

Five-Coordinate Geometry of Cadmium(II) with Octahedral Bidentate-*S*,*S* Complex-Ligand *cis*(*S*)-$[Co(aet)_2(en)]^+$ (aet = 2-aminoethanethiolate): Synthesis, Crystal Structures and Interconversion of S-Bridged $Co^{III}Cd^{II}$ Polynuclear Complexes

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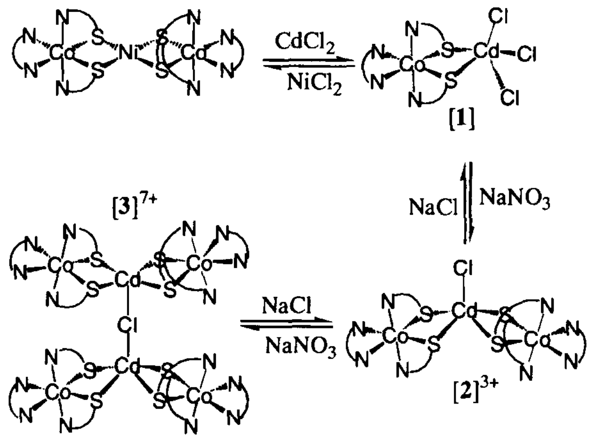
An S-bridged $Co^{III}Cd^{II}$ dinuclear complex molecule, $[CdCl_3\{Co(aet)_2(en)\}]^0$ ([**1**]) (aet = 2-aminoethanethiolate, en = ethylenediamine), was prepared by the reaction of an S-bridged $Co^{III}Ni^{II}Co^{III}$ trinuclear complex salt, $[Ni\{Co(aet)_2(en)\}_2]Cl_4$, with excess $CdCl_2$ in water. Treatment of [**1**] with $NaNO_3$ in water gave an S-bridged $Co^{III}Cd^{II}Co^{III}$ dinuclear complex salt, $[CdCl\{Co(aet)_2(en)\}_2](NO_3)_3$ ([**2**]$(NO_3)_3$), which was further converted to a $(Co^{III}Cd^{II}Co^{III})_2$ hexanuclear complex salt, $[Cd_2Cl\{Co(aet)_2(en)\}_4](NO_3)_7$ ([**3**]$(NO_3)_7$), by treatment with $NaNO_3$ in water. The crystal structures of [**1**], [**2**]$(NO_3)_3$ and [**3**]$(NO_3)_7$ were determined by X-ray crystallography. In [**1**] Cd^{II} ion is coordinated by three Cl^- ions besides two S atoms from one octahedral C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ unit, while each Cd^{II} ion in $[\mathbf{2}]^{3+}$ and $[\mathbf{3}]^{7+}$ is coordinated by one Cl^- ion besides four S atoms from two C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units. The coordination geometry of each Cd^{II} center in [**1**], $[\mathbf{2}]^{3+}$ and $[\mathbf{3}]^{7+}$ is described as a distorted trigonal-bipyramid, considering an angular structural parameter, χ, which is proposed as a modified index of trigonality. The reverse conversions of $[\mathbf{3}]^{7+}$ to $[\mathbf{2}]^{3+}$ and $[\mathbf{2}]^{3+}$ to [**1**] were also achieved by treatment with NaCl in water.

Coordinated thiolato S atoms in mononuclear cobalt(III) complexes tend to make bridges with other metal ions to form S-bridged polynuclear structures. In fact, a number of S-bridged polynuclear complexes composed of Co^{III} octahedral units have been prepared by the reactions of *fac*(*S*)-$[Co(aet)_3]$ or $[Co(aet)(en)_2]^{2+}$ (aet = 2-aminoethanethiolate, en = ethylenediamine) with a variety of metal ions, and their stereochemical and spectroscopic properties have been extensively studied.[1—14] On the other hand, no report has yet been published on S-bridged polynuclear complexes composed of octahedral *cis*(*S*)-$[Co(aet)_2(en)]^+$ units, mainly because of the great difficulty in isolating the mononuclear *cis*(*S*)-$[Co(aet)_2(en)]^+$,[15,16] compared with *fac*(*S*)-$[Co(aet)_3]$ and $[Co(aet)(en)_2]^{2+}$.

In 1992 we reported that the reaction of $[Ni(aet)_2]$ with $[CoCl_2(en)_2]Cl$ in water produces an S-bridged $Co^{III}Ni^{II}Co^{III}$ trinuclear complex salt, $[Ni\{Co(aet)_2(en)\}_2]Cl_4$, which is the first example of an S-bridged polynuclear structure composed of *cis*(*S*)-$[Co(aet)_2(en)]^+$ units.[17] The $Co^{III}Ni^{II}Co^{III}$ trinuclear structure in $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ was found to be relatively unstable in water to afford mononuclear *cis*(*S*)-$[Co(aet)_2(en)]^+$ species,[17,18] which suggests that other S-bridged polynuclear complexes composed of *cis*(*S*)-$[Co(aet)_2(en)]^+$ units can be prepared by the use of $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ as a starting complex instead of the mononuclear *cis*(*S*)-$[Co(aet)_2(en)]^+$. Thus, we examined the reactions of $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ with Cd^{II} or Pd^{II}, which prefers to take a four-coordinate geometry as well as Ni^{II}, expecting that the central Ni^{II} in $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ would be replaced by Cd^{II} or Pd^{II} to form the corresponding S-bridged trinuclear complexes. While an expected $Co^{III}Pd^{II}Co^{III}$ trinuclear complex salt, $[Pd\{Co(aet)_2(en)\}_2]Cl_4$, was obtained by the facile reaction of $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ with $Na_2[PdCl_4]$ in a ratio of 1 : 1,[19] the reaction with $CdCl_2$ under the same conditions did not produce a $Co^{III}Cd^{II}Co^{III}$ trinuclear complex salt, $[Cd\{Co(aet)_2(en)\}_2]Cl_4$. Instead, we found that the reaction of $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ with excess $CdCl_2$ gives an S-bridged $Co^{III}Cd^{II}$ dinuclear complex molecule, $[CdCl_3\{Co(aet)_2(en)\}]$ ([**1**]). In this paper we report on the complete description of synthesis, crystal structure and properties of [**1**], along with those of the $Co^{III}Cd^{II}Co^{III}$ trinuclear complex salt, $[CdCl\{Co(aet)_2(en)\}_2](NO_3)_3$ ([**2**]$(NO_3)_3$), and the $(Co^{III}Cd^{II}Co^{III})_2$ hexanuclear complex salt, $[Cd_2Cl\{Co(aet)_2(en)\}_4](NO_3)_7$ ([**3**]$(NO_3)_7$), which were readily derived from [**1**] by treatment with $NaNO_3$ in water (Scheme 1). A modified angular structure parameter was introduced to describe the five-coordinate geometry of the Cd^{II} center, which was uniformly found in [**1**], $[\mathbf{2}]^{3+}$ and $[\mathbf{3}]^{7+}$. A preliminary result has been presented.[20]

Experimental

Preparation of Complexes. $[CdCl_3\{Co(aet)_2(en)\}]$ ([1]). To a solution containing 0.20 g (0.23 mmol) of $[Ni\{Co(aet)_2(en)\}_2]Cl_4\cdot 6H_2O$[18] in 10 cm^3 of water was added 0.30 g (1.31 mmol) of



Scheme 1.

$CdCl_2\cdot2.5H_2O$. The mixture was stirred at 60 °C for 1 h and the resulting red-brown powder was collected by filtration. Dark-brown tetragonal-plate crystals of [**1**]$\cdot0.5H_2O$ suitable for X-ray analysis were obtained by allowing the filtrate to stand at room temperature for several days. Yield: 0.22 g (94% based on Co). Anal. Found: C, 14.19; H, 4.36; N, 10.97; Co, 11.7; Cd, 22.2%. Calcd for $[CdCl_3\{Co(C_2H_6NS)_2(C_2H_8N_2)\}]\cdot0.5H_2O$: C, 14.44; H, 4.24; N, 11.23; Co, 11.81; Cd, 22.52%. Visible-UV spectrum in H_2O [σ_{max}, 10^3 cm^{-1} (log ε, mol^{-1} dm^3 cm^{-1})]: 15.7 (2.0)^{sh}, 22.47 (2.83), 29.6 (3.4)^{sh}, 34.4 (4.0)^{sh}, 37.59 (4.18). The sh label denotes a shoulder. ^{13}C NMR spectrum in D_2O (ppm from DSS): δ = 32.63 for CH_2S of aet, 47.40 for CH_2N of en, and 54.14 for CH_2N of aet.

$[CdCl\{Co(aet)_2(en)\}_2](NO_3)_3$ ([2]$(NO_3)_3$). To a solution containing 0.10 g (0.20 mmol) of [**1**]$\cdot0.5H_2O$ in 7 cm^3 of warm water was added a solution containing 0.30 g of $NaNO_3$ in 2 cm^3 of water. The mixture was stirred at 50 °C for a few minutes, followed by allowing to it stand at room temperature for 1 d. The resulting dark-brown hexagonal-plate crystals, one of which was used for X-ray analysis, were collected by filtration. Yield: 0.06 g (64% based on Co). Anal. Found: C, 15.35; H, 4.95; N, 16.38; Co, 12.3; Cd, 12.1%. Calcd for $[CdCl\{Co(C_2H_6NS)_2(C_2H_8N_2)\}_2](NO_3)_3\cdot3H_2O$: C, 15.49; H, 4.98; N, 16.56; Co, 12.67; Cd, 12.08%. Visible-UV spectrum in H_2O [σ_{max}, 10^3 cm^{-1} (log ε, mol^{-1} dm^3 cm^{-1})]: 15.7 (2.2)^{sh}, 22.47 (3.12), 29.6 (3.7)^{sh}, 34.3 (4.3)^{sh}, 37.59 (4.49). ^{13}C NMR spectrum in D_2O (ppm from DSS): δ = 32.50 for CH_2S, 47.26 for CH_2N of en, and 54.11 for CH_2N of en.

$[Cd_2Cl\{Co(aet)_2(en)\}_4](NO_3)_7$ ([3]$(NO_3)_7$). To a solution containing 0.16 g (0.32 mmol) of [**1**]$\cdot0.5H_2O$ in 14 cm^3 of warm water was added a solution containing 4.80 g of $NaNO_3$ in 8 cm^3 of water. The mixture was stirred at 50 °C for a few minutes, followed by allowing it to stand at room temperature for 2 d. The resulting red-brown needle crystals, one of which was used for X-ray analysis, were collected by filtration. Yield: 0.10 g (68% based on Co). Anal. Found: C, 15.71; H, 4.84; N, 17.47; Co, 12.7; Cd, 11.8%. Calcd for $[Cd_2Cl\{Co(C_2H_6NS)_2(C_2H_8N_2)\}_4](NO_3)_7\cdot3H_2O$: C, 15.72; H, 4.73; N, 17.57; Co, 12.86; Cd, 12.26%. Visible-UV spectrum in H_2O [σ_{max}, 10^3 cm^{-1} (log ε, mol^{-1} dm^3 cm^{-1})]: 15.8 (2.7)^{sh}, 22.47 (3.47), 29.6 (4.0)^{sh}, 34.3 (4.7)^{sh}, 37.59 (4.89). ^{13}C NMR spectrum in D_2O (ppm from DSS): δ = 32.46 for CH_2S of aet, 47.27 for CH_2N of en, and 54.13 for CH_2N of aet.

This complex was also prepared by treatment of a solution containing [**2**]$(NO_3)_3\cdot3H_2O$ (0.05 g) in 5 cm^3 of water with $NaNO_3$ (1.50 g) dissolved in 2 cm^3 of water, followed by allowing it to stand at room temperature for 2 d. Yield: 0.04 g (81% based on Co). Anal. Found: C, 15.48; H, 4.66; N, 17.33%. Calcd for $[Cd_2Cl\{Co(C_2H_6NS)_2(C_2H_8N_2)\}_4](NO_3)_7\cdot3H_2O$: C, 15.72; H, 4.73; N, 17.57%.

Conversion of [3]$(NO_3)_7$ to [2]$(NO_3)_3$. To a solution of [**3**]$(NO_3)_7\cdot3H_2O$ (0.05 g) in 2 cm^3 of water were added a solution of NaCl (0.01 g) in 1 cm^3 of water and one drop of a saturated $NaNO_3$ aqueous solution. The mixture was stored in a refrigerator for 2 d and the resulting dark-brown plate crystals were collected by filtration. Yield: 0.02 g (39% based on Co). Anal. Found: C, 15.39; H, 5.01; N, 16.41%. Calcd for $[CdCl\{Co(C_2H_6NS)_2(C_2H_8N_2)\}_2](NO_3)_3\cdot3H_2O$: C, 15.49; H, 4.98; N, 16.56%.

Conversion of [3]$(NO_3)_7$ to [1]. To a solution of [**3**]$(NO_3)_7\cdot3H_2O$ (0.05 g) in 2 cm^3 of water was added a solution of NaCl (0.50 g) in 3 cm^3 of water. The mixture was allowed to stand at room temperature for 2 d, and the resulting dark-brown crystals were collected by filtration. Yield: 0.02 g (73% based on Cd). Anal. Found: C, 14.18; H, 4.36; N,11.27%. Calcd for $[CdCl_3\{Co(C_2H_6NS)_2(C_2H_8N_2)\}]\cdot0.5H_2O$: C, 14.44; H, 4.24; N, 11.23%.

Conversion of [2]$(NO_3)_3$ to [1]. To a solution of [**2**]$(NO_3)_3\cdot3H_2O$ (0.05 g) in 5 cm^3 of water was added a solution of NaCl (0.20 g) in 2 cm^3 of water. The mixture was allowed to stand at room temperature for 2 d, and the resulting dark-brown crystals were collected by filtration. Yield: 0.02 g (75% based on Cd). Anal. Found: C, 14.63; H, 4.07; N,11.27%. Calcd for $[CdCl_3\{Co(C_2H_6NS)_2(C_2H_8N_2)\}]\cdot0.5H_2O$: C, 14.44; H, 4.24; N, 11.23%.

Conversion of [1] to $[Ni\{Co(aet)_2(en)\}_2]Cl_4$. To a solution containing 0.05 g (0.10 mmol) of [**1**]$\cdot0.5H_2O$ in 5 cm^3 of warm water was added 0.15 g (6.3 mmol) of $NiCl_2\cdot6H_2O$. The mixture was stirred at 60 °C for 30 min, followed by cooling in a refrigerator overnight. The resulting dark red-brown crystals, which showed identical absorption spectra with $[Ni\{Co(aet)_2(en)\}_2]Cl_4$,[18] were collected by filtration. Yield: 0.04 g (94% based on Co). Anal. Found: C,16.78; H, 6.13; N,12.89%. Calc for $[Ni\{Co(C_2H_6NS)_2(C_2H_8N_2)\}_2]Cl_4\cdot6H_2O$: C,16.93; H,6.16; N,13.16%.

Measurements. The electronic absorption spectra were recorded with a JASCO Ubest-55 spectrophotometer. The ^{13}C NMR spectra were recorded with a Bruker AM-500 NMR spectrometer at the probe temperature in D_2O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference. The elemental analyses (C, H, N) were performed by the Analysis Center of the University of Tsukuba. The concentrations of Co and Cd 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.

Crystal Structure Determination. Single-crystal X-ray diffraction experiments were performed on an Enraf–Nonius CAD4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ = 0.71073 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 ω-2θ scan mode up to 2θ = 50°. The intensities were corrected for Lorentz and polarization effects. Empirical absorption corrections based on a series of ψ scans were also applied. The 2131, 5026 and 4221 independent reflections with $I > 2\sigma(I)$ of the 3167, 6159 and 6321 measured reflections were considered as "observed" and used for structure determinations of [**1**]$\cdot0.5H_2O$, [**2**]$(NO_3)_3\cdot3H_2O$ and [**3**]$(NO_3)_7\cdot3H_2O$, respectively.

The positions of Cd, Co, S and some other atoms for [**1**]$\cdot0.5H_2O$, [**2**]$(NO_3)_3\cdot3H_2O$ and [**3**]$(NO_3)_7\cdot3H_2O$ were determined by direct

Table 1. Crystallographic Data[a] for [**1**]·$0.5H_2O$, [**2**]$(NO_3)_3 \cdot 3H_2O$ and [**3**]$(NO_3)_7 \cdot 3H_2O$

	[**1**]·$0.5H_2O$	[**2**]$(NO_3)_3 \cdot 3H_2O$	[**3**]$(NO_3)_7 \cdot 3H_2O$
Formula	$C_6H_{21}CdCl_3CoN_4O_{0.5}S_2$	$C_{12}H_{46}CdClCo_2N_{11}O_{12}S_4$	$C_{24}H_{86}Cd_2ClCo_4N_{23}O_{24}S_8$
M	499.1	930.5	1833.6
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/a$	$P2/c$
a/Å	7.717(2)	15.030(4)	15.190(4)
b/Å	16.353(2)	14.822(2)	7.6291(9)
c/Å	13.194(3)	15.147(4)	28.878(9)
β/°	97.47(1)	95.71(1)	103.47(1)
V/Å^3	1651.0(4)	3357(1)	3254(1)
Z	4	4	2
μ, cm^{-1}	30.2	20.0	20.2
R_{int}	0.028	0.020	0.022
R $(I > 2\sigma(I))$[b]	0.032	0.066	0.055
R_w $(I > 2\sigma(I))$[c]	0.035	0.083	0.061

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

methods, 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 N and O atoms of the nitrate anions and water O atoms in [**3**]$(NO_3)_7 \cdot 3H_2O$, which were refined isotropically. All H atoms, except for water H atoms, were located and added to the calculations but not refined. In [**2**]$(NO_3)_3 \cdot 3H_2O$ one of the nitrate anions was disordered and appeared as two fragments which are superposed on each other. The site occupancy factor for the atoms of this nitrate anion (N(13a), O(31a), O(32a), O(33a), N(13b), O(31b), O(32b) and O(33b)) was fixed to 0.5. For the atoms in [**3**]$[NO_3]_7 \cdot 3H_2O$, Cl(1), N(14) and O(51) were constrained to the special positions of symmetry 2, while N(15) was constrained to the position of symmetry $\bar{1}$. The site occupancy factors of these atoms, besides N(13), O(31), O(32), O(33), O(41), O(42), O(43) and O(2w), were fixed to 0.5. All of the calculations were performed using the teXsan crystallographic software package.[21,22]

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 149517—149519.

Results and Discussion

Crystal Structures. X-ray structural analysis revealed that [**1**] is a complex molecule consisting of one $[Co(aet)_2(en)]^+$ unit and one Cd and three Cl atoms. A perspective drawing of [**1**] is given in Fig. 1, and the selected bond distances and angles are listed in Table 2. The Cd atom is coordinated by three Cl atoms, besides two thiolato S atoms of the $[Co(aet)_2(en)]^+$ unit, to form an S-bridged $Co^{III}Cd^{II}$ dinuclear structure in $[CdCl_3\{Co(aet)_2(en)\}]$. The bond angles subtended at the Cd atom require a distorted trigonal-bipyramidal coordination geometry with the S(1) and Cl(2) atoms at the axial positions (S(1)–Cd(1)–Cl(2) = 161.65(6)°, S(2)–Cd(1)–Cl(1) = 129.06(6)°, S(2)–Cd(1)–Cl(3) = 116.08(6)°, Cl(1)–Cd(1)–Cl(3) = 114.67(7)°). These two donor atoms make the longer bond distances to the Cd atom; the Cd(1)–S(1) bond distance (2.707(2) Å) is ca. 0.09 Å longer than the Cd(1)–S(2) distance (2.618(2) Å) and the Cd(1)–Cl(2) bond distance (2.624(2) Å) is ca. 0.13 Å longer than the averaged distance of Cd(1)–Cl(1) and Cd(1)–Cl(3) (2.495(2) Å). The $[Co(aet)_2(en)]^+$ unit in [**1**] has an approximately octahedral geometry with a C_2-*cis*(*S*) configuration. This configuration is the same as

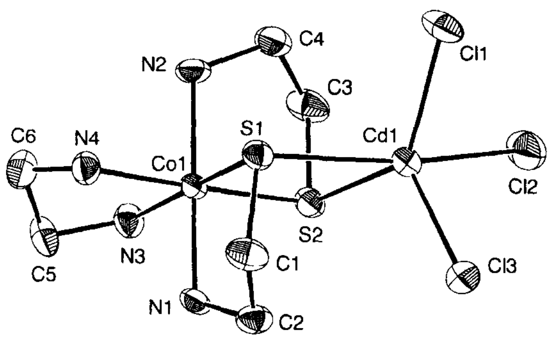


Fig. 1. A perspective views of the complex molecule [**1**] with the atomic labeling scheme. The Δ isomer is selected.

Table 2. Selected Bond Distances (Å) and Angles (°) for [**1**]

	Distances		
Cd(1)–Cl(1)	2.481(2)	Cd(1)–Cl(2)	2.624(2)
Cd(1)–Cl(3)	2.508(2)	Cd(1)–S(1)	2.707(2)
Cd(1)–S(2)	2.618(2)	Co(1)–S(1)	2.245(2)
Co(1)–S(2)	2.258(2)	Co(1)–N(1)	1.974(5)
Co(1)–N(2)	1.984(5)	Co(1)–N(3)	1.996(5)
Co(1)–N(4)	2.006(5)		
	Angles		
Cl(1)–Cd(1)–Cl(2)	87.84(6)	Cl(1)–Cd(1)–Cl(3)	114.67(7)
Cl(1)–Cd(1)–S(1)	92.77(5)	Cl(1)–Cd(1)–S(2)	129.06(6)
Cl(2)–Cd(1)–Cl(3)	96.90(7)	Cl(2)–Cd(1)–S(1)	161.65(6)
Cl(2)–Cd(1)–S(2)	90.28(6)	Cl(3)–Cd(1)–S(1)	99.49(6)
Cl(3)–Cd(1)–S(2)	116.08(6)	S(1)–Cd(1)–S(2)	75.13(5)
S(1)–Co(1)–S(2)	92.31(6)	S(1)–Co(1)–N(1)	87.7(2)
S(1)–Co(1)–N(3)	174.5(2)	S(2)–Co(1)–N(2)	88.2(2)
S(2)–Co(1)–N(4)	175.3(2)	N(1)–Co(1)–N(2)	179.1(2)
N(3)–Co(1)–N(4)	84.5(2)	Cd(1)–S(1)–Co(1)	95.13(6)
Cd(1)–S(2)–Co(1)	97.32(6)		

that observed for the $[Co(aet)_2(en)]^+$ units in the parental $Co^{III}Ni^{II}Co^{III}$ trinuclear complex, $[Ni\{Co(aet)_2(en)\}_2]^{4+}$,[17,18] which indicates that the conversion of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ to [1] occurs with retention of the configuration of the $[Co(aet)_2(en)]^+$ unit. The bond distances and angles concerning the C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ unit in [1] are similar to those found in $[Ni\{Co(aet)_2(en)\}_2]^{4+}$.[17,18] However, in [1] the Co–S bond distances (av 2.252(2) Å) are longer and the S–Co–S bond angle (92.31(6)°) is larger than the corresponding distances (av 2.238(1) Å) and angles (av 85.19(5)°) in $[Ni\{Co(aet)_2(en)\}_2]^{4+}$.

X-ray analysis for $[2](NO_3)_3 \cdot 3H_2O$ revealed the presence of a discrete complex cation, nitrate anions and water molecules. The number of nitrate anions implies that the complex cation is trivalent. As shown in Fig. 2, the complex cation $[2]^{3+}$ consists of two octahedral $[Co(aet)_2(en)]^+$ units and one Cd and one Cl atoms. The Cd atom is coordinated by one Cl atom, besides four S atoms from two $[Co(aet)_2(en)]^+$ units, to form an S-bridged $Co^{III}Cd^{II}Co^{III}$ trinuclear structure in $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$. The asymmetrical chelating mode of each $[Co(aet)_2(en)]^+$ unit toward Cd atom is the same as that found in [1], having one long and the other short Cd–S bond distance (Cd(1)–S(1) = 2.735(2) Å vs. Cd(1)–S(2) = 2.618(2) Å and Cd(1)–S(3) = 2.714(2) Å vs. Cd(1)–S(4) = 2.614(2) Å) (Table 3). Furthermore, the averaged Cd–S bond distance in $[2]^{3+}$ (2.670(2) Å) is very similar to that in [1] (2.663(2) Å) and the Cd–Cl bond distance (2.486(2) Å) in $[2]^{3+}$ corresponds well with the shortest Cd–Cl distance in [1] (Cd(1)–Cl(1) = 2.481(2) Å). Each $[Co(aet)_2(en)]^+$ unit has a C_2-*cis*(*S*) geometry, like the $[Co(aet)_2(en)]^+$ unit in [1], and its bond distances and angles are in good agreement with those in [1]. Considering the chiral configurations (Δ and Λ) of the two C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units, three isomers ($\Delta\Delta$, $\Lambda\Lambda$ and $\Delta\Lambda$) are possible for $[2]^{3+}$. The crystal of $[2](NO_3)_3 \cdot 3H_2O$ consists of the $\Delta\Delta$ and $\Lambda\Lambda$ isomers with an approximate C_2 symmetry, which combine to form the racemic compound.

X-ray analysis for $[3](NO_3)_7 \cdot 3H_2O$ indicated the presence of a discrete complex cation, nitrate anions and water molecules. The total occupancy factor of the nitrate anions implies that the entire complex cation is heptavalent. As shown in Fig. 3, the entire complex cation $[3]^{7+}$ consists of four octahedral $[Co(aet)_2(en)]^+$ units and two Cd and one Cl atoms. The Cl atom lies on a two-fold axis and thus only half of the complex cation corresponds to the asymmetric unit. Each Cd atom is coordinated by four S atoms from the two $[Co(aet)_2(en)]^+$ units to form an S-bridged $Co^{III}Cd^{II}Co^{III}$ trinuclear moiety. The two trinuclear moieties are connected with each other by a Cd–Cl–Cd linkage, which completes a novel $(Co^{III}Cd^{II}Co^{III})_2$ hexanuclear structure in $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$. As a result, each of the two Cd atoms is situated in a five-coordinate geometry with four S and one Cl donor atoms, like the Cd atoms in $[2]^{3+}$. It is worth noting that the Cd–Cl distance in $[3]^{7+}$ (2.544(1) Å) is longer than that found in $[2]^{3+}$ (2.486(2) Å), while the averaged

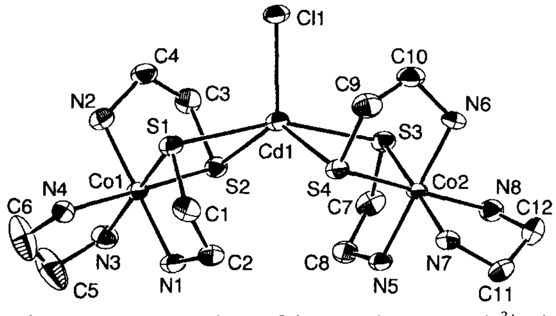


Fig. 2. A perspective views of the complex cation $[2]^{3+}$ with the atomic labeling scheme. The $\Delta\Delta$ isomer is selected.

Table 3. Selected Bond Distances (Å) and Angles (°) for $[2]^{3+}$

Distances			
Cd(1)–Cl(1)	2.486(2)	Cd(1)–S(1)	2.735(2)
Cd(1)–S(2)	2.618(2)	Cd(1)–S(3)	2.714(2)
Cd(1)–S(4)	2.614(2)	Co(1)–S(1)	2.255(2)
Co(1)–S(2)	2.269(2)	Co(1)–N(1)	1.992(6)
Co(1)–N(2)	1.968(6)	Co(1)–N(3)	1.995(6)
Co(1)–N(4)	1.987(6)	Co(2)–S(3)	2.248(2)
Co(2)–S(4)	2.257(2)	Co(2)–N(5)	1.981(5)
Co(2)–N(6)	1.982(6)	Co(2)–N(7)	1.997(6)
Co(2)–N(8)	1.995(6)		
Angles			
Cl(1)–Cd(1)–S(1)	99.13(5)	Cl(1)–Cd(1)–S(2)	117.20(6)
Cl(1)–Cd(1)–S(3)	101.87(6)	Cl(1)–Cd(1)–S(4)	111.20(6)
S(1)–Cd(1)–S(2)	75.00(5)	S(1)–Cd(1)–S(3)	158.89(5)
S(1)–Cd(1)–S(4)	95.36(5)	S(2)–Cd(1)–S(3)	97.00(5)
S(2)–Cd(1)–S(4)	131.53(6)	S(3)–Cd(1)–S(4)	75.12(5)
S(1)–Co(1)–S(2)	92.17(7)	S(1)–Co(1)–N(1)	87.4(2)
S(1)–Co(1)–N(3)	175.3(2)	S(2)–Co(1)–N(2)	87.1(2)
S(2)–Co(1)–N(4)	174.7(2)	N(1)–Co(1)–N(2)	178.7(2)
N(3)–Co(1)–N(4)	84.4(3)	S(3)–Co(2)–S(4)	92.30(7)
S(3)–Co(2)–N(5)	88.1(2)	S(3)–Co(2)–N(7)	175.6(2)
S(4)–Co(2)–N(6)	87.6(2)	S(4)–Co(2)–N(8)	174.5(2)
N(5)–Co(2)–N(6)	178.6(2)	N(7)–Co(2)–N(8)	84.7(2)
Cd(1)–S(1)–Co(1)	94.62(6)	Cd(1)–S(2)–Co(1)	97.52(6)
Cd(1)–S(3)–Co(2)	94.49(6)	Cd(1)–S(4)–Co(2)	97.04(6)

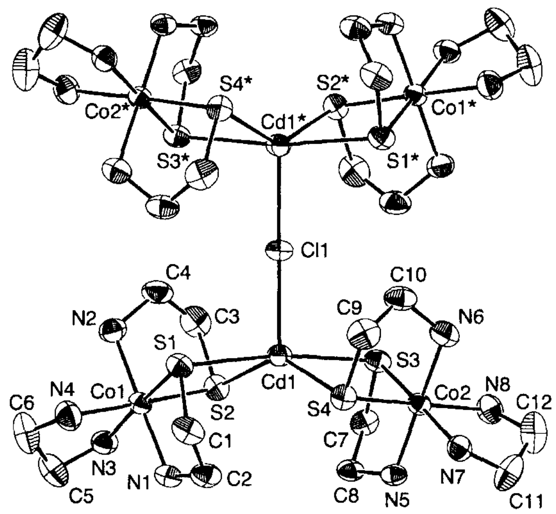


Fig. 3. A perspective views of the complex cation $[3]^{7+}$ with the atomic labeling scheme. The $\Delta\Delta\Delta\Delta$ isomer is selected.

Cd–S distance in $[\mathbf{3}]^{7+}$ (2.637(2) Å) is slightly shorter than that in $[\mathbf{2}]^{3+}$ (2.671(2) Å) (Tables 3 and 4). Each of four $[Co(aet)_2(en)]^+$ units adopts a C_2-*cis*(*S*) geometry, as does each $[Co(aet)_2(en)]^+$ unit in [**1**] and $[\mathbf{2}]^{3+}$, and its bond distances and angles are in good agreement with those in [**1**] and $[\mathbf{2}]^{3+}$. In $[\mathbf{3}]^{7+}$ either the Δ or Λ configurational C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ unit is selectively incorporated in the hexanuclear structure, giving only the $\Delta\Delta\Delta\Delta$ and $\Lambda\Lambda\Lambda\Lambda$ isomers with an approximate D_2 symmetry (Fig. 3).

The coordination geometry about the Cd^{II} atoms in $[\mathbf{2}]^{3+}$ and $[\mathbf{3}]^{7+}$ can be described as an intermediate between the trigonal bipyramid and square pyramid. For the coordination geometry of the five-coordinate complex, Addison et al. has introduced an angular structural index parameter, $\tau = (\beta - \alpha)/60$, where α and β represent two largest angles ($\beta > \alpha$); the τ value is zero for an ideal square pyramid ($\alpha = \beta = 180°$), while the value becomes unity for an ideal trigonal bipyramid ($\alpha = 120°, \beta = 180°$).[23] For $[\mathbf{2}]^{3+}$ and $[\mathbf{3}]^{7+}$ the τ values becomes 0.46 (α = S(2)–Cd(1)–S(4) = 131.53°, β = S(2)–Cd(1)–S(3) = 158.89(5)°) and 0.54 (α = S(2)–Cd(1)–S(4) = 139.13(8)°, β = S(2)–Cd(1)–S(3) = 171.34(7)°), respectively, which suggests a distorted square-pyramidal geometry for $[\mathbf{2}]^{3+}$ and a distorted trigonal-bipyramidal geometry for $[\mathbf{3}]^{7+}$. However, it is noticed that the three bond angles for $[\mathbf{2}]^{3+}$ (S(2)–Cd(1)–Cl(1) = 117.20(6)°, S(2)–Cd(1)–S(4) = 131.53(6)°, Cl(1)–Cd(1)–S(4) = 111.20(6)°), which correspond to the basal angles for the trigonal-bipyramidal geometry, are closer to the ideal trigonal angle of 120° than those for $[\mathbf{3}]^{7+}$ (S(2)–Cd(1)–Cl(1) = 110.2(1)°, S(2)–Cd(1)–S(4) = 139.13(8)°, Cl(1)–Cd(1)–S(4) = 110.6(1)°). Since the index parameter τ is based only on the two largest angles defined by four of five donor atoms, which correspond to the basal angles for the square-pyramid, we modified this index parameter as given in Eq. 1, so as to take into account the remaining one donor atom and the basal angles for the trigonal-bipyramid.

$$\chi = \{(\beta - \alpha) + (\gamma + \delta - \alpha)\}/180 = (\beta + \gamma + \delta - 2\alpha)/180 \quad (1)$$

In Eq. 1, α and β represent two largest angles defined by four of five donor atoms, B, C, D, and E ($\beta = B-\mathrm{M}-C$, $\alpha = D-\mathrm{M}-E$, $\beta > \alpha$), and γ and δ represent the angles concerning the remaining donor atom A ($\gamma = A-\mathrm{M}-D$, $\delta = A-\mathrm{M}-E$) (Chart 1). That is, β and α correspond to the basal angles for the square-pyramid, while γ, δ and α, correspond to the basal angles for the trigonal-bipyramid. For an ideal square-pyramidal geometry this index parameter χ is equal to zero ($\alpha = \beta = 180°$, $\gamma = \delta = 90°$; $\beta - \alpha = 0$, $\gamma + \delta - \alpha = 0$), while it becomes unity for an ideal trigonal-bipyramidal geometry ($\alpha = \gamma = \delta = 120°$, $\beta = 180°$; $\beta - \alpha = 60°$, $\gamma + \delta - \alpha = 120°$). The χ values for [**1**], $[\mathbf{2}]^{3+}$ and $[\mathbf{3}]^{7+}$ become 0.75, 0.69 and 0.63, respectively, which defines that all the Cd^{II} atoms in the present S-bridged polynuclear complexes have a distorted trigonal-bipyramidal geometry, rather than a square-pyramidal geometry. Moreover, it is seen from the χ values that the distortion from the trigonal bipyramid to square pyramid increases in the order of the $Co^{III}Cd^{II}$ dinuclear [**1**], the $Co^{III}Cd^{II}Co^{III}$ trinuclear $[\mathbf{2}]^{3+}$ and the $(Co^{III}Cd^{II}Co^{III})_2$ hexanuclear $[\mathbf{3}]^{7+}$.

Table 4. Selected Bond Distances (Å) and Angles (°) for $[\mathbf{3}]^{7+}$

Distances			
Cd(1)–Cl(1)	2.5438(9)	Cd(1)–S(1)	2.679(2)
Cd(1)–S(2)	2.599(2)	Cd(1)–S(3)	2.678(2)
Cd(1)–S(4)	2.591(2)	Co(1)–S(1)	2.260(3)
Co(1)–S(2)	2.262(3)	Co(1)–N(1)	1.974(7)
Co(1)–N(2)	1.979(8)	Co(1)–N(3)	2.008(8)
Co(1)–N(4)	1.992(8)	Co(2)–S(3)	2.266(3)
Co(2)–S(4)	2.269(3)	Co(2)–N(5)	1.972(7)
Co(2)–N(6)	1.969(8)	Co(2)–N(7)	1.997(8)
Co(2)–N(8)	1.988(8)		

Angles			
Cl(1)–Cd(1)–S(1)	93.89(7)	Cl(1)–Cd(1)–S(2)	110.2(1)
Cl(1)–Cd(1)–S(3)	94.57(8)	Cl(1)–Cd(1)–S(4)	110.6(1)
S(1)–Cd(1)–S(2)	76.84(7)	S(1)–Cd(1)–S(3)	171.34(7)
S(1)–Cd(1)–S(4)	101.68(8)	S(2)–Cd(1)–S(3)	98.42(7)
S(2)–Cd(1)–S(4)	139.13(8)	S(3)–Cd(1)–S(4)	77.03(7)
S(1)–Co(1)–S(2)	93.01(9)	S(1)–Co(1)–N(1)	87.5(2)
S(1)–Co(1)–N(3)	175.4(2)	S(2)–Co(1)–N(2)	87.2(2)
S(2)–Co(1)–N(4)	173.5(3)	N(1)–Co(1)–N(2)	179.1(3)
N(3)–Co(1)–N(4)	84.9(3)	S(3)–Co(2)–S(4)	92.73(9)
S(3)–Co(2)–N(5)	87.4(2)	S(3)–Co(2)–N(7)	174.7(2)
S(4)–Co(2)–N(6)	87.5(3)	S(4)–Co(2)–N(8)	174.5(3)
N(5)–Co(2)–N(6)	179.3(3)	N(7)–Co(2)–N(8)	84.6(3)
Cd(1)–S(1)–Co(1)	93.59(9)	Cd(1)–S(2)–Co(1)	95.70(9)
Cd(1)–S(3)–Co(2)	93.77(8)	Cd(1)–S(4)–Co(2)	96.06(9)
Cd(1)–Cl(1)–Cd(1*)	177.3(3)		

Synthesis and Structural Conversion. The reaction of the S-bridged $Co^{III}Ni^{II}Co^{III}$ trinuclear complex salt, $[Ni\{Co(aet)_2(en)\}_2]Cl_4$, with excess $CdCl_2$ in water gave a red-brown crystalline product ([**1**]$\cdot 0.5H_2O$) in high yield, while no reaction occurred with equimolar $CdCl_2$. The elemental and plasma emission analyses of this red-brown complex are in good agreement with the proposed formula of a complex salt, $[CdCl_2\{Co(aet)_2(en)\}]Cl \cdot 0.5H_2O$, but X-ray analysis demonstrated that [**1**] is the neutral complex molecule, $[CdCl_3\{Co(aet)_2(en)\}]$, in which the Cd^{II} ion is coordinated by three Cl^- ions, besides two S atoms from the C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ unit. These results are in contrast to those found for the reactions of $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ with $Na_2[PdCl_4]$ in water.[19] That is, $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ readily reacted with 1 molar equiv of $Na_2[PdCl_4]$ to form an S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear complex salt, [Pd{Co-

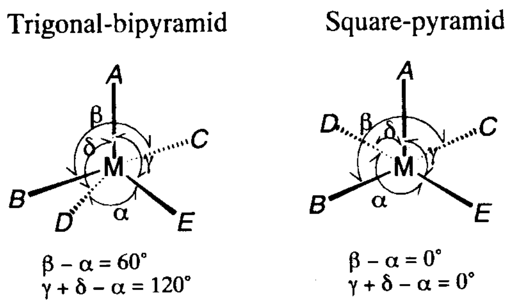


Chart 1.

$(aet)_2(en)\}_2]Cl_4$. Furthermore, the reaction of $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ with $Na_2[PdCl_4]$ in a ratio of 1 : 2 produced an S-bridged $Co^{III}Pd^{II}$ dinuclear complex salt, $[PdCl_2\{Co(aet)_2(en)\}]Cl$, in which the Pd^{II} ion has an distorted square-planar geometry, coordinated by two Cl^- ions besides two S atoms from the C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ unit.[19]

Although [**1**] forms a neural complex molecule in crystal, [**1**] is considerably soluble in water. As shown in Fig. 4, the electronic absorption spectrum of [**1**] in water is characterized by a d-d transition band with a shoulder at lower energy in the region of ca. $(18—24)\times 10^3\ cm^{-1}$ and an intense S-to-Co charge-transfer band composed of two components in the region of $(34—40)\times 10^3\ cm^{-1}$. This spectral behavior differs significantly from that of the parental $Co^{III}Ni^{II}Co^{III}$ trinuclear complex, $[Ni\{Co(aet)_2(en)\}_2]^{4+}$,[17,18] but resembles that observed for the *cis*(*S*)-$[Co(thiolato\text{-}S)_2(amine\text{-}N)_4]^+$-type mononuclear complexes.[16,24—26] In the ^{13}C NMR spectrum, [**1**] exhibits only three sharp signals in D_2O ($\delta = 32.63$ for CH_2S of aet, 47.40 for CH_2N of en, and 54.14 for CH_2N). Thus, it is considered that the C_2-*cis*(*S*) configuration of the $[Co(aet)_2(en)]^+$ unit observed in the crystal of [**1**]$\cdot 0.5H_2O$ is retained in solution. However, the molar conductivity of [**1**] in water gives the value of 333 $\Omega^{-1}\ cm^2\ mol^{-1}$. This suggests that [**1**] exists as a cationic complex in water, eliminating at least one Cl^- ion from the coordination sphere of the Cd^{II} center.

When [**1**] was treated with an appropriate amount of $NaNO_3$ in water, dark-red plate crystals of [**2**]$(NO_3)_3\cdot 3H_2O$ were obtained in reasonable yield. The plasma emission analysis indicated that [**2**]$(NO_3)_3\cdot 3H_2O$ contains Co and Cd atoms in a ratio of 2 : 1, and X-ray analysis demonstrated that $[\mathbf{2}]^{3+}$ is the cationic S-bridged $Co^{III}{}_2Cd^{II}$ trinuclear complex, $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$, in which the Cd^{II} center is coordinated by one Cl^- ion besides four S atoms from the two C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units. The absorption spectral curve of [**1**] in water coincides well with the curve of [**2**]$(NO_3)_3$ over the whole region. Furthermore, the ^{13}C NMR spectrum of [**1**] in D_2O is essentially the same as that of [**2**]$(NO_3)_3$,

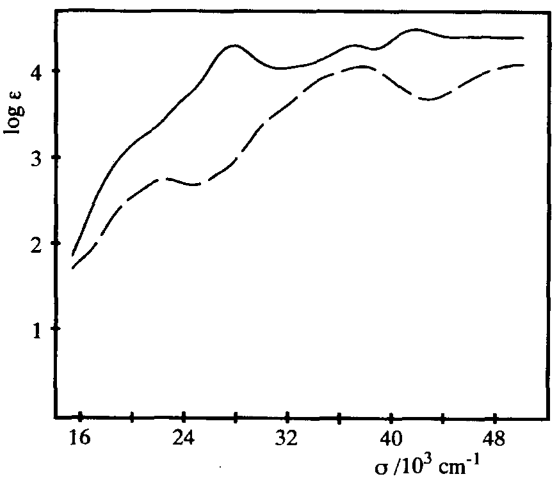


Fig. 4. Electronic absorption spectra of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (—) and [**1**] (- - -) in H_2O.

giving only three sharp signals for the aet and en ligands in the complex. Considering these facts and the result that [**2**]$(NO_3)_3$ is isolated from the aqueous solution of [**1**], one can assume that the $Co^{III}Cd^{II}$ dinuclear structure in [**1**] is readily converted at least in part to the $Co^{III}Cd^{II}Co^{III}$ trinuclear structure in $[\mathbf{2}]^{3+}$ in solution.

Treatment of [**2**]$(NO_3)_3\cdot 3H_2O$ with $NaNO_3$ in water was found to produce dark-red needle crystals of [**3**]$(NO_3)_7\cdot 3H_2O$, the absorption and ^{13}C NMR spectral features of which are essentially the same as those of [**2**]$(NO_3)_3\cdot 3H_2O$. [**3**]$(NO_3)_7\cdot 3H_2O$ was also obtained by treating [**1**]$\cdot 0.5H_2O$ with a large amount of $NaNO_3$ in water. While the plasma emission analysis suggested that $[\mathbf{3}]^{7+}$ contains Co and Cd atoms in the same ratio of 2 : 1 as does $[\mathbf{2}]^{3+}$, X-ray analysis revealed that $[\mathbf{3}]^{7+}$ has a novel $(Co^{III}Cd^{II}Co^{III})_2$ hexanuclear structure in $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$, which can be regarded as a dimer of the S-bridged $Co^{III}Cd^{II}Co^{III}$ trinuclear structure in $[\mathbf{2}]^{3+}$. When [**3**]$(NO_3)_7\cdot 3H_2O$ was treated with an appropriate amount of NaCl in water, plate crystals of [**2**]$(NO_3)_3\cdot 3H_2O$ were formed. [**2**]$(NO_3)_3$ was further reconverted into [**1**] by treatment with NaCl in water. These results clearly indicate that the S-bridged $Co^{III}Cd^{II}$ dinuclear, $Co^{III}Cd^{II}Co^{III}$ trinuclear and $(Co^{III}Cd^{II}Co^{III})_2$ hexanuclear structures with the C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units are interconvertible to one another by controlling the concentrations of Cl^- ion vs. NO_3^- ion in solution, where Cl^- and NO_3^- ions act as a ligand and a counter-anion, respectively (Scheme 1). In addition, it was found that [**1**] can be reverted back to $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ by treatment with excess $NiCl_2\cdot 6H_2O$ in water. Since the reactions of $[Pd\{Co(aet)_2(en)\}_2]Cl_4$ or $[PdCl_2\{Co(aet)_2(en)\}]Cl$ with excess $NiCl_2\cdot 6H_2O$ did not produce $[Ni\{Co(aet)_2(en)\}_2]Cl_4$,[19] it is considered that the Cd–S bonds in [**1**] are weaker than the Pd–S bonds in $[Pd\{Co(aet)_2(en)\}_2]^{4+}$. This is compatible with the Cd–S bond distances observed in [**1**] (av 2.663(2) Å), which are much longer than those in $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ (av 2.310(1) Å) and $[PdCl_2\{Co(aet)_2(en)\}]^+$ (av 2.271 (1) Å).[19]

In [**1**], $[\mathbf{2}]^{3+}$ and $[\mathbf{3}]^{7+}$ each Cd^{II} ion uniformly adopts a five-coordinate geometry, having at least one Cl^- ion in the coordination sphere. Furthermore, attempts to remove the bridging Cl^- ion from $[\mathbf{3}]^{7+}$ by treatment with a large amount of $NaNO_3$ in water were unsuccessful; only needle crystals of [**3**]$(NO_3)_7\cdot 3H_2O$ were isolated. Accordingly, it is reasonable to assume that the Cd^{II} ion with the C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units inherently prefers the five-coordinate geometry. The small S–Cd–S "bite" angles (75.13(5)° for [**1**], 75.00(5)° and 75.12(5)° for $[\mathbf{2}]^{3+}$ and 76.84(7)° and 77.03(7)° for $[\mathbf{3}]^{7+}$), which are restricted by the framework of the bidentate-*S*,*S* complex-ligand, C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$, besides the large covalent radius of the Cd^{II} ion, seem to be responsible for this geometrical preference.

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