Chiral-Selective Formation of S-Bridged $\mathrm{Co^{III}Pd^{II}Co^{III}}$ Trinuclear Complexes by Using *trans*(*N*)-$[\mathrm{Co(D\text{-}pen\text{-}}N,O,S)_2]^-$ as a Bidentate-*S*,*S* Complexed-Ligand (D-pen = D-Penicillaminate)

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The reaction of $[\mathrm{PdCl_2\{Co(aet)_2(en)\}}]^+$ (aet = 2-aminoethanethiolate) with *trans(N)*-$[\mathrm{Co(D\text{-}pen\text{-}}N,O,S)_2]^-$ (D-pen = D-penicillaminate) in water led to the formation of three optically active S-bridged $\mathrm{Co^{III}Pd^{II}Co^{III}}$ complexes, $[\mathrm{Pd\{Co(D\text{-}pen\text{-}}N,O,S)_2\}_2]^0$ (**1**), Λ-$[\mathrm{Pd\{Co(D\text{-}pen\text{-}}N,O,S)_2\}\{\mathrm{Co(aet)_2(en)}\}]^{2+}$ (Λ-**2**), and ΔΔ-$[\mathrm{Pd\{Co(aet)_2(en)\}_2}]^{4+}$ (ΔΔ-**3**). The molecular structure of Λ-**2** was determined by X-ray crystallography.

Since the discovery of an S-bridged $\mathrm{Co^{III}Ni^{II}Co^{III}}$ trinuclear complex with two C_2-*cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ units, $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$, which is readily formed from $[\mathrm{CoCl_2(en)_2}]^+$ and $[\mathrm{Ni(aet)_2}]$ in water,[1] our research interest has been directed toward S-bridged polynuclear complexes composed of bis(thiolato)cobalt(III) octahedral units. Recently, we have found that the reaction of $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$ with $[\mathrm{PdCl_4}]^{2-}$ in a ratio of 1:1 gives an S-bridged $\mathrm{Co^{III}Pd^{II}Co^{III}}$ trinuclear complex $[\mathrm{Pd\{Co(aet)_2(en)\}_2}]^{4+}$, while the corresponding 1:2 reaction produces an S-bridged $\mathrm{Co^{III}Pd^{II}}$ dinuclear complex $[\mathrm{PdCl_2\{Co(aet)_2(en)\}}]^+$.[2] Furthermore, $[\mathrm{PdCl_2\{Co(aet)_2(en)\}}]^+$ was found to be convertible to $[\mathrm{Pd\{Co(aet)_2(en)\}_2}]^{4+}$ by reacting with $[\mathrm{Ni\{Co(aet)_2(en)\}_2}]^{4+}$, which acts as a donor of the *cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ unit.[2] A remarkable feature of the trinuclear structure in $[\mathrm{M\{Co(aet)_2(en)\}_2}]^{4+}$ (M = $\mathrm{Ni^{II}}$, $\mathrm{Pd^{II}}$) is the selective formation of the ΔΔ and ΛΛ isomers, which is in contrast to the fact that all three possible isomers (ΔΔ, ΛΛ, and ΔΛ) are formed for the S-bridged trinuclear structure in $[\mathrm{M'\{Co(aet)_3\}_2}]^{2+\text{ or }3+}$ (M' = $\mathrm{Ni^{II}}$, $\mathrm{Co^{III}}$).[3] Thus, it is expected that either Δ- or Λ-$[\mathrm{PdCl_2\{Co(aet)_2(en)\}}]^+$ is selectively incorporated in the S-bridged $\mathrm{Co^{III}Pd^{II}Co^{III}}$ trinuclear structure by the reaction with some chiral bis(thiolato)cobalt(III) complex. In this paper, we wish to report that the reaction of $[\mathrm{PdCl_2\{Co(aet)_2(en)\}}]^+$ with *trans(N)*-$[\mathrm{Co(D\text{-}pen\text{-}}N,O,S)_2]^-$ [4] leads not only to the chiral-selective formation of Λ-$[\mathrm{Pd\{Co(D\text{-}pen\text{-}}N,O,S)_2\}\{\mathrm{Co(aet)_2(en)}\}]^{2+}$, but also to the production of ΔΔ-$[\mathrm{Pd\{Co(aet)_2(en)\}_2}]^{4+}$ and $[\mathrm{Pd\{Co(D\text{-}pen\text{-}}N,O,S)_2\}_2]^0$.

Treatment of $[\mathrm{PdCl_2\{Co(aet)_2(en)\}}]\mathrm{Cl\cdot 2H_2O}$ [2] with equimolar of *trans(N)*-$\mathrm{K}[\mathrm{Co(D\text{-}pen\text{-}}N,O,S)_2]\cdot\mathrm{2H_2O}$ [4] in water at 50 °C gave a deep brown solution, which was poured onto an SP-Sephadex C-25 column ($\mathrm{Na^+}$ form). Three bands, A-1 (yellow-green), A-2 (brown), and A-3 (red-brown), were eluted with water, a 0.3 mol $\mathrm{dm^{-3}}$ aqueous solution of NaCl, and a 0.5 mol $\mathrm{dm^{-3}}$ aqueous solution of NaCl, respectively. The formation ratio was ca. A-1:A-2:A-3 = 1:2:1, which was estimated from the electronic absorption spectral data. The electronic absorption and CD spectra of the A-3 eluate were identical with those of ΔΔ-$[\mathrm{Pd\{Co(aet)_2(en)\}_2}]^{4+}$ (ΔΔ-**3**) having a D_2 symmetrical S-bridged trinuclear structure,[2] and the elemental analytical data of the isolated brown complex were in good agreement with the formula of $[\mathrm{Pd\{Co(aet)_2(en)\}_2}]\mathrm{Cl_4\cdot 6H_2O}$.[5] These results indicate that the A-3 eluate contained only the ΔΔ isomer of $[\mathrm{Pd\{Co(aet)_2(en)\}_2}]^{4+}$.

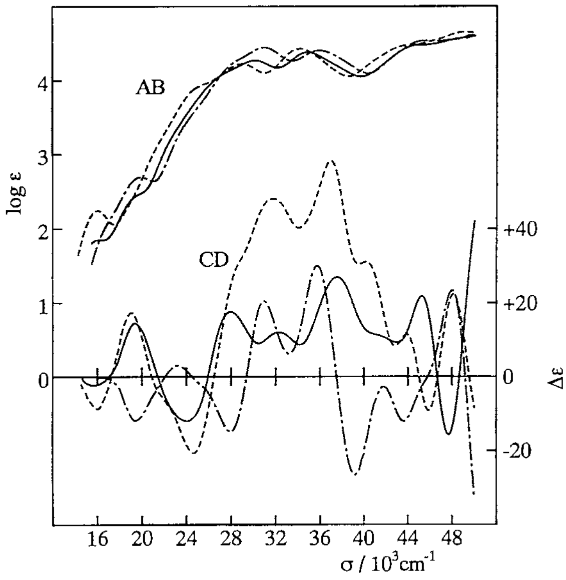

Figure 1. Electronic absorption and CD spectra of **1** (---), Λ-**2** (—), and ΔΔ-**3** (-·-) in water.

As illustrated in Figure 1, the absorption spectral behavior of the A-2 eluate is very similar to that of **3** over the whole region. In the ^{13}C NMR spectrum the brown complex (Λ-$\mathbf{2}\mathrm{Cl_2\cdot 5H_2O}$), which was isolated from the A-2 eluate, exhibits five signals besides three signals which coincide well with three signals observed for **3**.[6] From these facts and elemental analysis,[6] it is assumed that **2** has an S-bridged $\mathrm{Co^{III}Pd^{II}Co^{III}}$ trinuclear structure in $[\mathrm{Pd\{Co(D\text{-}pen\text{-}}N,O,S)_2\}\{\mathrm{Co(aet)_2(en)}\}]^{2+}$ having a C_2 symmetry. The CD spectrum of the A-2 eluate is almost enantiomeric to that of ΔΔ-**3**, except the region of 30 – 38 × 10^3 $\mathrm{cm^{-1}}$ (Figure 1), which suggests that the A-2 eluate contained only the Λ isomer of **2**.

The molecular structure and absolute configuration for Λ-**2** were established by a single-crystal X-ray analysis of the $\mathrm{PF_6^-}$ salt.[7] The number of the $\mathrm{PF_6^-}$ anions implies that the complex cation **2** is divalent. As shown in Figure 2, the complex cation **2** consists of C_2-*cis(S)*-$[\mathrm{Co(aet)_2(en)}]^+$ and *trans(N)*-$[\mathrm{Co(D\text{-}pen\text{-}}N,O,S)_2]^-$ octahedral units and one $\mathrm{Pd^{II}}$ atom. The two thiolato S atoms of each octahedral unit are bound to the central $\mathrm{Pd^{II}}$ atom to form a linear-type S-bridged $\mathrm{Co^{III}Pd^{II}Co^{III}}$ trinuclear structure having a C_2 symmetry. While this S-bridged trinuclear structure corresponds well with that of $[\mathrm{Pd\{Co(aet)_2(en)\}_2}]^{4+}$,[2] the central $\mathrm{PdS_4}$ sphere in **2** is not so distorted from a square-planar to a tetrahedral geometry, compared with that in $[\mathrm{Pd\{Co(aet)_2(en)\}_2}]^{4+}$; the dihedral angle between the Pd1S1S2 and Pd1S3S4 planes in **2** (8.4°) is smaller than the corresponding angle in **3** (14.0°). The absolute

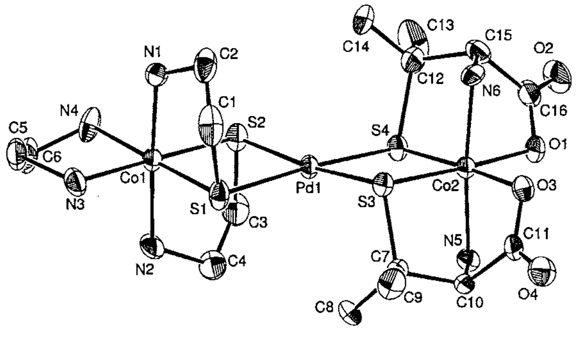

Figure 2. Perspective view of Λ-**2**. Selected bond distances (Å) and angles (°): Pd1-S1 = 2.329(3), Pd1-S2 = 2.331(4), Pd1-S3 = 2.335(3), Pd1-S4 = 2.317(3), Co1-S1 = 2.243(4), Co1-S2 = 2.263(4), Co1-N1 = 1.98(1), Co1-N2 = 2.01(1), Co1-N3 = 2.02(1), Co1-N4 = 2.02(1), Co2-S3 = 2.244(3), Co2-S4 = 2.228(4), Co2-O1 = 1.963(8), Co2-O3 = 1.957(9), Co2-N5 = 1.96(1), Co2-N6 = 1.97(1), S1-Pd1-S2 = 84.1(1), S3-Pd-S4 = 83.1(1), S1-Co1-S2 = 87.7(1), S3-Co2-S4 = 87.3(1).

configuration for the C_2-*cis(S)*-[Co(aet)$_2$(en)]$^+$ unit was determined to be Λ on the basis of the known *S* configuration of the asymmetric carbon atom in the D-pen ligand, and this absolute structure was supported by the Flack parameter (-0.0054(7)).[8] As can be seen from Figure 2, there exits little steric interaction between the Λ configurational C_2-*cis(S)*-[Co(aet)$_2$(en)]$^+$ unit and the *trans(N)*-[Co(D-pen-*N,O,S*)$_2$]$^-$ unit, in which the skew pair of the two five-membered *N,S*-chelate rings adopts the Λ configuration.

From the A-1 eluate, dark yellow-green complex (**1**·6H$_2$O) was isolated after passing through a QAE-Sephadex A-25 column (Cl$^-$ form) with water.[9] **1** is confidently assigned as a D_2 symmetrical trinuclear complex, [Pd{Co(D-pen-*N,O,S*)$_2$}$_2$]^0, in which the Pd^{II} atom is coordinated by four S atoms from two *trans(N)*-[Co(D-pen-*N,O,S*)$_2$]$^-$ units, by (i) elemental analysis, (ii) electronic absorption and CD spectroscopies, the spectral features of which coincide well with those of Λ-**2** (Figure 1), (iii) ^{13}C NMR spectroscopy which gives five signals, (iv) molar conductivity in water (1.5 Ω^{-1} cm^2 mol^{-1}), which is compatible with the non-electrolyte. **1** was also prepared by the reaction of *trans(N)*-K[Co(D-pen-*N,O,S*)$_2$]·2H$_2$O with Pd(NO$_3$)$_2$ in water, which supports this assignment.

In the present study, it was found that a novel S-bridged Co^{III}Pd^{II}Co^{III} trinuclear complex, [Pd{Co(D-pen-*N,O,S*)$_2$}-{Co(aet)$_2$(en)}]$^{2+}$ (**2**), is produced by the reaction of [PdCl$_2${Co(aet)$_2$(en)}]$^+$ with *trans(N)*-[Co(D-pen-*N,O,S*)$_2$]$^-$. This result clearly indicates that *trans(N)*-[Co(D-pen-*N,O,S*)$_2$]$^-$ functions as an effective bidentate-*S,S* complexed-ligand, which replaces the two Cl atoms in [PdCl$_2${Co(aet)$_2$(en)}]$^+$. Of two isomers (Δ and Λ) possible for **2**, only the Λ isomer was formed. To our knowledge, this is the first example of a chiral-selective formation of S-bridged polynuclear structure with use of a chiral complexed-ligand. Molecular model examinations reveal that a significant steric interaction comes into exist between the *N,S*-chelate rings of the C_2-*cis(S)*-[Co(aet)$_2$(en)]$^+$ and *trans(N)*-[Co(D-pen-*N,O,S*)$_2$]$^-$ units, when the C_2-*cis(S)*-[Co(aet)$_2$(en)]$^+$ unit adopts the Δ configuration. One may assume that Δ-[PdCl$_2${Co(aet)$_2$(en)}]$^+$ and excess *trans(N)*-[Co(D-pen-*N,O,S*)$_2$]$^-$ remain in solution. However, the reaction solution was found to contain little Δ-[PdCl$_2${Co(aet)$_2$(en)}]$^+$ and *trans(N)*-[Co(D-pen-*N,O,S*)$_2$]$^-$. Instead, the formation of [Pd{Co(D-pen-*N,O,S*)$_2$}$_2$]^0 (**1**) and ΔΔ-[Pd{Co(aet)$_2$(en)}$_2$]$^{4+}$ (ΔΔ-**3**), besides Λ-**2**, was recognized in a ratio of ca. **1**:Λ-**2**:ΔΔ-**3** = 1:2:1, which implies that metathesis occurs between Δ-[PdCl$_2$-{Co(aet)$_2$(en)}]$^+$ and *trans(N)*-[Co(D-pen-*N,O,S*)$_2$]$^-$ under relatively moderate conditions. Finally, it should be noted that the optical resolution of **3** has been achieved by fractional recrystallization with great difficulty.[2] On the other hand, the present procedure is straightforward and simple to afford ΔΔ-**3**. Thus, the use of *trans(N)*-[Co(D-pen-*N,O,S*)$_2$]$^-$ as a chiral complexed-ligand may be applicable for the preparation of a variety of optically active S-bridged polynuclear complexes.

References and Notes

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3 D. H. Busch and D. C. Jicha, *Inorg. Chem.*, **1**, 884 (1962); G. R. Brubaker and B. E. Douglas, *Inorg. Chem.*, **6**, 1562 (1967); T. Konno, K. Okamoto, and J. Hidaka, *Acta Crystallogr., Sect. C*, **49**, 222 (1993).

4 The *trans(N)* isomer of [Co(D-pen-*N,O,S*)$_2$]$^-$ has a *trans(N)·cis(O)·cis(S)* geometry. K. Okamoto, K. Wakayama, H. Einaga, S. Yamada, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **56**, 165 (1983).

5 Anal. Found: C, 15.78; H, 5.66; N, 12.20%. Calcd for [Pd{Co(aet)$_2$(en)}$_2$]Cl$_4$·6H$_2$O = C$_{12}$H$_{52}$Cl$_4$Co$_2$N$_8$O$_6$PdS$_4$: C, 16.03; H, 5.83; N, 12.47%. ^{13}C NMR spectrum in D$_2$O (δ, ppm from DSS): 35.6 (-CH$_2$S of aet), 46.6 (-CH$_2$N of en), 56.1 (-CH$_2$N of aet).

6 Anal. Found: C, 21.49; H, 5.23; N, 9.38%. Calcd for [Pd{Co(D-pen)$_2$}{Co(aet)$_2$(en)}]Cl$_2$·5H$_2$O = C$_{16}$H$_{48}$Cl$_2$Co$_2$N$_6$O$_9$PdS$_4$: C, 21.54; H, 5.42; N, 9.42%. ^{13}C NMR spectrum in D$_2$O (δ, ppm from DSS): 30.9 (-CH$_3$ of pen), 35.3 (-CH$_3$ of pen), 35.6 (-CH$_2$S of aet), 46.6 (-CH$_2$N of en), 54.3 (-C(CH$_3$)$_2$S of pen), 55.9 (-CH$_2$N of aet), 75.4 (-CH(COO)N of pen), 183.7 (-COO of pen).

7 Anal. Found: C, 17.86; H, 4.03; N, 7.88%. Calcd for [Pd{Co(D-pen)$_2$}{Co(aet)$_2$(en)}](PF$_6$)$_2$·2H$_2$O = C$_{16}$H$_{42}$Co$_2$F$_{12}$N$_6$O$_6$P$_2$PdS$_4$: C, 18.18; H, 4.00; N, 7.95%. Crystal data for Λ-**2**(PF$_6$)$_2$·2H$_2$O: *F. W.* 1057.0, orthorhombic, $P2_12_12_1$, a = 16.97(5), b = 20.08(7), c = 10.80(5) Å, V = 3681(19) Å^3, Z = 4, D_c = 1.91 g cm^{-3}, R (R_w) = 0.051 (0.065) for 3569 reflections with $I > 2\sigma(I)$.

8 H. D. Flack, *Acta Crystallogr., Sect A*, **39**, 876 (1983); H. D. Flack and G. Bernandinello, *Acta Crystallogr., Sect A*, **41**, 500 (1985).

9 Anal. Found: C, 25.92; H, 5.07; N, 5.93%. Calcd for [Pd{Co(D-pen)$_2$}$_2$]·6H$_2$O = C$_{20}$H$_{48}$Co$_2$N$_4$O$_{14}$PdS$_4$: C, 26.08; H, 5.25; N, 6.08%. ^{13}C NMR spectrum in D$_2$O (δ, ppm from DSS): 30.6 (-CH$_3$), 36.2 (-CH$_3$), 55.0 (-C(CH$_3$)$_2$S), 75.2 (-CH(COO)N), 183.5 (-COO).