First Geometrical Isomerization of $[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ Induced by Forming S-Bridged Structure with $\mathrm{Au^I}$ or $\mathrm{Ag^I}$: Crystal Structure of a $\mathrm{Co^{III}}_3\mathrm{Au^I}_3$ Hexanuclear Metallacycle $[\mathrm{Au}_3\{\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2\}_3]$ (D-pen = D-Penicillaminate)

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The reactions of *trans(N)*-$[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ with $\mathrm{Au^I}$ or $\mathrm{Ag^I}$ in water led to the formation of novel S-bridged $\mathrm{Co^{III}}_3\mathrm{M}_3$ hexanuclear metallacycles $[\mathrm{M}_3\{\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2\}_3]$ (M = $\mathrm{Au^I}$ (**1**), $\mathrm{Ag^I}$ (**2**)), in which $[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ units adopt a *trans(O)* geometry. The molecular structure of **1** was determined by X-ray crystallography.

Recently we reported that *trans(N)*-$[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ (D-pen = D-penicillaminate) having two thiolato S atoms replaces two Cl atoms in $[\mathrm{PdCl_2}\{\mathrm{Co(aet)_2(en)}\}]^+$ (aet = 2-aminoethanethiolate) to form an S-bridged $\mathrm{Co^{III}}_2\mathrm{Pd^{II}}$ trinuclear complex $[\mathrm{Pd}\{\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2\}\{\mathrm{Co(aet)_2(en)}\}]^{2+}$, retaining its *trans(N)* geometry.[1] From this result, it was suggested that *trans(N)*-$[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ can function as an effective didentate-*S,S* complex-ligand toward a variety of metal ions, besides square-planar $\mathrm{Pd^{II}}$ ion. Thus, as part of our goal to develop coordination chemistry of S-donating complex–ligands, we decided to investigate the binding ability of *trans(N)*-$[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ toward linear-type metal ions M = $\mathrm{Au^I}$, $\mathrm{Ag^I}$. Since it has been shown that the reaction of *fac(S)*-$[\mathrm{Co(aet)_3}]$ with linear $\mathrm{Ag^I}$ produces an S-bridged $\mathrm{Co^{III}}_2\mathrm{Ag^I}_3$ pentanuclear complex $[\mathrm{Ag}_3\{\mathrm{Co(aet)_3}\}_2]^{3+}$, in which two *fac(S)*-$[\mathrm{Co(aet)_3}]$ units are linked by three $\mathrm{Ag^I}$ ions,[2] we expected the formation of S-bridged $\mathrm{Co^{III}}_2\mathrm{M}_2$ tetranuclear complexes $[\mathrm{M}_2\{\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2\}_2]$, in which two *trans(N)*-$[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ are linked by two $\mathrm{Au^I}$ or $\mathrm{Ag^I}$ ions. However, the reactions were found to give cyclic $\mathrm{Co^{III}}_3\mathrm{M}_3$ hexanuclear complexes $[\mathrm{M}_3\{\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2\}_3]$ (M = $\mathrm{Au^I}$ (**1**), $\mathrm{Ag^I}$ (**2**)), accompanied by the geometrical isomerization of $[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ (Figure 1). In this paper we describe the formation and characterization of **1** and **2**.

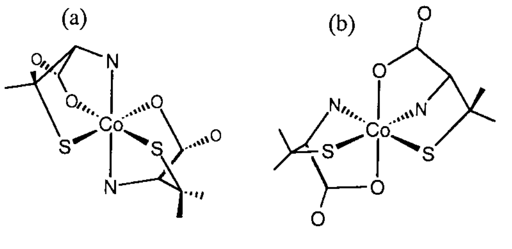

Figure 1. Two geometrical isomers, *trans(N)* (a) and *trans(O)* (b), for $[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$.

Treatment of an aqueous solution of *trans(N)*-$\mathrm{K}[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]\cdot 2\mathrm{H_2O}$ [3] with equimolar of $[\mathrm{AuCl}\{\mathrm{S(CH_2CH_2OH)_2}\}]$, which was freshly prepared from $\mathrm{Na[AuCl_4]}$ and 2,2'-thiodiethanol in water,[4] at room temperature gave greenish black hexagonal-plate crystals ($\mathbf{1}\cdot 15\mathrm{H_2O}$).[5] The elemental analysis of this complex is consistent with the 1:1 stoichiometry of $[\mathrm{Au}\{\mathrm{Co}(\mathrm{D}\text{-pen})_2\}]\cdot 5\mathrm{H_2O}$, and its structure was established by X-ray crystallography.[6] As shown in Figure 2, **1** is a neutral complex molecule consisting of three octahedral $[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ units and three $\mathrm{Au^I}$ atoms. A three-fold axis exists at the center of the structure, and therefore, only one-third of the molecule corresponds to the asymmetric unit. Two thiolato S atoms in each $[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ unit are bound to two approximately linear $\mathrm{Au^I}$ atoms, such that the three $[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ units are linked by three $\mathrm{Au^I}$ atoms in a cyclic form. Here it should be noted that each $[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ unit in **1** adopts a *trans(O)* geometry, which is distinct from the *trans(N)* geometry of the parental *trans(N)*-$[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ (Figure 1). The averaged Co–S bond distance (2.261(7) Å) is longer and the S–Co–S angle (91.1(2)°) is larger than the corresponding distance and angle observed for the *trans(N)*-$[\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2]^-$ unit in $[\mathrm{Pd}\{\mathrm{Co}(\mathrm{D}\text{-pen-}N,O,S)_2\}\{\mathrm{Co(aet)_2(en)}\}]^{2+}$ (average Co–S = 2.236(4) Å, S–Co–S = 87.3(1)°).[1] Two chiral configurations, *R* and *S*, are possible for each bridging thiolato S atom. However, all six bridging S atoms are unified to have the *R* configuration.[7] Thus, only one optically active isomer, $[trans(O)]_3(R)_6$, with an averaged D_3 symmetry exists in crystal.

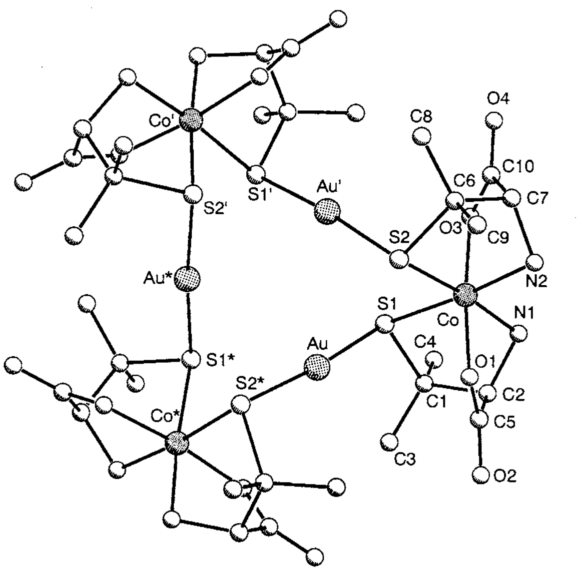

Figure 2. Perspective view of **1**. Selected bond distances (Å) and angles (°): Au-S1 = 2.314(7), Au-S2 = 2.308(8), Co-S1 = 2.271(7), Co-S2 = 2.252(7), Co-O1 = 1.90(2), Co-O3 = 1.93(2), Co-N1 = 1.99(2), Co-N2 = 1.98(2), S1-Au-S2 = 173.7(2), S1-Co-S2 = 91.1(2), Au···Au = 3.406(1).

1 is poorly soluble in water, and its absorption spectrum is characterized by two d–d absorption bands in the region of (16–22) × 10^3 cm^{-1}, besides one intense S-to-Co CT band at 31.4 × 10^3 cm^{-1} with a shoulder at the lower energy side (Figure 3). This absorption spectral behavior differs significantly from that of the parental mononuclear *trans(N)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$.[3] Furthermore, the solid state spectrum of **1** (nujol mull) is essentially the same as the spectrum of **1** in water. Accordingly, it is reasonable to assumed that the cyclic $Co^{III}{}_3Au^I{}_3$ hexanuclear structure of **1** observed in crystal is retained in solution. This is supported by its CD spectrum in water, which is markedly different from that of three moles of *trans(N)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$ over the whole region (Figure 3).[3] In the 500 MHz ^1H NMR spectrum in D_2O, **1** gives only two methyl (δ 1.36, 1.82) and one methine (δ 3.87) signals for the six D-pen ligands in the complex. This suggests that the $[trans(O)]_3(R)_6$ isomer with a D_3 symmetrical structure is selectively formed for **1**.

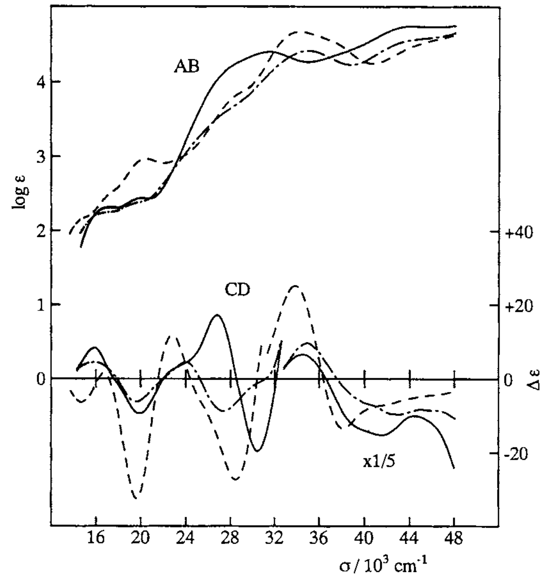

Figure 3. Electronic absorption and CD spectra of **1** (—), **2** (--), and *trans(N)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$ x 3 (---), in water. The absorption and CD spectral scales for **2** are arbitrary.

The reaction of *trans(N)*-$K[Co(\textsc{d}\text{-pen-}N,O,S)_2]\cdot 2H_2O$ with equimolar of $AgNO_3$ in water at room temperature also produced greenish black hexagonal-plate crystals ($\mathbf{2}\cdot 15H_2O$).[8] While single crystals suitable for X-ray analysis could not be grown, the product shows an almost overlapping IR spectrum to that of $\mathbf{1}\cdot 15H_2O$. Moreover, the solid state absorption spectrum of **2** gives two d-d absorption components in the region of (16–22) × 10^3 cm^{-1}, as does the spectrum of **1**. From these results and the elemental analysis, **2** is assignable to the S-bridged $Co^{III}{}_3Ag^I{}_3$ hexanuclear complex $[Ag_3\{Co(\textsc{d}\text{-pen})_2\}_3]$, in which three *trans(O)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$ units are linked by three Ag^I atoms in a cyclic form. The solubility of **2** in water is much lower than that of **1**, and therefore, the spectral measurements for **2** were carried out only qualitatively. As illustrated in Figure 3, the absorption spectral behavior of **2** resembles that of **1** in the region of (16–22) × 10^3 cm^{-1}, and the overall CD spectral pattern of **2** is in agreement with that of **1** except the region of (25–32) × 10^3 cm^{-1}. The absorption and CD spectral behavior supports that **2** has a cyclic $Co^{III}{}_3Ag^I{}_3$ hexanuclear structure composed of *trans(O)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$ units.

In the present study, it was found that the reactions of *trans(N)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$ with M = Au^I, Ag^I under moderate conditions gave the S-bridged $Co^{III}{}_3M_3$ hexanuclear metallacycles composed of three *trans(O)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$ units. This result obviously implies that *trans(N)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$ readily isomerizes to have a *trans(O)* geometry by forming S-bridged structure with linear Au^I or Ag^I ion. It is worth noting that the mononuclear *trans(O)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$ has not been isolated to date,[9] and furthermore, the reactions of *trans(N)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$ with Pd^{II} have been shown to form S-bridged polynuclear structures with retention of the *trans(N)* geometry.[1] Molecular model examinations reveal that the directionality of lone pairs on the two thiolato S atoms in *trans(N)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$ is not suitable for binding with two linear Au^I or Ag^I ions, but is best fitted for chelating to one square-planar metal ion. In contrast, *trans(O)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$ allows two thiolato S atoms to bind with two linear metal ions, as demonstrated by the crystal structure of **1**. Thus, the directionality of lone pairs on the coordinated thiolato S atoms is a key factor of controlling the S-bridged polynuclear structures.

References and Notes

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5 Anal. Found: C, 18.60; H, 4.21; N, 4.37%. Calcd for $[Au_3\{Co(pen)_2\}_3]\cdot 15H_2O$ = $C_{30}H_{84}Au_3Co_3N_6O_{27}S_6$: C, 18.76; H, 4.41; N, 4.37%. Yield: 74%.

6 Crystal data for $\mathbf{1}\cdot 15H_2O$: FW 1921.1, hexagonal, $P6_3$, a = 13.183(2) Å, c = 19.028(5) Å, V = 2863(1) $Å^3$, Z = 2, D_c = 2.23 g cm^{-3}, R (R_w) = 0.054 (0.057) for 1634 reflections with $I > 1.9\sigma(I)$.

7 The absolute configuration was determined 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 (−0.05(6)). H. D. Flack, *Acta Crystallogr., Sect A*, **39**, 876 (1983); H. D. Flack and G. Bernandinello, *Acta Crystallogr., Sect A*, **41**, 500 (1985).

8 Anal. Found: C, 21.84; H, 4.85; N, 5.07%. Calcd for $[Ag_3\{Co(pen)_2\}_3]\cdot 15H_2O$ = $C_{30}H_{84}Ag_3Co_3N_6O_{27}S_6$: C, 21.79; H, 5.12; N, 5.08%. Yield: 48%.

9 It has been shown that the green complex assigned to *trans(O)*-$[Co(\textsc{d}\text{-pen-}N,O,S)_2]^-$ in Ref. 3 is indeed Λ_{DDD}-*fac(S)*-$[Co(\textsc{d}\text{-pen-}N,S)_3]^{3-}$. K. Okamoto, T. Yonemura, T. Konno, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **65**, 794 (1992).