Stereoselective Preparation and Crystal Structures of $\Delta\Lambda$- and $\Delta\Delta$-[Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$ (aet = 2-Aminoethanethiolate): Conversion of a Racemic Co^{III}Hg^{II} Dinuclear to an Optically Active Co^{III}Hg^{II}Co^{III} Trinuclear Structure

Takumi Konno,* Hirokazu Honda, Yu Chikamoto, Tatsuya Kawamoto, Takashi Yoshimura,† and Masakazu Hirotsu†
Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043
†*Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376-8515*

(Received January 29, 2002; CL-020111)

The reaction of [HgBr$_2${Co(aet)$_2$(en)}]$^+$ with [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ selectively gave the *meso* isomer of an S-bridged Co^{III}Hg^{II}Co^{III} trinuclear complex, $\Delta\Lambda$-[Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$ ($\Delta\Lambda$-[**1**]$^{4+}$), while the optically active $\Delta\Delta$ isomer of [**1**]$^{4+}$ was produced by the corresponding reaction with *trans(N)*-[Co(D-pen-*N*, *O*, *S*)$_2$]$^-$.

Chirality is a fascinating subject in coordination chemistry, as well as in organic chemistry. However, progress in the field of chiral selective synthesis of polynuclear metal complexes is rather slow. Our research interest has been directed toward this subject, based on the linkage of bis(thiolato)-type *cis(S)*-[Co(aet)$_2$(en)]$^+$ octahedral units (aet = 2-aminoethanethiolate) with certain metal ion.[1–5] Previously, we have reported that the two *cis(S)*-[Co(aet)$_2$(en)]$^+$ units are linked by square-planar Ni^{II} or Pd^{II}, trigonal-bipyramidal Cd^{II}, and linear Au^I to form S-bridged polynuclear structures in [Ni^{II} or Pd^{II}{Co(aet)$_2$(en)}$_2$]$^{4+}$,[1,3] [CdCl{Co(aet)$_2$(en)}$_2$]$^{3+}$,[2] and [Au$_2${Co(aet)$_2$(en)}$_2$]$^{4+}$,[5] respectively. In these polynuclear complexes, the two *cis(S)*-[Co(aet)$_2$(en)]$^+$ units are regulated to have the same configuration to give only the racemic isomer ($\Delta\Delta/\Lambda\Lambda$). This chiral behavior is distinct from the fact that [M{Co(aet)$_3$}$_2$]$^{3+}$ (M = Co^{III}, Fe^{III}) composed of two tris(thiolato)-type *fac(S)*-[Co(aet)$_3$] units afford both the *racemic* and *meso* ($\Delta\Lambda$) isomers.[6] In order to clarify the effect of linking metal ion on the chiral selective aggregation of the *cis(S)*-[Co(aet)$_2$(en)]$^+$ units, we investigated the structures and properties of S-bridged polynuclear complexes of this class, introducing Hg^{II} which prefers to take a tetrahedral geometry. As a result, we found that only the *meso* isomer of an S-bridged Co^{III}Hg^{II}Co^{III} trinuclear complex, $\Delta\Lambda$-[Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$ ($\Delta\Lambda$-[**1**]$^{4+}$), is produced by the reaction of the newly prepared Co^{III}Hg^{II} dinuclear complex, [HgBr$_2${Co(aet)$_2$(en)}]$^+$,[7] with [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ which has shown to act as a donor of the *cis(S)*-[Co(aet)$_2$(en)]$^+$ unit.[1–3] To our surprise, however, treatment of [HgBr$_2${Co(aet)$_2$(en)}]$^+$ with the bis(thiolato)-type *trans(N)*-[Co(D-pen-*N*, *O*, *S*)$_2$]$^-$ [8] (D-pen = D-penicillaminate) resulted in the formation of an optically active $\Delta\Delta$ isomer of [Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$ ($\Delta\Delta$-[**1**]$^{4+}$), showing the chiral conversion of the racemic (Δ/Λ) to Δ configuration for *cis(S)*-[Co(aet)$_2$(en)]$^+$. Here we report the preparation and structural characterization of $\Delta\Lambda$- and $\Delta\Delta$-[**1**]$^{4+}$.

Treatment of [HgBr$_2${Co(aet)$_2$(en)}]Br[7] with [Ni{Co(aet)$_2$(en)}$_2$]Cl$_4$·6H$_2$O[1] in a 1 : 0.5 ratio in water (60 °C, 1 h) gave a dark brown solution, from which dark red-brown crystals ($\Delta\Lambda$-[**1**]Br$_3$Cl·4H$_2$O) were isolated in 81% yield.[9] The plasma emission analysis indicated that $\Delta\Lambda$-[**1**]$^{4+}$ contains Co and Hg atoms in a 2 : 1 ratio and its elemental analysis is in good agreement with the formula for the 2 : 1 adduct of [Co(aet)$_2$(en)]$^+$ and Hg^{II}. In the ^{13}C NMR spectrum, $\Delta\Lambda$-[**1**]$^{4+}$ gives only three sharp signals due to three kinds of methylene groups,[9] suggesting the existence of one isomer. The molecular structure of $\Delta\Lambda$-[**1**]$^{4+}$ was determined by X-ray analysis for its ClO$_4^-$ salt ($\Delta\Lambda$-[**1**](ClO$_4$)$_4$·4H$_2$O).[10] As shown in Figure 1, the complex cation consists of two octahedral C_2-*cis(S)*-[Co(aet)$_2$(en)]$^+$ units that are linked by one Hg^{II} atom, forming a linear-type S-bridged trinuclear structure in [Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$ (Co1–Hg1–Co2 = 176.00(5) °). The central Hg^{II} atom is coordinated by four thiolato S atoms from two terminal C_2-*cis(S)*-[Co(aet)$_2$(en)]$^+$ units to adopt an approximately tetrahedral geometry. This S-bridged trinuclear structure corresponds well with the MHg^{II}M structure in [Hg{M(L-*N*, *N*, *S*)$_2$}$_2$]$^{2+}$ composed of two octahedral *mer*-[M(L-*N*, *N*, *S*)$_2$] units (M = Fe^{II}, Ni^{II}; L = 2-[(3-aminopropyl)amino]ethanethiolate).[11] The Hg–S bond distances (2.521(4) Å –2.591(4) Å) in $\Delta\Lambda$-[**1**]$^{4+}$ are within the range normally observed for tetrahedral Hg^{II}S$_4$ spheres.[11,12] In $\Delta\Lambda$-[**1**]$^{4+}$, the two C_2-*cis(S)*-[Co(aet)$_2$(en)]$^+$ units have the Δ and Λ configurations to form the *meso* isomer. This is in wholly contrast to the fact that the corresponding trinuclear complexes, [Ni^{II} or Pd^{II}{Co(aet)$_2$(en)}$_2$]$^{4+}$, in which the two C_2-*cis(S)*-[Co(aet)$_2$(en)]$^+$ units are linked by square-planar Ni^{II} or Pd^{II}, selectively produce the *racemic* isomer.[1,3] Molecular model examinations reveal that in the *racemic* isomer of this linear-type Co^{III}Hg^{II}Co^{III} structure there exists a steric repulsion between the SCH$_2$ methylene groups of the two C_2-*cis(S)*-[Co(aet)$_2$(en)]$^+$ units.

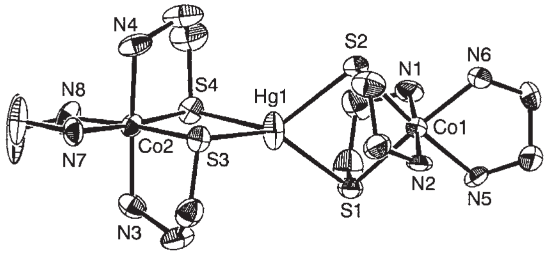

Figure 1. A perspective view of $\Delta\Lambda$-[**1**]$^{4+}$. Selected bond distances (Å) and angles (°): Hg1–S1 = 2.521(4), Hg1–S2 = 2.591(4), Hg1–S3 = 2.548(4), Hg1–S4 = 2.571(4), Co1–S1 = 2.250(4), Co1–S2 = 2.254(4), Co2–S3 = 2.261(4), Co2–S4 = 2.266(4), S1–Hg1–S2 = 80.8(1), S3–Hg1–S4 = 81.7(1), S1–Co1–S2 = 94.7(2), S3–Co2–S4 = 95.4(1).

A similar reaction of [HgBr$_2${Co(aet)$_2$(en)}]Br with *trans(N)*-K[Co(D-pen-*N*, *O*, *S*)$_2$]·2H$_2$O[8] having the Λ_D configuration (60 °C, 1 h) was carried out, expecting the formation of [Hg{Co(D-pen-*N*, *O*, *S*)$_2$}{Co(aet)$_2$(en)}]$^{2+}$, in which Hg^{II} is bound by *cis(S)*-[Co(aet)$_2$(en)]$^+$ and *trans(N)*-[Co(D-pen-*N*, *O*, *S*)$_2$]$^-$ units. However, the cation-exchange column chromatography of the reaction solution indicated that the desired divalent species were little formed. Instead, the formation of $[\mathbf{1}]^{4+}$ and $\Lambda_D\Lambda_D$-[Hg{Co(D-pen-$N,O,S)_2\}_2]^0$ was recognized.[13] Interestingly, $[\mathbf{1}]^{4+}$ thus obtained was CD active, showing a negative CD value at 530 nm. Furthermore, the ^{13}C NMR spectrum of $[\mathbf{1}]^{4+}$ exhibited additional signals, besides the three signals for $\Delta\Lambda$-$[\mathbf{1}]^{4+}$.[13] An optically pure $(-)^{CD}_{530}$ isomer of $[\mathbf{1}]^{4+}$, which shows only three ^{13}C NMR signals, was obtained by elongation of the reaction time to ca. 1.5 h,[14] although the yield was decreased because of the decomposition to other polynuclear species. The crystal structure of $(-)^{CD}_{530}$-$[\mathbf{1}]Cl_4{\cdot}4H_2O$ was established by X-ray analysis,[14] which demonstrated that $(-)^{CD}_{530}$-$[\mathbf{1}]^{4+}$ is an S-bridged $Co^{III}Hg^{II}Co^{III}$ complex composed of two C_2-*cis(S)*-$[Co(aet)_2(en)]^+$ units with the Δ configuration. As shown in Figure 2, the central Hg^{II} atom is situated in an environment markedly distorted from tetrahedral geometry, having two short (2.488(5) Å) and two long (2.772(6) Å) Hg–S bonds. In addition, one of Cl^- anions contacts with the Hg^{II} atom with a distance of 3.007(7) Å. Thus, the coordination geometry of the Hg^{II} atom in $\Delta\Delta$-$[\mathbf{1}]^{4+}$ may be regarded as a distorted trigonal-bipyramid with the S1 and S1′ atoms at apical positions (S1–Hg1–S1′ = 169.7(2)°, CL1–Hg1–S2 = 119.2(2)°, S2–Hg1–S2′ = 121.5(2)°), like the geometry of the Cd^{II} atom in $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$.[2] It is noticed that the trinuclear structure in $\Delta\Delta$-$[\mathbf{1}]^{4+}$ deviates significantly from linearity (Co1–Hg1–Co1′ = 144.9(1)°), which effectively decreases the steric repulsion between the two Δ configurational C_2-*cis(S)*-$[Co(aet)_2(en)]^+$ units.

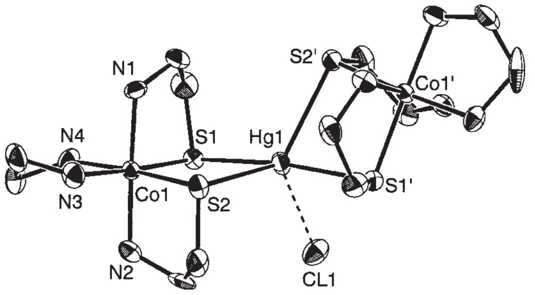

Figure 2. A perspective view of $\Delta\Delta$-$[\mathbf{1}]^{4+}$. One of Cl^- anions contacting with Hg^{II} is included. Selected bond distances (Å) and angles (°): Hg1–S1 = 2.488(5), Hg1–S2 = 2.772(6), Co1–S1 = 2.251(6), Co1–S2 = 2.256(6), S1–Hg1–S2 = 76.9(2), S1–Co1–S2 = 93.4(2).

In summary, it was found in this study that the replacement of the two Br atoms in $[HgBr_2\{Co(aet)_2(en)\}]^+$ by the two S atoms in C_2-*cis(S)*-$[Co(aet)_2(en)]^+$ produces the *meso* isomer of $[Hg\{Co(aet)_2(en)\}_2]^{4+}$ ($\Delta\Lambda$-$[\mathbf{1}]^{4+}$), in which the two C_2-*cis(S)*-$[Co(aet)_2(en)]^+$ units are linked by tetrahedral Hg^{II}. This result, together with the stereoselective formation of the *racemic* ($\Delta\Delta/\Lambda\Lambda$) isomer for [Ni or Pd$\{Co(aet)_2(en)\}_2]^{4+}$, indicates that the chirality of this class complexes can be controlled by the choice of the linking metal ion. Despite the stereoselective formation of the *meso* isomer for the reaction of $[HgBr_2\{Co(aet)_2(en)\}]^+$ with $[Ni\{Co(aet)_2(en)\}_2]^{4+}$, the optically active $\Delta\Delta$-$[\mathbf{1}]^{4+}$ was obtained by the corresponding reaction with *trans(N)*-[Co(D-pen-$N,O,S)_2]^-$.[15] Thus, the *racemic* (Δ/Λ) C_2-*cis(S)*-$[Co(aet)_2(en)]^+$ unit converted at least in part to the Δ form, representing a quite rare example of chiral amplification for polynuclear systems.

References and Notes

1 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).

2 T. Konno and K. Okamoto, *Chem. Lett.*, **1996**, 975; T. Konno, K. Tokuda, J. Sakurai, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **73**, 2767 (2000).

3 T. Konno, T. Machida, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **71**, 175 (1998).

4 T. Konno, N. Matsuno, K. Okamoto, and M. Hirotsu, *Chem. Lett.*, **1999**, 1243.

5 T. Konno, M. Hattori, T. Yoshimura, and M. Hirotsu, *Chem. Lett.*, **2002**, 230.

6 G. R. Brubaker and B. E. Douglas, *Inorg. Chem.*, **6**, 1562 (1967); R. E. DeSimone, T. Ontko, L. Wardman, and E. L. Blinn, *Inorg. Chem.*, **14**, 1313 (1975); T. Tokuda, Ph. D. Thesis, Gunma University, Gunma, Japan, 2000.

7 $[HgBr_2\{Co(aet)_2(en)\}]Br$ was prepared by the 1 : 2 reaction of $[Ni\{Co(aet)_2(en)\}_2]Br_4{\cdot}6H_2O$ with $HgBr_2$ in water. The $Co^{III}Hg^{II}$ dinuclear structure, in which Hg^{II} atom is tetrahedrally coordinated by two S atoms from one C_2-*cis(S)*-$[Co(aet)_2(en)]^+$ units and two Br atoms, was confirmed by X-ray analysis. Crystal Data: fw = 711.6, monoclinic, $C2/c$, $a = 25.202(5)$ Å, $b = 9.550(4)$ Å, $c = 14.262(3)$ Å, $\beta = 98.55(2)°$, $V = 3394(1)$ Å^3, $Z = 8$, $D_c = 2.79$ g cm^{-3}, $R(R_w) = 0.063$ (0.060) for 2239 reflections with $I > 1.9\sigma(I)$.

8 K. Okamoto, K. Wakayama, H. Einaga, S. Yamada, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **56**, 165 (1983). In *trans(N)*-[Co(D-pen-$N,O,S)_2]^-$, the skew pair of two N,S-chelate rings adopts the Λ configuration.[4]

9 Anal. Calcd for $[\mathbf{1}]Br_3Cl{\cdot}4H_2O$: C, 13.21; H, 4.43; N, 10.28%. Found: C, 13.02; H, 4.38; N, 10.25%. Visible-UV spectrum in H_2O [σ_{max}, 10^3 cm^{-1} (log ε, mol^{-1} dm^3 cm^{-1})]: 20.5 (2.9)^{sh}, 22.83 (3.04), 33.5 (4.1)^{sh}, 37.88 (4.78). ^{13}C NMR spectrum in D_2O (δ, ppm from DSS): 35.42 (CH_2S), 47.59 (CH_2NH_2 of en), 54.77 (CH_2NH_2 of aet).

10 Anal. Calcd for $[\mathbf{1}](ClO_4)_4{\cdot}4H_2O$: C, 11.88; H, 3.99; N, 9.23%. Found: C, 11.63; H, 4.01; N, 8.92%. Crystal Data: fw = 1213.1, monoclinic, $P2_1/n$, $a = 16.052(3)$ Å, $b = 13.362(3)$ Å, $c = 19.708(3)$ Å, $\beta = 111.75(1)°$, $V = 3926(1)$ Å^3, $Z = 4$, $D_c = 2.05$ g cm^{-3}, $R(R_w) = 0.058$ (0.057) for 3219 reflections with $I > 2.0\sigma(I)$.

11 M. Mikuriya, H. Tsutsumi, M. Handa, and Y. Sayama, *Bull. Chem. Soc. Jpn.*, **69**, 3489 (1996).

12 G. A. Bowmaker, I. G. Dance, B. C. Dobson, and D. A. Rogers, *Aust. J. Chem.*, **37**, 1607 (1984); N. Govindaswamy, J. Moy, M. Millar, and S. A. Koch, *Inorg. Chem.*, **31**, 5343 (1992); A. Silver, S. A. Koch, and M. Millar, *Inorg. Chim. Acta*, **205**, 9 (1993).

13 When the reaction solution was chromatographed on an SP-Sephadex C-25 column, a brown band containing $\Lambda_D\Lambda_D$-[Hg{Co(D-pen-$N,O,S)_2\}_2]^0$ and a red-brown band containing $[\mathbf{1}]^{4+}$ were eluted with water and a 0.5 mol dm^{-3} aqueous solution of NaCl, respectively. It was found from the absorption and CD spectral measurements that $[\mathbf{1}]^{4+}$ was formed in more than 90% yield (based on C_2-*cis(S)*-$[Co(aet)_2(en)]^+$ unit) having a ratio of $\Delta : \Lambda$ = ca. 7 : 3. ^{13}C NMR spectrum in D_2O (δ, ppm from DSS): 35.35 and 35.47 (CH_2S), 47.59 (CH_2NH_2 of en), 54.71 and 54.81 (CH_2NH_2 of aet).

14 The column chromatography showed that $\Delta\Delta$-$[\mathbf{1}]^{4+}$ was formed in less than 40% yield. Anal. Calcd for $[\mathbf{1}]Cl_4{\cdot}4H_2O$: C, 15.06; H, 5.06; N, 11.71%. Found: C, 15.17; H, 5.01; N, 11.45%. Visible-UV spectrum in H_2O [σ_{max}, 10^3 cm^{-1} (log ε, mol^{-1} dm^3 cm^{-1})]: 20.3 (2.8)^{sh}, 22.59 (2.92), 33.1 (4.2)^{sh}, 37.76 (4.76). CD spectrum in H_2O [σ_{max}, 10^3 cm^{-1} ($\Delta\varepsilon$, mol^{-1} dm^3 cm^{-1})]: 18.87 (−6.8), 21.93 (+10.3), 27.03 (−6.8), 33.11 (−49.0), 37.59 (+200.5). ^{13}C NMR spectrum in D_2O (δ, ppm from DSS): 35.76 (CH_2S), 47.59 (CH_2NH_2 of en), 54.62 (CH_2NH_2 of aet). Crystal Data: fw = 957.1, orthorhombic, $C222_1$, $a = 12.137(4)$ Å, $b = 12.351(5)$ Å, $c = 21.505(8)$ Å, $V = 3224(2)$ Å^3, $Z = 4$, $D_c = 1.97$ g cm^{-3}, $R(R_w) = 0.052$ (0.069) for 1984 reflections with $I > 2.0\sigma(I)$. The absolute configuration was determined to be $\Delta\Delta$ by the η parameter (1.04), and this absolute structure was supported by the CD spectral pattern which is similar to that of $\Delta\Delta$-[Ni or Pd$\{Co(aet)_2(en)\}_2]^{4+}$.[1,3]

15 The mechanism of this reaction may be explained by the equilibrium between Δ- and Λ-$[Co(aet)_2(en)]^+$ units and the predominant formation of the quasi-meso isomer ($\Lambda_D\Delta$) of [Hg{Co(D-pen-$N,O,S)_2\}\{Co(aet)_2(en)\}]^{2+}$, which is subject to disproportionation to $\Lambda_D\Lambda_D$-[Hg{Co(D-pen-$N,O,S)_2\}_2]^0$ and $\Delta\Delta$-$[\mathbf{1}]^{4+}$.