Synthesis, Structural Characterization, and Interconversion of S-Bridged Dinuclear and Hexanuclear Complexes Composed of *cis(S)*-$[Co(aet)_2(en)]^+$ and Trigonal-Bipyramidal Cadmium(II) (aet = 2-Aminoethanethiolate, en = Ethylenediamine)

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The reaction of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (**1**) with excess $CdCl_2$ gave an S-bridged $Co^{III}Cd^{II}$ dinuclear complex, $[CdCl_3\{Co(aet)_2(en)\}]$ (**2**), which is interconvertible to a $Co^{III}_4Cd^{II}_2$ hexanuclear complex, $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$ (**3**). X-Ray analyses of **2** and $\mathbf{3}(NO_3)_7$ indicated that each Cd atom in the complexes has a trigonal-bipyramidal geometry.

Coordinated thiolato S atoms in mononuclear Co(III) complexes have been recognized to bind with other metal ions to form S-bridged polynuclear complexes.[1-4] In fact, considerable progress has been made in the chemistry of S-bridged polynuclear complexes containing $[Co(aet)(en)_2]^{2+}$ or *fac(S)*-$[Co(aet)_3]$ units (aet = 2-aminoethanethiolate, en = ethylenediamine).[1-3] On the other hand, no S-bridged polynuclear complexes containing $[Co(aet)_2(en)]^+$ units have long been studied, because of the difficulty in preparation of $[Co(aet)_2(en)]^+$ used as a starting mononuclear complex.[5] We have recently found that the facile reaction of $[Ni(aet)_2]$ with $[CoCl_2(en)_2]^+$ gives an S-bridged $Co^{III}Ni^{II}Co^{III}$ trinuclear complex, $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (**1**), in which the central Ni^{II} atom is coordinated by four S atoms from two *C2-cis(S)*-$[Co(aet)_2(en)]^+$ units.[6] In order to better understand the chemistry of S-bridged polynuclear complexes composed of octahedral thiolato units, it is desirable to investigate other S-bridged polynuclear complexes composed of $[Co(aet)_2(en)]^+$ units. In this paper we wish to report that novel S-bridged $Co^{III}Cd^{II}$ polynuclear complexes with *C2-cis(S)*-$[Co(aet)_2(en)]^+$, which exhibit unique stereochemical behavior, can be prepared by using **1** as the starting complex.

The addition of $CdCl_2{\cdot}2.5H_2O$ (0.3 g) to an aqueous solution of $\mathbf{1}Cl_4{\cdot}6H_2O$ (0.2 g),[6] followed by stirring at 60 ℃, gave a red-brown powder ($\mathbf{2}{\cdot}0.5H_2O$, 0.22 g), which was collected by filtration.[7] Dark-red plate crystals of $\mathbf{2}{\cdot}0.5H_2O$ suitable for X-ray analysis were obtained by allowing the filtrate to stand at room temperature for several days. X-Ray structural analysis revealed that **2** is a complex molecule consisting of one $[Co(aet)_2(en)]^+$ unit and one Cd and three Cl atoms.[8] As shown in Figure 1, the Cd atom is coordinated by two thiolato S atoms of the $[Co(aet)_2(en)]^+$ unit and three Cl atoms to form the 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 S1 and Cl3 atoms in the axial positions.[8,9] The Co atom has an approximately octahedral geometry with a *C2-cis(S)* configuration. This configuration is the same as that observed for the $[Co(aet)_2(en)]^+$ units in **1**,[6] which indicates that the metal replacement reaction of **1** occurs with retention of the geometry of the *C2-cis(S)*-$[Co(aet)_2(en)]^+$ unit. The bond distances and angles concerning the *C2-cis(S)*-$[Co(aet)_2(en)]^+$ unit in **2** are similar to those in **1**.[6] However, it is noticed that in **2** the Co-S bond distances (av. 2.251(2) Å) are longer and the S-Co-S bond angle (92.26(6) °) is larger than the corresponding distances (av. 2.238(1) Å) and angles (av. 85.19(5) °) in **1**.

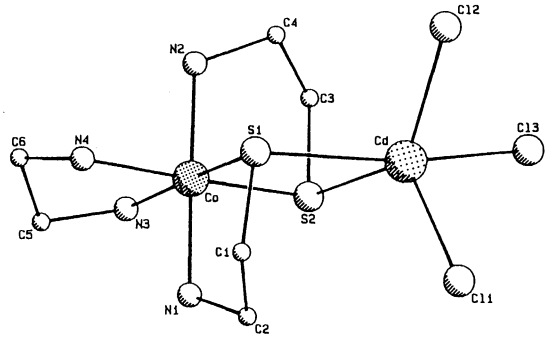

Figure 1. Perspective view of $[CdCl_3\{Co(aet)_2(en)\}]$ (**2**).

Treatment of **2** (0.16 g) with a large amount of $NaNO_3$ (4.8 g) in water, followed by standing at room temperature, gave dark-red needle crystals ($\mathbf{3}(NO_3)_7{\cdot}3H_2O$, 0.19 g).[10] X-Ray analysis of one of these crystals revealed the presence of a complex cation, nitrate anions, and water molecules.[11] As shown in Figure 2, the complex cation **3** consists of four *C2-cis(S)*-$[Co(aet)_2(en)]^+$ units and two Cd and one Cl atoms. This is consistent with the plasma emission analysis which gave the value of Co:Cd = 2:1.[10] Each Cd atom is coordinated by four S atoms from the two *C2-cis(S)*-$[Co(aet)_2(en)]^+$ units to form an S-bridged CoCdCo trinuclear unit. The two trinuclear units are connected with each other by a Cd-Cl-Cd linkage, completing the unprecedented $Co^{III}_4Cd^{II}_2$ hexanuclear structure in $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$. As a result, each Cd atom in **3** adopts a distorted trigonal-bipyramidal geometry as does the Cd atom in **2**. The bond distances and angles concerning the *C2-cis(S)*-$[Co(aet)_2(en)]^+$ units in **3** are in good agreement with those in **2**, except the slightly longer Co-S distances (av. 2.265(2) Å). Two chiral configurations, Δ and Λ, are possible for each of the four *C2-cis(S)*-$[Co(aet)_2(en)]^+$ units. However, either the Δ or Λ configuration is selectively incorporated in the hexanuclear structure in **3**, forming only the $\Delta\Delta\Delta\Delta$ and $\Lambda\Lambda\Lambda\Lambda$ isomers with a D_2 symmetry (Figure 2).

The electronic absorption curve of **2** in water,[7] which is dominated by a d-d transition band at 445 nm and a sulfur-to-cobalt charge-transfer band at 266 nm, coincides well with the curve of $\mathbf{3}(NO_3)_7$ over the whole region.[10] Furthermore, the ^{13}C NMR spectrum of **2** [7] is essentially the same as that of $\mathbf{3}(NO_3)_7$,[9] giving only three sharp signals for the aet and en ligands in the complex. Considering these facts and that $\mathbf{3}(NO_3)_7$ was isolated from the aqueous solution of **2**, it is likely that the dinuclear structure in **2** is converted to the hexanuclear structure in **3** in solution. On the other hand, treatment of $\mathbf{3}(NO_3)_7{\cdot}3H_2O$ (50 mg) with a large amount of NaCl (500 mg) in water, followed by standing at room temperature, produced $\mathbf{2}{\cdot}H_2O$ in a quantitative yield (26 mg, 93%).[12] These results indicate that the S-bridged $Co^{III}Cd^{II}$ dinuclear and $Co^{III}_4Cd^{II}_2$

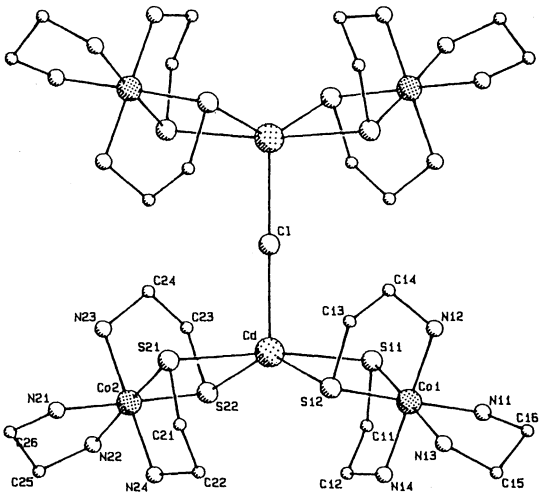

Figure 2. Perspective view of $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$ (**3**).

hexanuclear structures are interconvertible to each other only by controlling the concentrations of Cl^- ion in solution.

In the present study, it was found that the replacement of the Ni^{II} atom in $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ (**1**Cl_4) is achieved by the reaction with excess $CdCl_2$ in water. However, the reaction product was not a corresponding S-bridged $Co^{III}Cd^{II}Co^{III}$ trinuclear complex $[Cd\{Co(aet)_2(en)\}_2]^{4+}$, but a neutral dinuclear complex $[CdCl_3\{Co(aet)_2(en)\}]$ (**2**), in which the Cd atom is situated in a trigonal-bipyramidal environment. When **2** was treated with a large amount of $NaNO_3$ in water, a cationic $Co^{III}_4Cd^{II}_2$ hexanuclear complex $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$ (**3**) was produced. In **3** each Cd^{II} atom also adopts a trigonal-bipyramidal geometry, coordinated by a bridging Cl atom besides four S atoms from the two *C2-cis(S)*-$[Co(aet)_2(en)]^+$ units. Attempts to remove the bridging Cl atom from **3** by treating with a large amount of $NaNO_3$ in water were unsuccessful. Accordingly, it is reasonable to assume that the $Co^{III}Cd^{II}$ polynuclear structures composed of *C2-cis(S)*-$[Co(aet)_2(en)]^+$ units are stabilized by the preference of Cd(II) for the trigonal-bipyramidal geometry. The large covalent radius of the Cd^{II} atom and the small S-Cd-S bite angle restricted by the *C2-cis(S)*-$[Co(aet)_2(en)]^+$ metalloligand seem to be responsible for this geometrical preference.

References and Notes

1 R. H. Lane, N. S. Pantaleo, J. K. Farr, W. M. Coney, and M. G. Newton, *J. Am. Chem. Soc.*, **100**, 1610 (1978); M. J. Heeg, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **18**, 2036 (1979); M. J. Heeg, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **19**, 554 (1980).

2 D. H. Busch and D. C. Jicha, *Inorg. Chem.*, **1**, 884 (1962); R. E. DeSimone, T. Ontko, L. Wardman, and E. L. Blinn, *Inorg. Chem.*, **14**, 1313 (1975); D. W. Johnson and T. R. Brewer, *Inorg. Chim. Acta*, **151**, 221 (1988).

3 T. Konno, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **63**, 3027 (1990); T. Konno, T. Nagashio, K. Okamoto, and J. Hidaka, *Inorg. Chem.*, **31**, 1160 (1992).

4 J. Suades, X. Solans, M. F-Altaba, and M. Aguilo, *Inorg. Chim. Acta*, **99**, 1 (1985); K. Okamoto, S. Aizawa, T. Konno, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **59**, 3859 (1986); K. Okamoto, T. Yonemura, T. Konno, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **65**, 794 (1992).

5 C. Stein, S. Bouma, J. Carlson, C. Cornelius, J. Maeda, C. Weschler, E. Deutsch, and K. O. Hodgson, *Inorg. Chem.*, **15**, 1183 (1976); H. Umehara, Ph. D. Thesis, University of Tsukuba, 1988; T. Yonemura, K. Okamoto, T. Ama, H. Kawaguchi, and T. Yasui, *Chem. Lett.*, **1993**, 1123.

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

7 Anal. Found: C, 14.35; H, 4.15; N, 10.90; Co, 11.7; Cd, 22.2%. Calcd for $[CdCl_3\{Co(C_2H_6NS)_2(C_2H_8N_2)\}]\cdot 0.5H_2O$: C, 14.44; H, 4.24; N, 11.23; Co, 11.8; Cd, 22.5%. Absorption spectrum in H_2O [ν_{max}, 10^3 cm^{-1} (log ε , mol^{-1} dm^3 cm^{-1})]: 15.72 (1.96)^{sh}, 22.47 (2.83), 29.59 (3.38)^{sh}, 34.36 (4.02)^{sh}, 37.59 (4.18), 48.31 (4.17)^{sh}. The sh label denotes a shoulder. ^{13}C NMR spectrum in D_2O (δ, ppm from DSS): 32.62 (CH_2S), 47.40 (CH_2NH_2 of en), 54.14 (CH_2NH_2 of aet).

8 Crystal data: *F. W.* = 499.1, monoclinic, $P2_1/c$ (No. 14), a = 7.717(2), b = 16.353(2), c = 13.194(3) Å, β = 97.47(1) °, V = 1651.0(5) $Å^3$, Z = 4, Dc = 2.03 g cm^{-3}, $R(Rw)$ = 0.035 (0.038) for 2249 reflections. Selected bond distances (Å) and angles (°): Cd-Cl1 = 2.508(2), Cd-Cl2 = 2.482(2), Cd-Cl3 = 2.624(2), Cd-S1 = 2.707(2), Cd-S2 = 2.617(2), av. Co-S = 2.251(2), av. Co-N_{aet} = 1.977(5), av. Co-N_{en} = 1.999(5), Cl1-Cd-Cl2 = 114.71(6), Cl1-Cd-S2 = 116.07(6), Cl2-Cd-S2 = 129.03(6), Cl3-Cd-S1 = 161.60(5), S1-Cd-S2 = 75.11(5), S1-Co-S2 = 92.26(6), S1-Co-N1 = 87.8(1), S2-Co-N2 = 88.2(2), N3-Co-N4 = 84.4(2), Cd-S1-Co = 95.14(6).

9 The equatorial-equatorial and axial-equatorial angles (114.71(6) – 129.03(6) ° and 75.11(5) – 95.14(6) °) are close to the ideal angles of 120 ° and 90 ° for a trigonal bipyramid.

10 Anal. Found: C, 15.48; H, 4.66; N, 17.33; Co, 12.7; Cd, 11.8%. Calcd for $[Cd_2Cl\{Co(C_2H_6NS)_2(C_2H_8N_2)\}_4](NO_3)_7\cdot 3H_2O$: C, 15.72; H, 4.73; N, 17.57; Co, 12.9; Cd, 12.3%. Absorption spectrum in H_2O [ν_{max}, 10^3 cm^{-1} (log ε , mol^{-1} dm^3 cm^{-1})]: 15.87 (2.71)^{sh}, 22.47 (3.47), 29.59 (4.04)^{sh}, 34.25 (4.72)^{sh}, 37.59 (4.89), 48.31 (5.16). ^{13}C NMR spectrum in D_2O (δ, ppm from DSS): 32.46 (CH_2S), 47.27 (CH_2NH_2 of en), 54.13 (CH_2NH_2 of aet).

11 Crystal data: *F. W.* = 1833.6, monoclinic, $P2/c$ (No. 13), a = 15.190(4), b = 7.629(1), c = 28.878(9) Å, β =103.47(1) °, V = 3255(1) $Å^3$, Z = 2, Dc = 1.87 g cm^{-3}, $R(Rw)$ = 0.054 (0.058) for 4432 reflections. Cd-Cl = 2.5437(6), Cd-S11 = 2.679(2), Cd-S12 = 2.600(2), Cd-S21 =2.677(2), Cd-S22 = 2.591(2), av. Co-S = 2.265(2), av. Co-N_{aet} = 1.982(7), av. Co-N_{en} = 2.006(7), Cl-Cd-S12 = 110.1(1), Cl-Cd-S22 = 110.7(1), S12-Cd-S22 = 139.13(7), S11-Cd-S21 = 171.41(6), S11-Cd-S12 = 76.83(7), S21-Cd-S22 = 77.07(7), S11-Co1-S12 = 92.99(8), S11-Co1-N11 = 88.1(2), S12-Co1-N12 = 87.6(2), N13-Co1-N14 = 85.4(3), S21-Co2-S22 = 92.71(9), S21-Co2-N21 = 87.6(2), S22-Co2-N22 = 87.8(2), N23-Co2-N24 = 85.2(3), av. Cd-S-Co = 94.78(8).

12 Anal. Found: C,14.19; H, 4.38; N, 10.95%. Calcd for $[CdCl_3\{Co(C_2H_6NS)_2(C_2H_8N_2)\}]\cdot H_2O$: C, 14.18; H, 4.36; N, 11.03%.