Anion-controlled Preparation of Chiral S-Bridged $\mathrm{Co^{III}Pt^{II}_2}$ and $\mathrm{Co^{III}_2Pt^{II}_2}$ Complexes Consisting of $[\mathrm{Co}(\text{D-penicillaminato-}N,O,S)_2]^-$ and $[\mathrm{Pt(CH_3NH_2)_2}]^{2+}$ Units

Asako Igashira-Kamiyama, Junji Fujioka, Tomoki Kodama, Tatsuya Kawamoto, and Takumi Konno*
Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043

(Received March 6, 2006; CL-060261; E-mail: konno@ch.wani.osaka-u.ac.jp)

Treatment of *trans*(*N*)-$[\mathrm{Co}(\text{D-pen-}N,O,S)_2]^-$ with *trans*-$[\mathrm{PtCl_2(CH_3NH_2)_2}]$ in water, followed by the addition of NaCl and $\mathrm{NaClO_4}$, gave chiral S-bridged $\mathrm{Co^{III}Pt^{II}_2}$ and $\mathrm{Co^{III}_2Pt^{II}_2}$ complexes with *trans*(*O*)-$[\mathrm{Co}(\text{D-pen-}N,O,S)_2]^-$ units, respectively. The $\mathrm{Co^{III}Pt^{II}_2}$ complex reacted with the racemic *fac*(*S*)-$[\mathrm{Co(aet)_3}]$ to form a chiral $\mathrm{Co^{III}_2Pt^{II}_2}$ complex with *trans*(*O*)-$[\mathrm{Co}(\text{D-pen-}N,O,S)_2]^-$ and Δ-*fac*(*S*)-$[\mathrm{Co(aet)_3}]$ units.

During the past decade, considerable attention has been drawn to the rational synthesis of chiral metal compounds in the field of coordination stereochemistry.[1] This is stimulated by the growing interest in the design and creation of well-organized metallo-supramolecular species, the overall structures of which can be controlled by the chirality of their building blocks.[2] Our research interest has been directed toward this subject, focused on the aggregation of chiral octahedral complex-units containing simple aminothiolate-type ligands.[3,4] Recently, we have shown that $[\mathrm{Co}(\text{D-pen-}N,O,S)_2]^-$ (D-pen = D-penicillaminate) can be aggregated by transition-metal ions to form S-bridged polynuclear structures.[5] Interestingly, the reactions of *trans*(*N*)-$[\mathrm{Co}(\text{D-pen-}N,O,S)_2]^-$ with linear $\mathrm{Ag^+}$ or $\mathrm{Au^+}$ were accompanied by the *trans*(*N*)-to-*trans*(*O*) isomerization to give a $\mathrm{Co^{III}_3M_3}$ hexanuclear structure in $[\mathrm{M_3}\{\mathrm{Co}(\text{D-pen-}N,O,S)_2\}_3]$ ($\mathrm{M = Ag^I}$ and $\mathrm{Au^I}$),[5b] while the corresponding reactions with square-planar $[\mathrm{PdCl_4}]^{2-}$ or $[\mathrm{PtCl_4}]^{2-}$ proceeded with retention of *trans*(*N*) to produce a $\mathrm{Co^{III}M'Co^{III}}$ trinuclear structure in $[\mathrm{M'}\{\mathrm{Co}(\text{D-pen-}N,O,S)_2\}_2]$ ($\mathrm{M' = Pd^{II}}$ and $\mathrm{Pt^{II}}$).[5a,5c] In this context, we started to investigate the reactions of *trans*(*N*)-$[\mathrm{Co}(\text{D-pen-}N,O,S)_2]^-$ with *trans*-$[\mathrm{PtCl_2(RNH_2)_2}]$ that could be available as a linear linker for the construction of S-bridged structures,[4b] in order to elucidate factors dominating the stereochemistry of chiral polynuclear complexes. Here, we report that the reaction with *trans*-$[\mathrm{PtCl_2(CH_3NH_2)_2}]$ does not afford an expected $\mathrm{Co^{III}_3Pt^{II}_3}$ hexanuclear complex analogous to $[\mathrm{M_3}\{\mathrm{Co}(\text{D-pen-}N,O,S)_2\}_3]$ but leads to the isolation of a $\mathrm{Co^{III}Pt^{II}_2}$ trinuclear and a $\mathrm{Co^{III}_2Pt^{II}_2}$ tetranuclear complexes, the structures of which are controlled by the anions employed. The chiral-selective formation of an analogous $\mathrm{Co^{III}_2Pt^{II}_2}$ complex by the reaction of the $\mathrm{Co^{III}Pt^{II}_2}$ complex with *fac*(*S*)-$[\mathrm{Co(aet)_3}]$ (aet = 2-aminoethanethiolate) is also reported.

The 1:1 reaction of *trans*(*N*)-$\mathrm{K}[\mathrm{Co}(\text{D-pen-}N,O,S)_2]$[6a] with *trans*-$[\mathrm{PtCl_2(CH_3NH_2)_2}]$[6b] in water in an ice bath gave a dark brown solution, from which black crystals ([**1**]Cl) were isolated by adding aqueous NaCl.[7] The absorption spectrum of [**1**]Cl in water showed a d–d band at ca. $16 \times 10^3\,\mathrm{cm^{-1}}$ and an intense S-to-Co CT band at ca. $28 \times 10^3\,\mathrm{cm^{-1}}$ with a shoulder at lower energy, while its CD spectrum gives positive, negative, and positive CD bands from lower energy in this region.[8] These spectral features are reminiscent of those of the S-bridged hexanuclear complexes, $[\mathrm{M_3}\{\mathrm{Co}(\text{D-pen-}N,O,S)_2\}_3]$.[5b] However, the elemental analytical data of [**1**]Cl do not match with the formula for a 1:1 adduct of $[\mathrm{Co}(\text{D-pen})_2]^-$ and $[\mathrm{Pt(CH_3NH_2)_2}]^{2+}$, but with that for a 1:2 adduct. The crystal structure of [**1**]Cl was determined by X-ray crystallography.[9] As shown in Figure 1, the complex cation $[\mathbf{1}]^+$ contains one octahedral $[\mathrm{Co}(\text{D-pen-}N,O,S)_2]^-$ unit that is bound by two *trans*-$[\mathrm{PtCl(CH_3NH_2)_2}]^+$ moieties, forming a S-bridged $\mathrm{Co^{III}Pt^{II}_2}$ trinuclear structure. The $[\mathrm{Co}(\text{D-pen-}N,O,S)_2]^-$ unit in $[\mathbf{1}]^+$ adopts a *trans*(*O*) geometry, which implies the occurrence of the geometrical isomerization. The coordination environment about each $\mathrm{Pt^{II}}$ atom is roughly square-planar, with three sites being coordinated by a thiolato S and two amine N atoms and the remaining site trans to a S atom being occupied by a Cl atom. The two $\mathrm{Pt^{II}}$ square-planes face to each other with a Pt···Pt distance of 3.2866(9) Å and a twist angle of ca. 55°, such that each of two amine groups forms an intramolecular N–H···O hydrogen bond with an adjacent carboxylato O atom (N···O = 2.859(9) Å). The S–Co–S (93.4(1)°) and S–Pt–Cl (170.98(7)°) angles in $[\mathbf{1}]^+$ are deviated from the ideal angles of 90° and 180°. In $[\mathbf{1}]^+$, the two bridging S atoms have the *R* chiral configuration to give the [*trans*(*O*)](*R*)$_2$ isomer with a crystallographic C_2 symmetry.[10] Note that the two terminal Cl atoms are hydrogen bonded with amine groups of a neighboring $\mathrm{Co^{III}Pt^{II}_2}$ cation (av N···Cl = 3.199(8) Å), constructing a 1D-chain structure.[8]

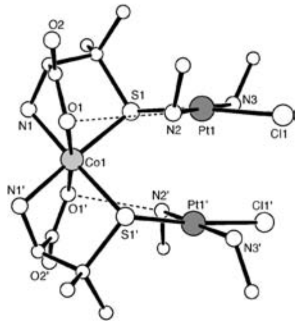

Figure 1. A perspective view of $[\mathbf{1}]^+$.

When aqueous $\mathrm{NaClO_4}$ was added to the 1:1 reaction mixture, instead of aqueous NaCl, black crystals of $[\mathbf{2}](\mathrm{ClO_4})_2$ were isolated.[7] While the overall absorption and CD spectral features of $[\mathbf{2}](\mathrm{ClO_4})_2$ are similar to those of [**1**]Cl, notable differences are observed in more minute detail.[8] Furthermore, the elemental analytical data of $[\mathbf{2}](\mathrm{ClO_4})_2$ are consistent with the formula for a 1:1 adduct of $[\mathrm{Co}(\text{D-pen})_2]^-$ and $[\mathrm{Pt(CH_3NH_2)_2}]^{2+}$. From these results, the formation of a $\mathrm{Co^{III}_3Pt^{II}_3}$ hexanuclear structure analogous to $[\mathrm{M_3}\{\mathrm{Co}(\text{D-pen-}N,O,S)_2\}_3]$ was anticipated. However, X-ray analysis revealed that $[\mathbf{2}]^{2+}$ has a $\mathrm{Co^{III}_2Pt^{II}_2}$ tetranuclear structure, in which two octahedral $[\mathrm{Co}(\text{D-pen-}N,O,S)_2]^-$ units are connected by two *trans*-$[\mathrm{Pt(CH_3NH_2)_2}]^{2+}$ units (Figure 2).[9] Each $[\mathrm{Co}(\text{D-pen-}N,O,S)_2]^-$ unit in $[\mathbf{2}]^{2+}$ adopts a *trans*(*O*) geometry, as does the unit in $[\mathbf{1}]^+$. The square-planar geometry about

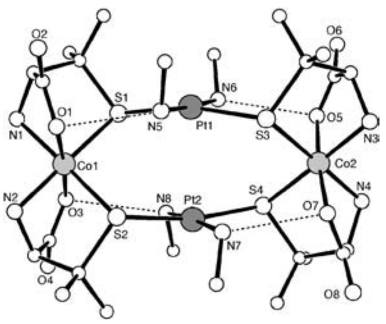

Figure 2. A perspective view of [**2**]$^{2+}$.

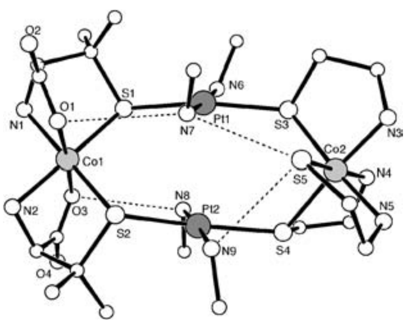

Figure 3. A perspective view of [**3**]$^{3+}$.

two Pt^{II} atoms and the relative arrangement of two Pt^{II} planes (Pt···Pt = 3.1735(4) Å, twist angle = ca. 49°) in [**2**]$^{2+}$ are similar to those in [**1**]$^{+}$. However, the S–Co–S (av 97.17(5)°) and S–Pt–S (av 167.96(4)°) angles are much more deviated from the ideal angles. This disadvantage appears to be compensated by the four intramolecular N–H···O hydrogen bonds (av N···O = 2.931(5) Å). The bridging S atoms in [**2**]$^{2+}$ also have the *R* configuration to form the [*trans*(*O*)]$_2$(*R*)$_4$ isomer with an averaged D_2 symmetry.[10]

It was recognized that [**1**]$^{+}$ is converted into [**2**]$^{2+}$ on treating with equimolar of *trans*(*N*)-[Co(D-pen-*N*,*O*,*S*)$_2$]$^{-}$ in water in an ice bath. Prompted by this result, we carried out the reaction of [**1**]$^{+}$ with *fac*(*S*)-[Co(aet)$_3$][6c] under the same conditions. When the reaction solution was chromatographed on an SP-Sephadex C-25 column, a dark green band containing [**3**]$^{3+}$ was eluted with 0.3 mol dm^{-3} aqueous NaClO$_4$, after the swept of the column with 0.2 mol dm^{-3} aqueous NaClO$_4$. The presence of a single isomer having aet and D-pen ligands in [**3**]$^{3+}$ was confirmed by the ^{1}H and ^{13}C NMR spectra,[10] and the elemental analytical data of [**3**](ClO$_4$)$_3$ isolated from the eluate were consistent with the formula for a 1:1:2 adduct of [Co(D-pen)$_2$]$^{-}$, [Co(aet)$_3$], and [Pt(CH$_3$NH$_2$)$_2$]$^{2+}$.[7] Indeed, X-ray analysis demonstrated that [**3**](ClO$_4$)$_3$ is a S-bridged Co$^{III}{}_2$Pt$^{II}{}_2$ tetranuclear complex, in which [Co(aet)$_3$] and [Co(D-pen)$_2$]$^{-}$ units are spanned by two *trans*-[Pt(CH$_3$NH$_2$)$_2$] linkers (Figure 3).[9] Again, the [Co(D-pen-*N*,*O*,*S*)$_2$]$^{-}$ unit in [**3**]$^{3+}$ has a *trans*(*O*) geometry. The [Co(aet)$_3$] unit adopts the *fac*(*S*) geometry, as does the starting mononuclear *fac*(*S*)-[Co(aet)$_3$]. This is in contrast to the fact that the linkage of two [Co(aet)$_3$] units with a square planar Pd^{II} or Pt^{II} was accompanied by the *fac*(*S*)-to-*mer*(*S*) isomerization.[4a] The overall tetranuclear structure in [**3**]$^{3+}$ (av S–Pt–S = 165.9(3)°, N–Pt–N = 176(1)°, S–Co–S = 95.9(4)°) resembles that in [**2**]$^{2+}$, except the presence of *fac*(*S*)-[Co(aet)$_3$] unit, in place of *trans*(*O*)-[Co(D-pen-*N*,*O*,*S*)$_2$]$^{-}$ unit. In [**3**]$^{3+}$, two amine groups form intramolecular hydrogen bonds with a nonbridging S atom (av N···S = 3.29(3) Å),[4b] which in turn weaken the N–H···O hydrogen bonds (av N···O = 3.30(4) Å). An interesting aspect of this reaction is that the Δ isomer of *fac*(*S*)-[Co(aet)$_3$] is selectively incorporated in the tetranuclear structure.[11] This result indicates that [**1**]$^{+}$ could serve as a "chiral molecular nipper" that enantioselectively catches a chiral molecule.

In summary, this study showed several unique, noteworthy features, involving (i) the controlled isolation of S-bridged trinuclear and tetranuclear structures in [**1**]$^{+}$ and [**2**]$^{2+}$ by the choice of counter ions (Cl^{-} vs ClO$_4{}^{-}$), (ii) the formation of a tetranuclear structure in [**2**]$^{2+}$ rather than a less hindered hexanuclear structure analogous to [M$_3${Co(D-pen-*N*,*O*,*S*)$_2$}$_3$], despite the bulkiness of *trans*-[Pt(CH$_3$NH$_2$)$_2$] linker, which is most likely ascribed to the tight N–H···O hydrogen-bonding interaction, and (iii) the potential utility of [**1**]$^{+}$ as a "chiral molecular nipper." Investigation of the reactions with other *trans*-[PtCl$_2$-(RNH$_2$)$_2$] complexes is currently underway.

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7 Calcd for [**1**]Cl·3H$_2$O = [{PtCl(CH$_3$NH$_2$)$_2$}$_2${Co(D-pen)$_2$}]Cl·3H$_2$O: C, 16.36; H, 4.31; N, 8.17%. Found: C, 16.37; H, 4.01; N, 8.24%. Yield: 68%. Calcd for [**2**](ClO$_4$)$_2$·2H$_2$O = [{Pt(CH$_3$-NH$_2$)$_2$}$_2${Co(D-pen)$_2$}$_2$](ClO$_4$)$_2$·2H$_2$O: C, 19.80; H, 4.15; N, 7.70%. Found: C, 19.76; H, 4.44; N, 7.55%. Yield: 17%. Calcd for [**3**](ClO$_4$)$_3$·2H$_2$O·NaClO$_4$ = [{Pt(CH$_3$NH$_2$)$_2$}$_2${Co(D-pen)$_2$}-{Co(aet)$_3$}](ClO$_4$)$_3$·2H$_2$O·NaClO$_4$: C, 14.90; H, 3.75; N, 7.82%. Found: C, 14.84; H, 3.76; N, 7.58%.

8 See Supporting Information.

9 Crystal data for [**1**]Cl·3H$_2$O: fw 1028.13, Orthorhombic, $C222_1$, $a = 9.489(3)$, $b = 18.998(5)$, $c = 17.470(5)$ Å, $V = 3149.3(14)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 2.168$ g/cm^3, $R_1 = 0.035$ ($I > 2\sigma(I)$). Crystal data for [**2**](ClO$_4$)$_2$·8H$_2$O·4NaClO$_4$: fw 2053.84, Orthorhombic, $P2_12_12_1$, $a = 10.8286(16)$, $b = 20.198(2)$, $c = 29.719(3)$ Å, $V = 6500.0(14)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 2.099$ g/cm^3, $R_1 = 0.030$ ($I > 2\sigma(I)$). Crystal data for [**3**](ClO$_4$)$_3$·2H$_2$O·NaClO$_4$: fw 1611.90, Hexagonal, $P6_3$, $a = 19.879(5)$, $c = 22.926(12)$ Å, $V = 7846(5)$ Å^3, $Z = 6$, $D_{\text{calcd}} = 2.047$ g/cm^3, $R_1 = 0.063$ ($I > 2\sigma(I)$).

10 In the ^{1}H and ^{13}C NMR spectra, each of [**1**]$^{+}$, [**2**]$^{2+}$, and [**3**]$^{3+}$ gives a single set of signals. See Supporting Information.

11 The Δ isomer of *fac*(*S*)-[Co(aet)$_3$] corresponds to the *trans*(*O*) isomer of [Co(D-pen-*N*,*O*,*S*)$_2$]$^{-}$, in which the skew pair of two *O*,*S*-chelate rings has the Δ configuration.