The First S-Bridged $Co^{III}Cd^{II}Co^{III}$ and $Co^{III}Cd^{II}_2Co^{III}$ Structures Controlled by Chirality of Mono(thiolato)-Type Cobalt(III) Units

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Treatment of the *racemic* Δ/Λ-$[Co(aet)(en)_2]^{2+}$ (aet = 2-aminoethanethiolate) with Cd^{II} in the presence of excess Cl^- in water gave $\Delta\Lambda$-$[CdCl_4\{Co(aet)(en)_2\}_2]^{2+}$ ($\Delta\Lambda$-$[\mathbf{1}]^{2+}$), while the corresponding reaction using the optically active Λ-$[Co(aet)(en)_2]^{2+}$ produced $\Lambda\Lambda$-$[Cd_2Cl_7\{Co(aet)(en)_2\}_2]^+$ ($\Lambda\Lambda$-$[\mathbf{2}]^+$). The crystal structures of these complexes were determined by X-ray crystallography.

The ligating ability of coordinated thiolato groups toward transition metal ions is of current increasing interest, in relevance to the rational construction of heterometallic polynuclear and polymeric structures that exhibit unique chemical properties.[1] For the mono(thiolato)-type cobalt(III) system, this subject was initially studied by Deutsch and co-workers, who carried out the reactions of $[Co(aet)(en)_2]^{2+}$ (aet = 2-aminoethanethiolate) or $[Co(tga)(en)_2]^+$ (tga = mercaptoacetate) with heavy metal ions.[2] They have shown that Ag^I and Hg^{II} form S-bridged adducts with $[Co(aet)(en)_2]^{2+}$ or $[Co(tga)(en)_2]^+$ in solution and in the solid state, some of which have been structurally characterized.[2,3] On the other hand, it has been believed that Cd^{II} and Zn^{II} do not form detectable adducts, because no absorption spectral changes are recognized in the course of the reactions.[2a] Recently, we have found that treatment of $[Ni\{Co(aet)_2(en)\}_2]Cl_4$ with $CdCl_2$ produces an S-bridged $Co^{III}Cd^{II}$ dinuclear complex $[CdCl_3\{Co(aet)_2(en)\}]$, indicating the ligating ability of thiolato groups in $[Co(aet)_2(en)]^+$ toward Cd^{II}.[4] This result, together with our recent interest in the aggregation of mono(thiolato)-type cobalt(III) octahedrons,[3,5] prompted us to reexamine the reaction of $[Co(aet)(en)_2]^{2+}$ with Cd^{II}. As a result, we found that solid samples involving Co^{III}–S–Cd^{II} linkages can be isolated from $[Co(aet)(en)_2]^{2+}$ and Cd^{II} and that their S-bridged structures are controlled by the chirality of $[Co(aet)(en)_2]^{2+}$, the results of which are presented here.

Treatment of an aqueous solution (10 cm^3) of the *racemic* Δ/Λ-$[Co(aet)(en)_2](ClO_4)_2$[6a] (0.18 g, 0.40 mmol) with $CdCl_2\cdot 2.5H_2O$ (0.05 g, 0.20 mmol) at room temperature did not cause the solution color change, and its absorption spectrum was identical with that of $[Co(aet)(en)_2](ClO_4)_2$, as previously reported by Deutsch et al.[2a] However, the addition of excess NaCl (1.0 g) to the reaction mixture, followed by allowing to stand at room temperature, led to the formation of dark brown crystals ($\Delta\Lambda$-$[\mathbf{1}](ClO_4)_2$).[7] X-ray fluorescence spectrometry showed the presence of Co and Cd atoms in $\Delta\Lambda$-$[\mathbf{1}](ClO_4)_2$, and its elemental analytical data were in agreement with the formula of the 2:1 adduct $[Co(aet)(en)_2]_2[CdCl_2]Cl_2(ClO_4)_2$. While $\Delta\Lambda$-$[\mathbf{1}](ClO_4)_2$ exhibits an absorption spectrum identical with that of $[Co(aet)(en)_2](ClO_4)_2$ in water, its solid state spectral feature (nujol mull) is quite different. That is, for $\Delta\Lambda$-$[\mathbf{1}](ClO_4)_2$ the *d–d* absorption shoulder at ~600 nm characteristically observed for $[Co(aet)(en)_2](ClO_4)_2$ disappears with the absorption peak shift from 482 to 493 nm, which is suggestive of the binding of a thiolato group in $[Co(aet)(en)_2]^{2+}$ with Cd^{II}.

The crystal structure of $\Delta\Lambda$-$[\mathbf{1}](ClO_4)_2$ was determined by X-ray structural analysis.[8] As shown in Figure 1a, the complex cation $\Delta\Lambda$-$[\mathbf{1}]^{2+}$ consists of two octahedral $[Co(aet)(en)_2]^{2+}$ units and a square-planar $[CdCl_4]^{2-}$ unit. The thiolato S atom of each $[Co(aet)(en)_2]^{2+}$ unit is bound to an apical site of the $[CdCl_4]^{2-}$ unit to form an S-bridged $Co^{III}Cd^{II}Co^{III}$ trinuclear structure. As a result, the central Cd^{II} atom is situated in a quasi octahedral environment surrounded by two S and four Cl atoms.[9] This S-bridged trinuclear structure is reminiscent of the S-bridged $Co^{III}Ag^{I}Co^{III}$ structure in $[Ag\{Co(aet)(en)_2\}_2]^{5+}$.[2a,3b] However, in $\Delta\Lambda$-$[\mathbf{1}]^{2+}$ the two $[Co(aet)(en)_2]^{2+}$ units adopt the Δ and Λ configuration to give a *meso* form, which is distinct from a *racemic* form ($\Delta\Delta/\Lambda\Lambda$) found in $[Ag\{Co(aet)(en)_2\}_2]^{5+}$. The distance between each S atom and the central metal in $\Delta\Lambda$-$[\mathbf{1}]^{2+}$ (Cd–S = 2.716(1) Å) is much longer than that in $[Ag\{Co(aet)(en)_2\}_2]^{5+}$ (Ag–S = 2.400(1) Å),[3b] indicative of the weak coordination of thiolato groups toward Cd^{II}. Of note is the presence of intramolecular hydrogen bonds between each of two Cl atoms (Cl2, Cl2′) and two en amine groups in $\Delta\Lambda$-$[\mathbf{1}]^{2+}$,[8,10] which would compensate for the weak Cd–S bonds so as to sustain the $Co^{III}Cd^{II}Co^{III}$ structure. In addition, each of the two remaining Cl atoms (Cl1, Cl1′) forms an intermolecular hydrogen bond with an en amine group belonging to the adjacent $Co^{III}Cd^{II}Co^{III}$ cation, constructing a 2D grid-like structure (Figure 1b).

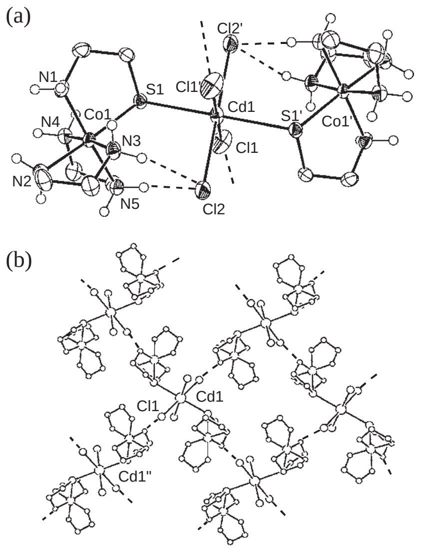

Figure 1. Perspective view of $\Delta\Lambda$-$[\mathbf{1}]^{2+}$. Selected bond distances (Å): Co1–S1 = 2.251(2), Cd1–S1 = 2.716(1), Cd1–Cl1 = 2.624(2), Cd1–Cl2 = 2.669(2). NH···Cl distances (Å): N3–Cl2 = 3.259(5), N5–Cl2 = 3.359(5), N1′–Cl1 = 3.216(5).

A similar 2:1 reaction of the optically active Λ-$[Co(aet)(en)_2](ClO_4)_2$[6b] with $CdCl_2 \cdot 2.5H_2O$ in water also produced dark brown crystals (ΛΛ-$[\mathbf{2}]Cl_{0.5}(ClO_4)_{0.5}$).[11] However, its elemental analytical data do not match with the formula of the 2:1 adduct, but with that of the 2:2 adduct $[Co(aet)(en)_2]_2[CdCl_2]_2Cl_{3.5}(ClO_4)_{0.5}$. X-ray structural analysis established that the complex cation ΛΛ-$[\mathbf{2}]^+$ has a unique $Co^{III}Cd^{II}{}_2Co^{III}$ tetranuclear structure composed of two Λ-$[Co(aet)(en)_2]^{2+}$ units and a $[Cd_2Cl_7]^{3-}$ moiety (Figure 2).[12] In ΛΛ-$[\mathbf{2}]^+$ the two Λ-$[Co(aet)(en)_2]^{2+}$ units are linked by a $[CdCl_4]^{2-}$ unit to form an S-bridged $Co^{III}Cd^{II}Co^{III}$ trinuclear moiety, to which a $[CdCl_3]^-$ fragment is attached through two Cl-bridges (Cl3, Cl4). While the S-bridged $Co^{III}Cd^{II}Co^{III}$ moiety in ΛΛ-$[\mathbf{2}]^+$ corresponds well with the trinuclear structure of ΔΛ-$[\mathbf{1}]^{2+}$, the Cd–S bond distances (average 2.623(1) Å) in ΛΛ-$[\mathbf{2}]^+$ are shorter than those in ΔΛ-$[\mathbf{1}]^{2+}$, which would be related to the elongated Cd1–Cl3 and Cd1–Cl4 bonds (average 2.790(2) Å) owing to the bridging with Cd2 atom. The coordination geometry about Cd2 atom appears to be a square-pyramid with five Cl donors, but its apical site contacts with the thiolato group (Cd2···S1 = 3.072(2) Å). In ΛΛ-$[\mathbf{2}]^+$ there exist two sets of intramolecular hydrogen bonds between two Cl atoms (Cl1, Cl4) and en amine groups, which are similar to that found in ΔΛ-$[\mathbf{1}]^{2+}$. However, ΛΛ-$[\mathbf{2}]^+$ possesses an intermolecular NH···Cl hydrogen bonding interaction quite different from that in ΔΛ-$[\mathbf{1}]^{2+}$. That is, one Cl atom (Cl3) bound to Cd1 atom is not participated in the hydrogen bonding interaction. Instead, two Cl atoms (Cl5, Cl7) bound to Cd2 atom, as well as Cl2 atom bound to Cd1 atom, form NH···Cl intermolecular hydrogen bonds, such that each $Co^{III}Cd^{II}{}_2Co^{III}$ cation is connected with the four adjacent cations to construct a 3D hydrogen bonding network structure.

In summary, it was found that the 2:1 reaction of Δ/Λ-$[Co(aet)(en)_2]^{2+}$ with Cd^{II} in the presence of excess Cl^- affords an S-bridged $Co^{III}Cd^{II}Co^{III}$ trinuclear complex (ΔΛ-$[\mathbf{1}]^{2+}$), consistent with the reaction stoichiometry. This result first demonstrates that a single thiolato group bound to a Co^{III} center does coordinate to Cd^{II} assisted by the introduction of appropriate co-ligands. Interestingly, the corresponding 2:1 reaction using Λ-$[Co(aet)(en)_2]^{2+}$ did not produce a $Co^{III}Cd^{II}Co^{III}$ trinuclear complex, but led to the crystallization of a $Co^{III}Cd^{II}{}_2Co^{III}$ tetranuclear complex (ΛΛ-$[\mathbf{2}]^+$). Here, it should be noted that ΔΛ-$[\mathbf{1}]^{2+}$ or ΛΛ-$[\mathbf{2}]^+$ was also produced, even when Δ/Λ- or Λ-$[Co(aet)(en)_2]^{2+}$ was reacted with Cd^{II} in a 1:1 ratio. Thus, the polynuclear structures derived from $[Co(aet)(en)_2]^{2+}$ and Cd^{II} are remarkably dependent on the chirality of the Co^{III} units, rather than the reaction stoichiometry. Since ΔΛ-$[\mathbf{1}]^{2+}$ and ΛΛ-$[\mathbf{2}]^+$ have similar intramolecular NH···Cl hydrogen bonds, the formation of a favorable intermolecular NH···Cl hydrogen bonding network, which is highly affected by the chiral configuration of the Co^{III} units, would play an essential role in the determination of $Co^{III}Cd^{II}$ polynuclear structures constructed.

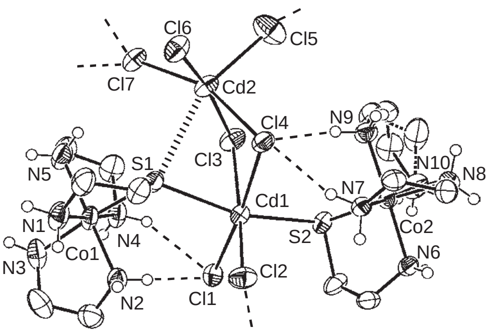

Figure 2. Perspective view of ΛΛ-$[\mathbf{2}]^+$. Selected bond distances (Å): Co1–S1 = 2.267(2), Co2–S2 = 2.256(2), Cd1–S1 = 2.656(1), Cd1–S2 = 2.589(1), Cd1–Cl1 = 2.639(2), Cd1–Cl2 = 2.563(2), Cd1–Cl3 = 2.843(2), Cd1–Cl4 = 2.737(2), Cd2–Cl3 = 2.703(2), Cd2–Cl4 = 2.638(1), Cd2–Cl5 = 2.517(2), Cd2–Cl6 = 2.581(2), Cd2–Cl7 = 2.520(1). NH···Cl distances (Å): N2–Cl1 = 3.278(5), N4–Cl1 = 3.374(5), N7–Cl4 = 3.219(4), N9–Cl4 = 3.376(5), N3′–Cl5 = 3.114(6), N2′–Cl2 = 3.276(5), N7′–Cl7 = 3.248(4), N1′–Cl7 = 3.275(5).

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7 Anal. Calcd for $[\mathbf{1}](ClO_4)_2$: C, 14,96; H, 4.60; N, 14.53%. Found: C, 14.85, H, 4.35; N, 14.51%. Yield: 53%.

8 Crystal data for ΔΛ-$[\mathbf{1}](ClO_4)_2$: fw = 481.8, monoclinic, $P2_1/n$, $a = 8.555(1)$, $b = 13.882(1)$, $c = 13.567(1)$ Å, $\beta = 96.04(1)°$, $V = 1602.1(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.997$ g cm^{-3}, $R = 0.043$ for 4661 reflections with $I > 2.0\sigma(I)$.

9 Octahedral Cd^{II} species with thiolato donors are quite rare; only two structurally characterized compounds (Cd–S = 2.46–2.72 Å) have been reported. I. G. Dance, R. G. Garbutt, and D. C. Craig, *Aust. J. Chem.*, **39**, 1449 (1986); I. Casals, P. González-Duarte, W. Clegg, C. Forces-Forces, F. H. Cano, M. Martíbez-Ripoll, M. Gómez, and X. Solans, *J. Chem. Soc., Dalton Trans.*, **1991**, 2511.

10 It has been shown that the averaged distance for 314 examples of NH_2···Cl hydrogen bonds is 3.299(6) Å. T. Steiner, *Acta Crystallogr., Sect. B*, **54**, 456 (1998).

11 Anal. Calcd for $[\mathbf{2}]Cl_{0.5}(ClO_4)_{0.5} \cdot 1.5H_2O$: C, 13.37; H, 4.39; N, 12.99%. Found: C, 13.36, H, 4.39; N, 12.77%. Yield: 85% (based on Cd). The absorption spectral curve of **2** in the solid state is very similar to that of **1**, showing an absorption peak at 497 nm.

12 Crystal data for ΛΛ-$[\mathbf{2}]Cl_{0.5}(ClO_4)_{0.5} \cdot H_2O$: fw = 1069.0, trigonal, $P3_221$, $a = 14.195(2)$, $c = 31.337(3)$ Å, $V = 5468(1)$ Å^3, $Z = 6$, $D_{calcd} = 1.951$ g cm^{-3}, $R = 0.038$ for 10612 reflections with $I > 2.0\sigma(I)$.

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