure of one of the racemic isomers for **1** has been reported.[9] In this paper we report on the complete description of synthesis, separation, optical resolution, and spectroscopic characterizations of the obtained isomers for **1**, along with the crystal structures of the two pairs of racemic isomers.

Experimental Section

Preparation of $\Delta AA\Delta/\Lambda CC\Lambda$- and $\Delta CC\Delta/\Lambda AA\Lambda$-$[\{Co_2(aet)_2\}\{Co(aet)_3\}_2](NO_3)_4$ (1a(NO$_3$)$_4$ and 1b(NO$_3$)$_4$). Method 1. To a green

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(1) (a) Jicha, D. C.; Busch, D. H. *Inorg. Chem.* **1962**, *1*, 872. (b) Jicha, D. C.; Busch, D. H. *Inorg. Chem.* **1962**, *1*, 878. (c) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1970**, *9*, 1878. (d) Konno, T.; Yonenobu, K.; Hidaka, J.; Okamoto, K. *Inorg. Chem.* **1994**, *33*, 861.

(2) Root, C. A.; Busch, D. H. *Inorg. Chem.* **1968**, *7*, 789.

(3) Hay, R. W.; Galyer, A. L.; Lawrance, G. A. *J. Chem. Soc., Dalton Trans.* **1976**, 939.

(4) Barrera, H.; Suades, J.; Perucard, M. C.; Brianso, J. L. *Polyhedron* **1984**, *3*, 839.

(5) Turner, M. A.; Driessen, W. E.; Reedijk, J. *Inorg. Chem.* **1990**, *29*, 3331.

(6) (a) Colpas, G. J., Kumar, M. R.; Day, O.; Maroney, M. J. *Inorg. Chem.* **1990**, *29*, 4779. (b) Colpas, G. J.; Day, R. O.; Maroney, M. J. *Inorg. Chem.* **1992**, *31*, 5053.

(7) (a) Mills, D. K.; Hsiao, Y. M.; Farmer, P. J.; Atnip, E. V.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 1421. (b) Farmer, P. J.; Solouki, T.; Mills, D. K.; Soma, T.; Russell, D. H.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4601. (c) Tuntulani, T.; Reibenspies, J. H.; Farmer, P. J.; Darensbourg, M. Y. *Inorg. Chem.* **1992**, *31*, 3497. (d) Musie, M.; Farmer, P. J.; Tuntulani, T.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1996**, *35*, 2176.

(8) Konno, T.; Okamoto, K.; Hidaka, J. *Inorg. Chem.* **1992**, *31*, 160. (b) Konno, T.; Hidaka, J.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1353.

(9) Konno, T.; Okamoto, K. *Chem. Lett.* **1995**, 675.

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suspension containing 2.0 g (9.5 mmol) of $[Ni(aet)_2]^{1a}$ in 40 cm^3 of water was added 2.4 g (9.5 mmol) of $[CoCl(NH_3)_5]Cl_2$.[10] The mixture was stirred at room temperature for 1 day and then filtered to remove an insoluble green powder. To the black filtrate was added 20 cm^3 of a saturated $NaNO_3$ aqueous solution, followed by cooling in a refrigerator for 1 day. The resulting black crystals (**1a**$(NO_3)_4$) contaminated with a small amount of green powder were recrystallized from water by adding a few drops of a saturated $NaNO_3$ aqueous solution. One of the recrystallized crystals was used for the X-ray analysis. Yield: 0.44 g. Anal. Calcd for $[Co_4(C_2H_6NS)_8](NO_3)_4\cdot 2H_2O$: C, 17.02; H, 4.64; N, 14.89; Co, 20.88. Found for **1a**$(NO_3)_4$: C, 16.91; H, 4.80; N, 14.59; Co, 20.60. ^{13}C NMR spectrum in D_2O (ppm from DSS): δ 30.70, 33.20, 33.81, and 37.69 for CH_2S; δ 48.82, 49.27, 49.37, and 51.05 for CH_2N.

A portion of the black reaction solution obtained by the method described above was poured onto a cation-exchange column of SP-Sephadex C-25 (Na^+ form, 4.5 × 110 cm). After the column had been swept with water and then with a 0.3 mol dm^{-3} aqueous solution of NaCl, the adsorbed band was eluted with a 0.4 mol dm^{-3} aqueous solution of NaCl. Two dark brown bands were eluted. It was found from the absorption spectral measurements that the earlier moving band and the later moving one contained **1a** and **1b**, respectively (ca. **1a**:**1b** = 4:1). The eluate of **1b** was concentrated to a small volume, and the deposited NaCl was filtered off. The desalted filtrate was then passed through an anion-exchange column of QAE-Sephadex A-25 (NO_3^- form, 4.0 × 80 cm) by eluting with water. The eluate was concentrated to a small volume with a rotary evaporator, followed by cooling in a refrigerator for several days. The resulting fine black crystals (**1b**$(NO_3)_4$) were collected by filtration. Crystals of a suitable size for X-ray analysis were obtained by recrystallization from water at room temperature. Anal. Calcd for $[Co_4(C_2H_6NS)_8](NO_3)_4\cdot 2H_2O$: C, 17.02; H, 4.64; N, 14.89; Co, 20.88. Found for **1b**$(NO_3)_4$: C, 17.06; H, 4.66; N, 14.60; Co, 20.68. ^{13}C NMR spectrum in D_2O (ppm from DSS): δ 29.75, 32.74, 33.16, and 37.77 for CH_2S; δ 49.14, 49.21, 49.65, and 52.76 for CH_2N.

Method 2. To a green suspension containing 2.0 g (9.5 mmol) of $[Ni(aet)_2]^{1a}$ in 40 cm^3 of water was added 2.7 g (9.5 mmol) of *trans*-$[CoCl_2(en)_2]Cl$.[11] The mixture was stirred at room temperature for 1 day and then filtered to remove a brown powder of $[Ni\{Co(aet)_2(en)\}_2]Cl_4$[8] contaminated with an insoluble green powder. The black filtrate was allowed to stand in a refrigerator for 1 day, which gave brown microcrystals of $[Ni\{Co(aet)_2(en)\}_2]Cl_4$. After the microcrystals had been filtered off, to the black filtrate was added 20 cm^3 of a saturated $NaNO_3$ aqueous solution. The mixture was stored in a refrigerator for 2 days and the resulting black crystals (**1a**$(NO_3)_4\cdot 2H_2O$, 0.50 g) were collected by filtration. When the remaining filtrate was allowed to stand in a refrigerator for several days, a brown powder (0.05 g) containing **1a**$(NO_3)_4$ and **1b**$(NO_3)_4$ was precipitated. **1a**$(NO_3)_4$ and **1b**$(NO_3)_4$ were separated by the same column chromatographic technique as described in method 1.

1a and **1b** were also formed using *cis*-$[CoCl_2(en)_2]Cl$ [11] instead of *trans*-$[CoCl_2(en)_2]Cl$.

Reaction of $[CoCl_2(en)_2]Cl$ with aet. To a solution containing 1.00 g (3.50 mmol) of $[CoCl_2(en)_2]Cl$ in 15 cm^3 of water was added 0.54 g (7.00 mmol) of Haet. The mixture was stirred at room temperature for 3 h, followed by storing in a refrigerator for several days. The resulting black crystals (0.15 g), which show an absorption spectrum identical with that of $[Co\{Co(aet)_3\}_2]^{3+}$,[12] were collected by filtration. It was found from SP-Sephadex C-25 column chromatography that **1** is little formed in this reaction.

Optical Resolution of 1a and 1b. An aqueous solution of **1a**$(NO_3)_4\cdot 2H_2O$ was chromatographed on an SP-Sephadex C-25 column (Na^+ form, 2.4 × 40 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 0.4 mol dm^{-3} aqueous solution of NaCl. Each eluate of the two bands was concentrated to a small volume, and the concentrated solution was used for the CD spectral measurement. The concentration of each eluate was evaluated on the basis of the absorption spectral data of the racemic salt **1a**$(NO_3)_4\cdot 2H_2O$. It was found from the CD spectral measurements that the earlier and the later moving bands in the column contained the $(+)^{CD}_{550}$ and the $(-)^{CD}_{550}$ isomers, respectively, which show CD curves enantiomeric to each other.

Table 1. Crystallographic Data[a] for **1a**$(NO_3)_4\cdot 2H_2O$ and **1b**$(NO_3)_4\cdot 2H_2O$

	1a$(NO_3)_4\cdot 2H_2O$	**1b**$(NO_3)_4\cdot 2H_2O$
empirical formula	$C_{16}H_{52}N_{12}O_{14}S_8Co_4$	$C_{16}H_{52}N_{12}O_{14}S_8Co_4$
fw	1128.9	1128.9
space group	$P\bar{1}$ (No. 2)	*Cc* (No. 9)
a, Å	13.585(3)	26.633(6)
b, Å	15.132(3)	10.204(1)
c, Å	10.699(2)	15.907(4)
β, deg	101.46(1)	
β, deg	104.78(1)	110.33(1)
γ, deg	95.89(1)	
V, $Å^3$,	2056.6(8)	4053(6)
Z	2	4
ρ_{calc}, g cm^{-3}	1.82	1.85
μ, cm^{-}	20.4	20.7
R^b	0.049	0.037
$R_w{}^c$	0.054	0.042

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

1b was also optically resolved by the same column chromatographic technique as described above. It was found from the CD spectral measurements that the earlier and the later moving bands in the column contained the $(+)^{CD}_{550}$ and the $(-)^{CD}_{550}$ isomers, respectively.

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 in the complexes were determined with a Nippon Jarrel-Ash ICPA-575 ICP spectrophotometer. The molar conductivities of the complexes were measured with a Horiba DS-14 conductivity meter at 23 °C in water.

X-ray Structure Determination. Single-crystal X-ray diffraction experiments were performed on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710$ 73 Å). 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 $15° < 2\theta < 20°$. The intensity data were collected by the $\omega - 2\theta$ scan mode up to $2\theta = 50°$. The intensities were corrected for Lorentz and polarization effects. Empirical absorption corrections based on a series of ψ scans were also applied. The 5353 and 2977 independent reflections with $F_o > 3\sigma(F_o)$ of the 7659 and 7852 measured reflections were considered as "observed" and used for structure determinations of **1a**$(NO_3)_4\cdot 2H_2O$ and **1b**$(NO_3)_4\cdot 2H_2O$, respectively.

The positions of Co and S atoms for **1a**$(NO_3)_4\cdot 2H_2O$ and **1b**$(NO_3)_4\cdot 2H_2O$ were determined by direct methods, and the remaining non-H atom positions were found by successive difference Fourier techniques.[13] The structures were refined by full-matrix least-squares techniques using the MOLEN crystallographic software package.[13] One of four nitrate anions for **1a**$(NO_3)_4\cdot 2H_2O$ was disordered, and its O atoms (O41a, O42a, O43a, O41b, O42b, and O43b) were refined isotropically with a site occupancy factor of 0.5. All other non-H atoms were refined anisotropically. H atoms were not included in the calculations.

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(10) Schlessinger, G. G. *Inorg. Synth.* **1967**, *9*, 160.

(11) Bailar, J. C., Jr. *Inorg. Synth.* **1946**, *2*, 222.

(12) (a) Busch, D. H.; Jicha, D. C. *Inorg. Chem.* **1962**, *1*, 884. (b) Brubaker, G. R.; Douglas, B. E. *Inorg. Chem.* **1967**, *6*, 1562. (c) Heeg, M. J.; Blinn, E. L.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 1118. (d) Miyanowaki, S.; Konno, T.; Okamoto, K.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2987. (e) Konno, T.; Aizawa, S; Hidaka, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 585.

(13) Fair, C. K. *MOLEN, Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

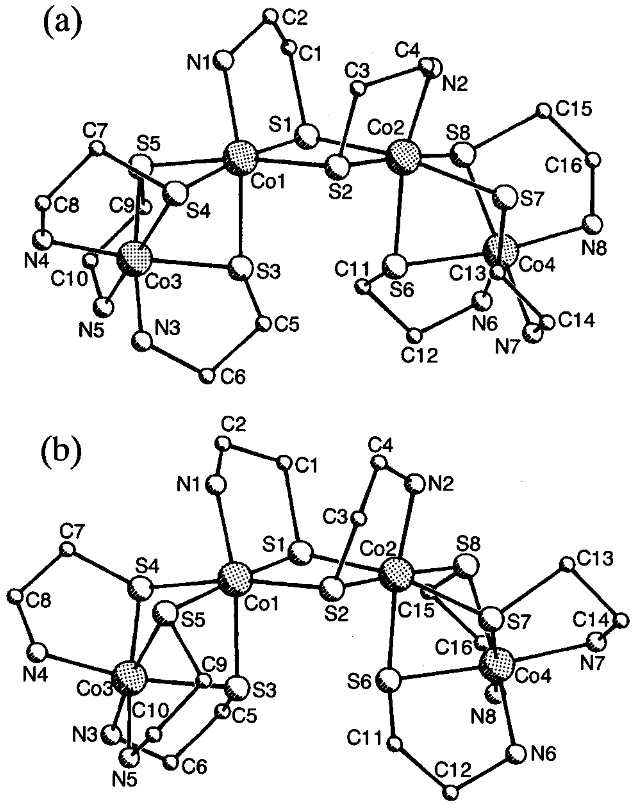

Figure 1. Perspective views of the complex cation **1a** (the $\Delta AA\Delta$ isomer) (a) and the compex cation **1b** (the $\Lambda AA\Lambda$ isomer) (b) with the atomic labeling scheme.

Results and Discussion

Crystal Structure of 1a. The X-ray structural analysis for **1a**$(\mathrm{NO_3})_4$ revealed the presence of a discrete complex cation, four nitrate anions, and two water molecules. The number of nitrate anions implies that the complex cation is tetravalent. This is compatible with the observed molar conductivity in water of 505 Ω^{-1} cm^2 mol^{-1}, which is in agreement with those of the 1:4 electrolytes, $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]\mathrm{Cl_4}$ (507 Ω^{-1} cm^2 mol^{-1}) and $[\mathrm{Pd_2\{Ni(aet)_2\}_4}]\mathrm{Br_4}$ (532 Ω^{-1} cm^2 mol^{-1}).[1d,8b] A perspective drawing of the complex cation **1a** is given in Figure 1a, and the selected bond distances and angles are listed in Table 2.

The complex cation **1a** consists of four cobalt atoms and eight aet ligands. Each of the two outer cobalt atoms is chelated by three aet ligands to form a distorted octahedral *fac(S)*-$[\mathrm{Co(aet)_3}]$ unit with a $\mathrm{CoN_3S_3}$ chromophore. On the other hand, the two inner cobalt atoms, each of which is chelated by one aet ligand, are linked to each other by a double sulfur bridge to form a $[\mathrm{Co_2(aet)_2}]^{4+}$ core. To this $[\mathrm{Co_2(aet)_2}]^{4+}$ core is bound each of the two *fac(S)*-$[\mathrm{Co(aet)_3}]$ units by a triple sulfur bridge, completing the S-bridged tetranuclear structure in $[\{\mathrm{Co_2(aet)_2}\}\{\mathrm{Co(aet)_3}\}_2]^{4+}$ with a boat-type metal array (Co1–Co2–Co4 = 136.04(4)°, Co2–Co1–Co3 = 136.28(4)°, Co1–Co2 = 3.347(1) Å, Co1–Co3 = 2.926(1) Å, Co2–Co4 = 2.929(1) Å). As a result, each of the inner cobalt atoms is surrounded by one nitrogen and five sulfur atoms in a distorted octahedral geometry.

The bond distances and angles concerning the *fac(S)*-$[\mathrm{Co(aet)_3}]$ units in **1a** (average Co–S = 2.223(2) Å, Co–N = 2.005(7) Å, S–Co–S = 83.35(8)°, N–Co–N = 93.5(3)°) (Table 2) are similar to those observed in $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ (average Co–S = 2.238(7) Å, Co–N = 1.996(8) Å, S–Co–S = 84.5(8)°, N–Co–N = 94.6(6)°), in which two *fac(S)*-$[\mathrm{Co(aet)_3}]$ units are bound to the central cobalt atom in a linear-type metal array.[12c] The three sulfur atoms of each *fac(S)*-$[\mathrm{Co(aet)_3}]$ unit in **1a** are not equally bound to the $[\mathrm{Co_2(aet)_2}]^{4+}$ core. That is, the Co–$\mathrm{S_{trans(S)}}$ bonds of Co1–S4, Co1–S5, Co2–S7, and Co2–S8 (average 2.297(2) Å) are ca. 0.04 Å longer than the Co–$\mathrm{S_{trans(N)}}$ bonds of Co1–S3 and Co2–S6 (average 2.257(2) Å). This can be explained by the mutual structural trans influence due to the coordinated thiolato sulfur atom.[14] Here it should be noted that the Co–$\mathrm{S_{trans(S)}}$ bond distances in **1a** are longer than the Co–$\mathrm{S_{trans(S)}}$ ones of the central $\mathrm{CoS_6}$ environment in $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ (average 2.262(11) Å). Furthermore, the Co–S–Co bridging angles between the inner and outer cobalt atoms in **1a** (average 81.03(7)°) are larger than those in $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ (average 78.8(4)°). The longer Co–S distances and the larger Co–S–Co angles permit the greater Co1–Co3 and Co2–Co4 separations (average 2.928(1) Å) in **1a**, compared with the Co–Co separations (average 2.857(1) Å) in $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$. Though the presence of Co–Co interaction in $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ has not been substantiated, it is reasonable to assume that, if any, the Co–Co bonding interaction in **1a** with a boat-type metal array is weaker than that in $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ with a linear-type metal array, which is responsible for the greater Co–Co separations in **1a**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1a**

Distances

Co1–S1	2.230(1)	Co3–S3	2.206(2)
Co1–S2	2.276(2)	Co3–S4	2.251(2)
Co1–S3	2.254(2)	Co3–S5	2.206(2)
Co1–S4	2.301(2)	Co3–N3	1.998(6)
Co1–S5	2.287(2)	Co3–N4	2.001(5)
Co1–N1	1.992(6)	Co3–N5	2.020(6)
Co2–S1	2.268(2)	Co4–S6	2.211(2)
Co2–S2	2.251(1)	Co4–S7	2.224(2)
Co2–S6	2.260(2)	Co4–S8	2.240(2)
Co2–S7	2.325(2)	Co4–N6	1.995(7)
Co2–S8	2.276(2)	Co4–N7	2.007(6)
Co2–N2	1.988(6)	Co4–N8	2.009(5)

Angles

S1–Co1–S2	84.06(6)	S5–Co3–N3	172.6(2)
S1–Co1–S4	173.25(8)	S5–Co3–N5	88.4(2)
S1–Co1–N1	89.0(1)	N3–Co3–N4	92.4(2)
S2–Co1–S5	170.91(7)	N3–Co3–N5	94.0(2)
S2–Co1–N1	100.5(2)	N4–Co3–N5	94.7(3)
S3–Co1–S4	81.45(6)	S6–Co4–S7	82.43(7)
S3–Co1–S5	80.32(7)	S6–Co4–S8	83.80(6)
S3–Co1–N1	168.2(2)	S6–Co4–N6	88.7(2)
S4–Co1–S5	81.13(6)	S6–Co4–N8	172.0(2)
S1–Co2–S2	83.78(6)	S7–Co4–S8	85.05(8)
S1–Co2–S7	168.11(8)	S7–Co4–N6	171.1(2)
S1–Co2–N2	104.0(2)	S7–Co4–N7	88.4(2)
S2–Co2–S8	173.50(8)	S8–Co4–N7	173.3(2)
S2–Co2–N2	88.4(1)	S8–Co4–N8	88.4(2)
S6–Co2–S7	79.18(7)	N6–Co4–N7	92.7(3)
S6–Co2–S8	81.90(7)	N6–Co4–N8	93.4(3)
S6–Co2–N2	166.0(2)	N7–Co4–N8	93.8(2)
S7–Co2–S8	81.96(6)	Co1–S1–Co2	96.14(6)
S3–Co3–S4	83.65(7)	Co1–S2–Co2	95.34(6)
S3–Co3–S5	83.19(6)	Co1–S3–Co2	82.00(6)
S3–Co3–N3	89.6(2)	Co1–S4–Co3	80.03(6)
S3–Co3–N4	172.4(2)	Co1–S5–Co3	81.26(6)
S4–Co3–S5	84.04(7)	Co2–S6–Co4	81.88(6)
S4–Co3–N4	89.0(2)	Co2–S7–Co4	80.14(7)
S4–Co3–N5	171.8(1)	Co2–S8–Co4	80.88(6)

Considering the absolute configurations of the outer (Δ and Λ configurations due to the skew pair of chelate rings) and the inner (*C* and *A* configurations due to the arrangement of the

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(14) (a) Elder, R. C.; Florian, L. R.; Lake, R. E.; Yacynych, A. M. *Inorg. Chem.* **1973**, *12*, 2690. (b) Stein, C.; Bouma, S.; Carlson, J.; Cornelius, C.; Maeda, J.; Weschler, C.; Deutsch, E.; Hodgson, K. O. *Inorg. Chem.* **1976**, *15*, 1183.

ligating atoms) cobalt chiral centers,[15] 10 isomers, $\Delta CC\Delta$ and $\Lambda AA\Lambda$ (racemic, C_2 symmetry), $\Delta AA\Delta$ and $\Lambda CC\Lambda$ (racemic, C_2 symmetry), $\Delta CC\Lambda$ and $\Delta AA\Lambda$ (racemic, C_1 symmetry), $\Delta CA\Delta$ and $\Lambda CA\Lambda$ (racemic, C_1 symmetry), $\Delta CA\Lambda$ (meso), and $\Delta AC\Lambda$ (meso) are possible for $[\{Co_2(aet)_2\}\{Co(aet)_3\}_2]^{4+}$. The isomer of **1a** illustrated in Figure 1a has the Δ configuration for the two outer cobalt centers, while the absolute configuration for the two inner cobalt centers is designated *A*, given that the order of precedence of the ligating atoms is $S_{inner-chelating} > S_{inner-non-chelating} > S_{outer} > N$.[16] Thus, the crystal of **1a** consists of the $\Delta AA\Delta$ and $\Lambda CC\Lambda$ isomers, which combine to form the racemic compound, as indicated by the space group $P\bar{1}$ and $Z = 2$. This is consistent with the fact that **1a** was optically resolved. All the aet chelate rings of the two *fac(S)*-[Co(aet)$_3$] units adopt a distinct gauche form with the *lel* conformation (λ conformation for the $\Delta AA\Delta$ isomer and the δ conformation for the $\Lambda CC\Lambda$ isomer). On the other hand, the two aet chelate rings of the $[Co_2(aet)_2]^{4+}$ core possess the δ and λ conformations, which avoid the steric interaction between these chelate rings.

Crystal Structure of 1b. The X-ray structural analysis for **1b**$(NO_3)_4$ showed the presence of a discrete tetravalent complex cation, four nitrate anions, and two water molecules. This is compatible with the observed molar conductivity in water of 520 Ω^{-1} cm^2 mol^{-1}. As shown in Figure 1b, the complex cation **1b** has the same S-bridged tetracobalt(III) structure as **1a**, in which two *fac(S)*-[Co(aet)$_3$] units are bound to the $[Co_2(aet)_2]^{4+}$ core to form $[\{Co_2(aet)_2\}\{Co(aet)_3\}_2]^{4+}$ with a boat-type metal array (Co1−Co2−Co4 = 136.74(6)°, Co3−Co1−Co2 = 137.26(5)°, Co1−Co2 = 3.325(1) Å, Co1−Co3 = 2.930(2) Å, Co2−Co4 = 2.923(2) Å). The bond distances and angles in **1b** are quite similar to those observed in **1a** (Table 3). However, it is noteworthy that the bond angles subtended at the inner sulfur atoms in **1b** (Co1−S1−Co2 = 94.8(1)°, Co1−S2−Co2 = 94.8(1)°, Co1−S1−C1 = 97.9(4)°, Co2−S2−C3 = 98.4(5)°, Co2−S1−C1 = 110.3(3)°, Co1−S2−C3 = 117.1(3)°) are more deviated from the ideal tetrahedral angle of 109.5°, compared with the corresponding angles in **1a** (Co1−S1−Co2 = 96.14(6)°, Co1−S2−Co2 = 95.34(6)°, Co1−S1−C1 = 98.7(2)°, Co2−S2−C3 = 99.6(2)°, Co2−S1−C1 = 113.7(2)°, Co1−S2−C3 = 111.4(2)°), which may be related to the formation ratio **1a** > **1b**. The crystal of **1b** is a racemic compound of a pair of enantiomers, $\Delta CC\Delta$ and $\Lambda AA\Lambda$, which can be discriminated from **1a** composed of the $\Delta AA\Delta$ and $\Lambda CC\Lambda$ isomers. The conformational behavior of the aet chelate rings in **1b** is the same as that observed in **1a**. That is, all the aet chelate rings of the two *fac(S)*-[Co(aet)$_3$] units adopt the *lel* conformation, while the two aet chelate rings of the $[Co_2(aet)_2]^{4+}$ core have the δ and λ conformations.

Synthesis and Characterization. In this study a novel S-bridged tetracobalt(III) complex, $[\{Co_2(aet)_2\}\{Co(aet)_3\}_2]^{4+}$ (**1**), was isolated from the reaction of [Ni(aet)$_2$] with $[CoCl(NH_3)_5]^{2+}$ in water at room temperature. A similar reaction of [Ni(aet)$_2$] with $[CoCl_2(en)_2]^+$ in a ratio of 1:1 also produced **1** besides the S-bridged Co^{III}Ni^{II}Co^{III} trinuclear complex $[Ni\{Co(aet)_2(en)\}_2]^{4+}$, though the 1:2 reaction of [Ni(aet)$_2$] and $[CoCl_2(en)_2]^+$ has been shown to give only $[Ni\{Co(aet)_2(en)\}_2]^{4+}$.[8] Since the direct reaction of $[CoCl_2(en)_2]Cl$ with aet under the same conditions produced only $[Co\{Co(aet)_3\}_2]^{3+}$ as the S-bridged polynuclear complex, it is obvious that Ni^{II} ion plays a significant role in the formation of **1**. However, the addition of $NiCl_2$ to this reaction formed only a trace amount of **1** besides the main product of $[Co\{Co(aet)_3\}_2]^{3+}$. These results suggest that **1** is constructed by way of some intermediate having a Ni^{II}−SR−Co^{III} μ_2-thiolato structure.

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

Distances			
Co1−S1	2.234(3)	Co3−S3	2.223(3)
Co1−S2	2.289(2)	Co3−S4	2.243(3)
Co1−S3	2.256(3)	Co3−S5	2.226(3)
Co1−S4	2.299(2)	Co3−N3	2.045(9)
Co1−S5	2.277(3)	Co3−N4	1.962(7)
Co1−N1	2.004(9)	Co3−N5	2.077(9)
Co2−S1	2.282(2)	Co4−S6	2.214(3)
Co2−S2	2.227(3)	Co4−S7	2.223(3)
Co2−S6	2.280(3)	Co4−S8	2.230(3)
Co2−S7	2.318(2)	Co4−N6	1.978(8)
Co2−S8	2.271(3)	Co4−N7	2.069(8)
Co2−N2	1.990(8)	Co4−N8	1.924(9)
Angles			
S1−Co1−S2	84.65(9)	S5−Co3−N3	170.5(3)
S1−Co1−S5	175.4(1)	S5−Co3−N5	90.3(3)
S1−Co1−N1	91.1(3)	N3−Co3−N4	95.0(3)
S2−Co1−S4	170.1(1)	N3−Co3−N5	93.5(4)
S2−Co1−N1	99.5(2)	N4−Co3−N5	97.6(4)
S3−Co1−S4	80.33(9)	S6−Co4−S7	83.5(1)
S3−Co1−S5	81.4(1)	S6−Co4−S8	83.9(1)
S3−Co1−N1	169.5(3)	S6−Co4−N6	91.0(2)
S3−Co1−S5	82.08(9)	S6−Co4−N7	174.2(3)
S1−Co2−S2	85.0(1)	S7−Co4−S8	84.9(1)
S1−Co2−S7	167.9(1)	S7−Co4−N7	91.4(3)
S1−Co2−N2	97.3(2)	S7−Co4−N8	172.2(2)
S2−Co2−S8	176.5(1)	S8−Co4−N6	174.8(2)
S2−Co2−N2	89.1(3)	S8−Co4−N8	87.6(2)
S6−Co2−S7	79.95(9)	N6−Co4−N7	92.2(4)
S6−Co2−S8	81.5(1)	N6−Co4−N8	92.1(3)
S6−Co2−N2	172.9(2)	N7−Co4−N8	91.1(4)
S7−Co2−S8	81.8(1)	Co1−S1−Co2	94.8(1)
S3−Co3−S4	82.3(1)	Co1−S2−Co2	94.8(1)
S3−Co3−S5	83.3(1)	Co1−S3−Co2	81.70(8)
S3−Co3−N3	87.8(2)	Co1−S4−Co3	80.33(8)
S3−Co3−N4	168.9(2)	Co1−S5−Co3	81.2(1)
S4−Co3−S5	84.5(1)	Co2−S6−Co4	81.12(9)
S4−Co3−N4	86.9(2)	Co2−S7−Co4	80.10(8)
S4−Co3−N5	173.3(2)	Co2−S8−Co4	81.0(1)

Of 10 isomers possible for **1**, the $\Delta AA\Delta/\Lambda CC\Lambda$ (**1a**) and $\Delta CC\Delta/\Lambda AA\Lambda$ (**1b**) isomers were formed, of which structures were determined by X-ray crystallography. As shown in Figure 2 and Table 4, the electronic absorption spectra of **1a** and **1b** are characterized by the intense absorption bands at around 22 × 10^3, 28 × 10^3, and 38 × 10^3 cm^{-1}. Though their absorption curves roughly coincide with each other over the whole region, a notable difference is observed in more minute detail. That is, at around 28 × 10^3 cm^{-1} **1a** gives an absorption band with a distinct shoulder at the lower energy side, while the corresponding band for **1b** has a vague shoulder at the higher energy side. No significant absorption spectral changes with time were noticed for **1a** and **1b**, at least for several hours. Furthermore, each ^{13}C NMR spectrum in D_2O gives four CH_2S and four CH_2NH_2 methylene carbon signals for the eight aet ligands in the complex. The absorption and ^{13}C NMR spectral behavior implies that the quasi-C_2-symmetrical S-bridged tetranuclear structures observed in crystals of **1a** and **1b** are retained in solution.

Each of **1a** and **1b** was optically resolved into the $(+)^{CD}_{550}$ and $(-)^{CD}_{550}$ isomers by SP-Sephadex C-25 column chromatography using $[Sb_2((R,R)\text{-tartarato})_2]^{2-}$ as the resolving agent. The CD spectra of $(+)^{CD}_{550}$-**1a** and $(+)^{CD}_{550}$-**1b** are illustrated in Figure 2, and their data are summarized in Table 4. The CD curves of $(+)^{CD}_{550}$-**1a** and $(+)^{CD}_{550}$-**1b** resemble that of $\Delta\Delta$-$[Co\{Co(aet)_3\}_2]^{3+}$ (Figure 3a)[12b,d] especially in the energy

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[15] Block, B. P.; Powell, W. H.; Fernelius, W. C. *Inorganic Chemical Nomenclature*; American Chemical Society: Washington, DC, 1990.

[16] Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

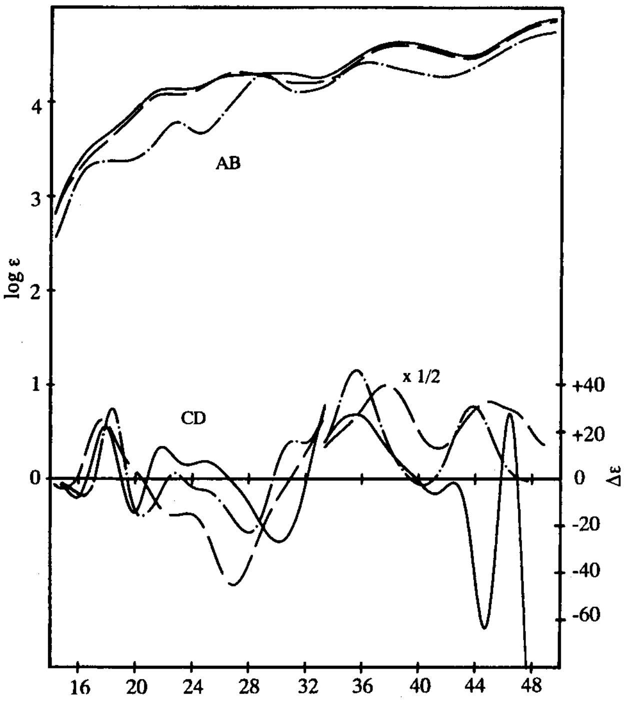

Figure 2. Electronic absorption and CD spectra of $(+)_{550}^{\mathrm{CD}}$-**1a** (—), $(+)_{550}^{\mathrm{CD}}$-**1b** (— — —), and ΔΔ-$[\mathrm{Co}\{\mathrm{Co(aet)_3}\}_2]^{3+}$ (—•—) in H_2O.

Table 4. Electronic Absorption and CD Spectral Data

abs max: $\sigma/10^3$ cm^{-1} (log ϵ/mol^{-1} dm^3 cm^{-1})	CD extrema: $\sigma/10^3$ cm^{-1} ($\Delta\epsilon$/mol^{-1} dm^3 cm^{-1})
Δ*AA*Δ-$[\{\mathrm{Co_2(aet)_2}\}\{\mathrm{Co(aet)_3}\}_2]^{4+}$ ($(+)_{550}^{\mathrm{CD}}$-**1a**)	
22.03 (4.14) sh[a]	15.87 (−0.86)
29.85 (4.30)	17.85 (+22.21)
38.46 (4.63)	19.92 (−14.42)
	21.79 (+13.66)
	30.21 (−26.70)
	35.46 (+55.12)
	44.84 (−129.5)
	46.30 (+67.68)
Δ*CC*Δ-$[\{\mathrm{Co_2(aet)_2}\}\{\mathrm{Co(aet)_3}\}_2]^{4+}$ ($(+)_{550}^{\mathrm{CD}}$-**1b**)	
22.03 (4.08) sh	14.90 (−4.71)
27.17 (4.31)	17.61 (+25.42)
38.46 (4.60)	22.62 (−16.19)
	26.95 (−48.11)
	37.45 (+81.37)
	44.64 (+61.64)

[a] The sh label denotes a shoulder.

region lower than 20 × 10³ cm⁻¹, giving a minor negative and a major positive CD band from the lower energy side. Thus, $(+)_{550}^{\mathrm{CD}}$-**1a** and $(+)_{550}^{\mathrm{CD}}$-**1b** are tentatively assigned as the Δ*AA*Δ and Δ*CC*Δ isomers, respectively. Assuming that this assignment is correct and that the CD contribution from the outer and the inner cobalt chiral centers are additive, the CD curves calculated from the expressions, $1/2[\Delta\epsilon\{(+)_{550}^{\mathrm{CD}}$-**1a**$\} + \Delta\epsilon\{(+)_{550}^{\mathrm{CD}}$-**1b**$\}]$ and $1/2[\Delta\epsilon\{(+)_{550}^{\mathrm{CD}}$-**1a**$\} - \Delta\epsilon\{(+)_{550}^{\mathrm{CD}}$-**1b**$\}]$ would represent the CD contributions from the two outer cobalt centers with the Δ configuration and from the two inner cobalt centers with the *A* configuration, respectively (eqs 1 and 2).

$$1/2[\Delta\epsilon(\Delta AA\Delta) + \Delta\epsilon(\Delta CC\Delta)] = \Delta\epsilon(\Delta\Delta) \qquad (1)$$

$$1/2[\Delta\epsilon(\Delta AA\Delta) - \Delta\epsilon(\Delta CC\Delta)] = \Delta\epsilon(AA) \qquad (2)$$

As shown in Figure 3, the CD curve calculated from the equation $1/2[\Delta\epsilon\{(+)_{550}^{\mathrm{CD}}$-**1a**$\} + \Delta\epsilon\{(+)_{550}^{\mathrm{CD}}$-**1b**$\}]$ coincides well with the observed CD curve of ΔΔ-$[\mathrm{Co}\{\mathrm{Co(aet)_3}\}_2]^{3+}$ which has the CD contribution from the two terminal cobalt centers with the Δ configuration. Accordingly, it is confidently assigned that the $(+)_{550}^{\mathrm{CD}}$-**1a** and $(+)_{550}^{\mathrm{CD}}$-**1b** isomers have the Δ*AA*Δ and Δ*CC*Δ configurations, while the $(-)_{550}^{\mathrm{CD}}$-**1a** and $(-)_{550}^{\mathrm{CD}}$-**1b** isomers, which show CD spectra enantiomeric to those of $(+)_{550}^{\mathrm{CD}}$-**1a** and $(+)_{550}^{\mathrm{CD}}$-**1b**, have the Λ*CC*Λ and Λ*AA*Λ configurations.

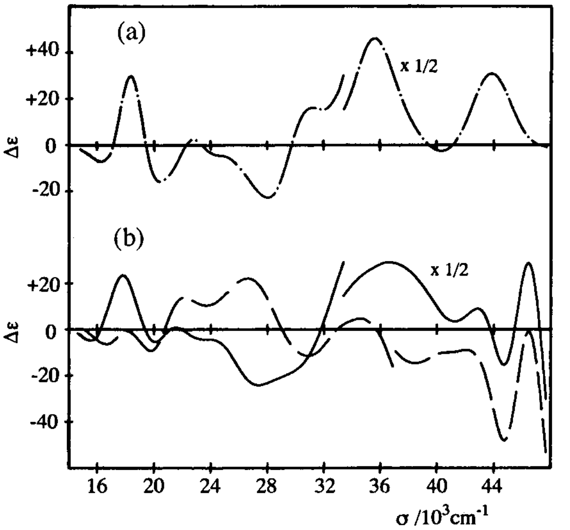

Figure 3. The observed CD curve of ΔΔ-$[\mathrm{Co}\{\mathrm{Co(aet)_3}\}_2]^{3+}$ (—•—) (a) and the calculated CD curves for $1/2[\Delta\epsilon\{(+)_{550}^{\mathrm{CD}}$-**1a**$\} + \Delta\epsilon\{(+)_{550}^{\mathrm{CD}}$-**1b**$\}]$ (—) and $1/2[\Delta\epsilon\{(+)_{550}^{\mathrm{CD}}$-**1a**$\} - \Delta\epsilon\{(+)_{550}^{\mathrm{CD}}$-**1b**$\}]$ (— — —) (b).

Concluding Remarks

In the present work, it was found that the S-bridged tetracobalt(III) complex $[\{\mathrm{Co_2(aet)_2}\}\{\mathrm{Co(aet)_3}\}_2]^{4+}$ (**1**) is formed by the reactions of $[\mathrm{Ni(aet)_2}]$ with $[\mathrm{CoCl(NH_3)_5}]^{2+}$ or $[\mathrm{CoCl_2(en)_2}]^{+}$ in water under moderate conditions. This result indicates that the bidentate-*N,S* ligand aet completely transfers from nickel(II) to cobalt(III). In these reactions the well-known S-bridged tricobalt(III) complex $[\mathrm{Co}\{\mathrm{Co(aet)_3}\}_2]^{3+}$, which has been prepared by reacting *fac(S)*-$[\mathrm{Co(aet)_3}]$ with $\mathrm{Co^{2+}}$ or $[\mathrm{CoX(NH_3)_5}]^{2+}$ (X = Cl, Br),[12a,e] was little formed. It has been shown that $[\mathrm{Co}\{\mathrm{Co(aet)_3}\}_2]^{3+}$ is the stable end product of the reactions of *fac(S)*-$[\mathrm{Co(aet)_3}]$ with reducing metal ions such as $\mathrm{Cr^{2+}}$ and $\mathrm{Fe^{2+}}$ or oxidizing metal ions such as $\mathrm{Ce^{4+}}$ and $\mathrm{V^{4+}}$,[16] and no other S-bridged polycobalt(III) complexes with aet have been discovered. Thus, the ligand transfer reaction found in this work may be adopted to prepare novel S-bridged polynuclear complexes, which are unable to be obtained by normal preparative methods. **1** formed two pairs of racemic isomers, **1a** (Δ*AA*Δ/Λ*CC*Λ) and **1b** (Δ*CC*Δ/Λ*AA*Λ), which were separated and optically resolved. To our knowledge, this is the first example of the formation of two pairs of racemic isomers for the S-bridged polynuclear complexes with aet; one racemic and/or one meso isomer have been formed.[1,8,12,17−27] The configu-

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(17) (a) DeSimone, R. E.; Ontko, T.; Wardman, L.; Blinn, E. L. *Inorg. Chem.* **1975**, *14*, 1313. (b) Blinn, E. L.; Butlar, P.; Chapman, K. M.; Harris, S. *Inorg. Chim. Acta* **1977**, *24*, 139.

(18) (a) Brubaker, G. R.; Henk, M. G.; Johnson, D. W. *Inorg. Chim. Acta* **1985**, *100*, 201. (b) Johnson, D. W.; Brewer, T. R. *Inorg. Chim. Acta* **1988**, *151*, 222. (c) Konno, T.; Okamoto, K.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3027. (d) Konno, T.; Okamoto, K.; Hidaka, J. *Acta Crystallogr., Sect. C* **1993**, *49*, 222.

(19) (a) Konno, T.; Aizawa, S.; Okamoto, K.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 792. (b) Konno, T.; Nakamura, K.; Okamoto, K.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2582. (c) Konno, T.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 610.

rational assignment of the optically active isomers for **1** was successfully made by the CD curve analysis, based on the assumption that the CD contributions from the inner and the outer cobalt chiral centers are additive. This fact indicates that the additivity on CD, which has been recognized mainly for the mononuclear cobalt(III) system,[28] can be applied for the S-bridged polynuclear system with aet or its related sulfur-containing ligand.

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Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for **1a**$(NO_3)_4\cdot 2H_2O$ and **1b**$(NO_3)_4\cdot 2H_2O$ (16 pages). Ordering information is given on any current masthead page.

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(20) (a) Konno, T.; Okamoto, K.; Hidaka, J. *Chem. Lett.* **1990**, 1043. (b) Konno, T.; Okamoto, K.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 101. Konno, T.; Kageyama, T.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1957.

(21) (a) Konno, T.; Okamoto, K.; Hidaka, J. *Inorg. Chem*. **1991**, *30*, 2253. (b) Konno, T.; Nagashio, T.; Okamoto, K.; Hidaka, J. *Inorg. Chem*. **1992**, *31*, 1160. (c) Konno, T.; Okamoto, K.; Hidaka, J. *Inorg. Chem*. **1994**, *33*, 538. (d) Okamoto, K.; Konno, T.; Hidaka, J. *J. Chem. Soc., Dalton Trans.* **1994**, 533. (e) Kageyama, Y.; Konno, T.; Okamoto, K.; Hidaka, J. *Inorg. Chim. Acta* **1995**, *239*, 19.

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

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

(24) Konno, T.; Yoshinari, Y.; Okamoto, K. *Chem. Lett.* **1995**, 989.

(25) Konno, T.; Okamoto, K. *Chem. Lett.* **1996**, 975.

(26) Konno, T.; Okamoto, K. *Chem. Lett.* **1996**, 977.

(27) Konno, T.; Okamoto, K. *Inorg. Chem.* **1997**, *36*, 1403.

(28) (a) Hawkins, C. J. *Absolute Configuration of Metal Complexes*; John Wiley & Sons Ltd.: New York, 1971. (b) Konno. T.; Okamoto, K.; Einaga, H.; Hidaka, J. *Chem. Lett.* **1983**, 969. (c) Konno, T.; Okamoto, K.; Einaga, H.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1119.