2b: Yield: 98%; elemental analysis calcd for $C_{16}H_{22}Br_4N_2Zn_2$ (%): C 27.73, H 3.18, N 4.04, Br 46.16, Zn 18.89; found: C 27.59, H 3.09, N 3.98, Br 45.50, Zn 18.83; ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25°C): $\delta = 1.16$ (d, $^3J(H,H) = 1.6$ Hz, 3H; CH_3), 4.04 (m, 1H,CH), 4.35(dd, $^3J(H,H) = 12.6$ Hz, $^2J(H,H) = 3.0$ Hz, 1H; CH_2), 4.71(dd, $^3J(H,H) = 12.6$ Hz, $^2J(H,H) = 8.4$ Hz, 1H; CH_2), 8.16 (t, $^3J(H,H) = 6.6$ Hz, 2H; C_5H_5N), 8.62 (t, $^3J(H,H) = 6.6$ Hz, 1H; C_5H_5N), 8.97 (d, $^3J(H,H) = 6.6$ Hz, 2H; C_5H_5N).

Catalysis reaction: All the coupling reactions were conducted in a 100-mL stainless-steel bomb equipped with a magnet bar and an electrical heater. The reactor was charged with the appropriate catalyst and epoxide, and pressurized with CO_2 (≈ 1.4 MPa). The bomb was then heated to a specified temperature with the addition of CO_2 (up to 3.4 MPa) from a reservoir tank to maintain a specified pressure. After the reaction, the bomb was cooled to room temperature and the remaining epoxide was removed. The product mixtures were analyzed by GC, HPLC, and GC-MS. Solid catalyst mixtures were characterized by NMR spectroscopy.

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[1] A. Behr, *Carbon Dioxide Activation by Metal Complexes*, VCH, New York, **1988**.

[2] D. J. Darensbourg, M. W. Holtcamp, *Coord. Chem. Rev.* **1996**, *153*, 155–174.

[3] R. Nomura, A. Ninagawa, H. Matsuda, *J. Org. Chem.* **1980**, *45*, 3735–3738.

[4] H. Kisch, R. Millini, I. J. Wang, *Chem. Ber.* **1986**, *119*, 1090–1094.

[5] T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, *Chem. Commun.* **1997**, 1129–1130.

[6] M. Ratzenhofer, H. Kisch, *Angew. Chem.* **1980**, *92*, 302; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 317–318.

[7] D. J. Darensbourg, M. W. Holtcamp, *Macromolecules* **1995**, *28*, 7577–7579.

[8] W. Dümler, H. Kisch, *Chem. Ber.* **1990**, *123*, 277–283.

[9] C. Postmus, J. R. Ferraqo, W. Wozniak, *Inorg. Chem.* **1967**, *6*, 2030–2032.

[10] Data for the crystal structure analyses were measured on a CAD-4 diffractometer. **2b**: monoclinic, $P2(1)/c$, $a = 8.8690(10)$, $b = 10.615(2)$, $c = 13.229(3)$ Å, $\alpha = 90.02(2)$, $\beta = 104.15(2)$, $\gamma = 90.020(10)°$, $V = 1207.6(4)$ Å^3, $Z = 4$, $R1 = 0.0481$, $wR^2 = 0.1110$ ($I > 2\sigma I$); $R1 = 0.0505$, $wR^2 = 0.1126$ (all data). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-148670. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[11] R. L. Geerts, J. C. Huffman, K. G. Caulton, *Inorg. Chem.* **1986**, *25*, 1803–1805.

[12] D. J. Darensbourg, S. A. Niezgoda, J. D. Draper, J. H. Reibenspies, *J. Am. Chem. Soc.* **1998**, *120*, 4690–4698.

[13] M. Kunert, M. Brauer, O. Klobes, H. Gorls, E. Dinjus, E. Anders, *Eur. J. Inorg. Chem.* **2000**, 1803–1809.

[14] D. J. Darensbourg, M. W. Holtcamp, G. E. Struck, M. S. Zimmer, S. A. Niezgoda, P. Rainey, J. B. Robertson, J. D. Draper, J. H. Reibenspies, *J. Am. Chem. Soc.* **1999**, *121*, 107–116.

[15] T. Tsuda, S. I. Sanada, K. Ueda, T. Saegusa, *Inorg. Chem.* **1976**, *15*, 2329–2332.

[16] See the Supporting Information for the ^{1}H NMR spectrum of the reaction mixture.

Rational Construction of Chiral Octanuclear Metallacycles Consisting of Octahedral Co^{III}, Square-Planar Pd^{II}, and Linear Au^I or Ag^I Ions[**]

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While self-assembly of organic molecules assisted by metal ions has attracted much interest in the field of supermolecular chemistry,[1] our research interest has been directed to assembly of octahedral metal complexes with simple thiolate ligands, such as 2-aminoethanethiolate (aet) and L-cysteinate (L-cys). It has been shown that the assembly of these types of complexes can be achieved by facile reactions with a variety of metal ions, which utilize the binding ability of a coordinated thiolato sulfur atom toward a second metal ion.[2–7] For example, a number of trinuclear $[M'\{M(aet)_3\}_2]^{n+}$ ($M' = Fe^{III}$, Co^{III}, Ni^{II}),[4] pentanuclear $[M'_3\{M(aet)_3\}_2]^{n+}$ ($M' = Ag^{I}$, Hg^{II}),[5] and octanuclear $[M'_4O\{M(aet)_3\}_4]^{6+}$ ($M' = Co^{II}$, Zn^{II}) complexes,[6] in which two or four equivalents of *fac*(*S*)-$[M(aet)_3]$ ($M = Co^{III}$, Rh^{III}, Ir^{III}) are assembled by forming sulfur-bridged structures with octahedral, linear, or tetrahedral metal ions, have been prepared and their unique stereochemical and spectroscopic properties have been clarified. In these polynuclear structures, all the three thiolato sulfur atoms in each *fac*(*S*)-$[M(aet)_3]$ unit bridge two metal centers and thus, further assembly of these polynuclear complexes assisted by additional metal ions would not be promising. In this context, it is desirable to prepare sulfur-bridged polynuclear complexes, in which thiolato sulfur atoms are still available for bridging, in order to expand the assembly chemistry based on thiolato metal complexes. One way to do this is to introduce a four-coordinate metal ion, such as $M' = Pd^{II}$, Pt^{II}, at the center of the linear trinuclear structure in $[M'\{M(aet)_3\}_2]^{2+}$. While the reaction of *fac*(*S*)-$[Co(aet)_3]$ with $[PdCl_4]^{2-}$ in a 1:1 ratio produced a sulfur-bridged $Co^{III}_2Pd^{II}_3$ pentanuclear complex, $[Pd_2\{Pd(aet)_2\}\{Co(aet)_3\}_2]^{4+}$, in which all of the eight thiolato sulfur atoms from two *fac*(*S*)-$[Co(aet)_3]$ and one *cis*(*S*)-$[Pd(aet)_2]$ units are bound to two square-planar Pd^{II} ions,[7g] we found that the corresponding 2:1 reaction under milder conditions gives the desired trinuclear complex $[Pd\{Co(aet)_3\}_2]^{2+}$, $[\mathbf{1}]^{2+}$, which readily

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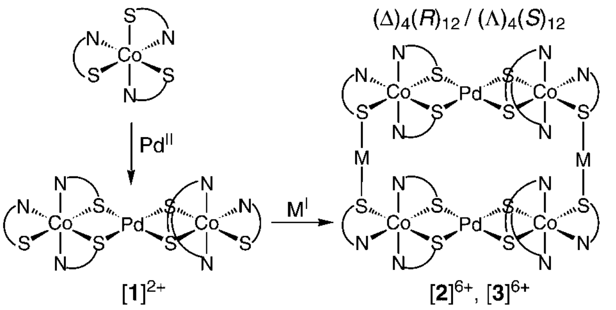
reacts with Ag^I or Au^I to afford cyclic sulfur-bridged octanuclear complexes $[M'_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$ ($M' = Au^I$ ($[\mathbf{2}]^{6+}$), Ag^I ($[\mathbf{3}]^{6+}$); Scheme 1). Interestingly, *fac*(*S*)-$[Co(aet)_3]$ was found to isomerize to adopt a *mer*(*S*) geometry in $[\mathbf{1}]^{2+}$, which is the key factor to form a cyclic sulfur-bridged structure in $[\mathbf{2}]^{6+}$ and $[\mathbf{3}]^{6+}$. In this Communication, we report the synthesis and fascinating stereochemical properties of $[\mathbf{1}]^{2+}$, $[\mathbf{2}]^{6+}$, and $[\mathbf{3}]^{6+}$, along with the crystal structures of $[\mathbf{2}]^{6+}$ and $[\mathbf{3}]^{6+}$. To the best of our knowledge, this is the first example of chiral metallacycles composed of three kinds of metal ions with different oxidation states and coordination geometries: octahedral Co^{III}, square-planar Pd^{II}, and linear Ag^I or Au^I ions.



Scheme 1. Synthesis of $[\mathbf{2}]^{6+}$ and $[\mathbf{3}]^{6+}$, by way of $[\mathbf{1}]^{2+}$.

The reaction of *fac*(*S*)-$[Co(aet)_3]$[4a] with $Na_2[PdCl_4]$ in a 2:1 ratio gave an almost black solution, from which a green-black powder ($[\mathbf{1}]Cl_2 \cdot 5H_2O$) was isolated by adding an aqueous solution of NaCl. The nitrate salt of this complex ($[\mathbf{1}](NO_3)_2 \cdot 1.5H_2O$) was obtained by adding an aqueous solution of $NaNO_3$ to the reaction solution. The elemental and plasma emission analyses of the chloride and nitrate salts are in good agreement with the formulas for the expected $Co^{III}Pd^{II}Co^{III}$ trinuclear $[Pd\{Co(aet)_3\}_2]^{2+}$ complex. When a dark green-brown aqueous solution of $[\mathbf{1}]Cl_2 \cdot 5H_2O$ was treated with a colorless aqueous solution containing $[AuCl\{S(CH_2CH_2OH)_2\}]$,[8] the intense absorption band at 336 nm characteristic for $[\mathbf{1}]^{2+}$ shifted to a higher energy side (327 nm) and, from the reaction solution, dark green-brown microcrystals ($[\mathbf{2}]Cl_6 \cdot 16H_2O$) were isolated. The plasma emission analysis indicated that $[\mathbf{2}]^{6+}$ contains Co, Pd, and Au atoms in a 2:1:1 ratio and the elemental analysis is also consistent with the 2:1:1 stoichiometry of $[Co(aet)_3]_2 \cdot PdCl_2 \cdot AuCl \cdot 8H_2O$.

The structure of $[\mathbf{2}]^{6+}$ was established by a single crystal X-ray analysis of $[\mathbf{2}]Cl_6 \cdot 16H_2O$.[9] As shown in Figure 1, the entire complex cation $[\mathbf{2}]^{6+}$ consists of four $[Co(aet)_3]$ units and two Pd^{II} and two Au^I atoms. Two of the three thiolato sulfur atoms in each octahedral $[Co(aet)_3]$ unit are bound to one Pd^{II} atom to form a linear sulfur-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear moiety, $[Pd\{Co(aet)_3\}_2]^{2+}$ (average bond lengths [Å] are Co–S 2.269(2) and Pd–S 2.323(2)). The two trinuclear moieties are connected with each other by two linear S-Au-S linkages (Au–S = 2.285(2) Å, S-Au-S = 178.85(7)°), completing a cyclic $Co^{III}_4Pd^{II}_2Au^I_2$ octanuclear structure in $[Au_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$. Here it should be noted that each $[Co(aet)_3]$ unit in $[\mathbf{2}]^{6+}$ adopts a *mer*(*S*) geometry, which is distinct from the *fac*(*S*) geometry of the parental *fac*(*S*)-$[Co(aet)_3]$.[4a, 6b] Two chiral configurations, Δ and Λ, are possible for each *mer*(*S*)-$[Co(aet)_3]$ unit. However, either the Δ or Λ configurational *mer*(*S*)-$[Co(aet)_3]$ unit is selectively incorporated in the octanuclear structure in $[\mathbf{2}]^{6+}$ to give only the $\Delta\Delta\Delta\Delta$ or $\Lambda\Lambda\Lambda\Lambda$ isomers. In addition, all 12 asymmetric bridging sulfur atoms are unified to have the *R* configuration for the $(\Delta)_4$ and the *S* configuration for the $(\Lambda)_4$ isomer. Thus, only a pair of enantiomers of approximately D_2 symmetry, $(\Delta)_4(R)_{12}$ and $(\Lambda)_4(S)_{12}$, exist in the crystal; the latter isomer is illustrated in Figure 1. When the solution mixture of $[\mathbf{1}]^{2+}$ with $[AuCl\{S(CH_2CH_2OH)_2\}]$ was chromatographed on an SP-Sephadex C-25 column (eluent 1.0 M aqueous NaCl), only one band for $[\mathbf{2}]^{6+}$ eluted. Furthermore, the ^{13}C NMR spectrum of $[\mathbf{2}]Cl_6$ in D_2O exhibits six methylene carbon signals for twelve aet ligands in the complex. These results indicate that the racemate of $(\Delta)_4/(\Lambda)_4$ with a D_2 symmetrical structure was selectively formed for $[\mathbf{2}]^{6+}$, taking account of the X-ray analytical result. This is supported by the fact that $[\mathbf{2}]^{6+}$ was resolved, by column chromatography (SP-Sephadex C-25, eluent 0.5 M aqueous $[Sb_2((R,R)\text{-tartrate})_2]^{2-}$), into the $(+)^{CD}_{260}$ and $(-)^{CD}_{260}$ isomers, which show CD spectra consistent with their enantiomeric relationship.

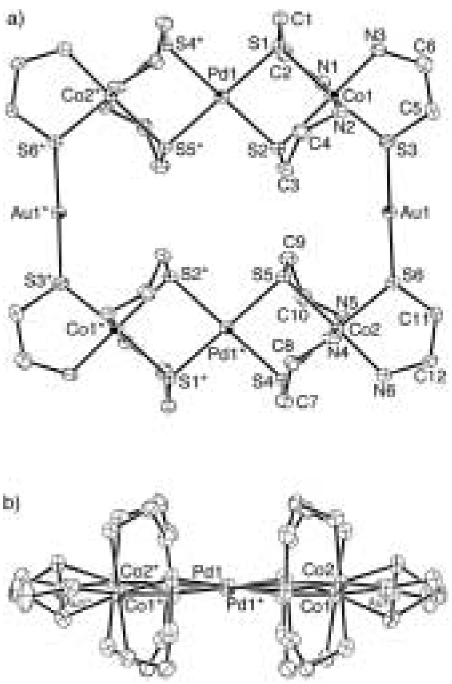


Figure 1. a) Plan and b) elevation of the complex cation $[\mathbf{2}]^{6+}$.

As illustrated in Figure 2, the absorption spectrum of two moles of $[\mathbf{1}]^{2+}$ coincides well with that of $[\mathbf{2}]^{6+}$. In its ^{13}C NMR spectrum, $[\mathbf{1}]^{2+}$ gives six signals at similar magnetic fields as the signals for $[\mathbf{2}]^{6+}$. From this behavior, $[\mathbf{1}]^{2+}$ is assigned to the sulfur-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear complex, $[Pd\{Co(aet)_3\}_2]^{2+}$, the structure of which is essentially the same as that of the $Co^{III}Pd^{II}Co^{III}$ trinuclear moiety found in $[\mathbf{2}]^{6+}$. That is, in $[\mathbf{1}]^{2+}$ a Pd^{II} ion is coordinated by four thiolato sulfur atoms from two *mer*(*S*)-$[Co(aet)_3]$ units to form the $(\Delta)_2/(\Lambda)_2$ racemate. Consistent with this assignment, $[\mathbf{1}]^{2+}$ was resolved into the $(+)^{CD}_{260}$ and $(-)^{CD}_{260}$ optical isomers by fractional crystallization of its $[Sb_2((R,R)\text{-tartrate})_2]^{2-}$ diastereo-

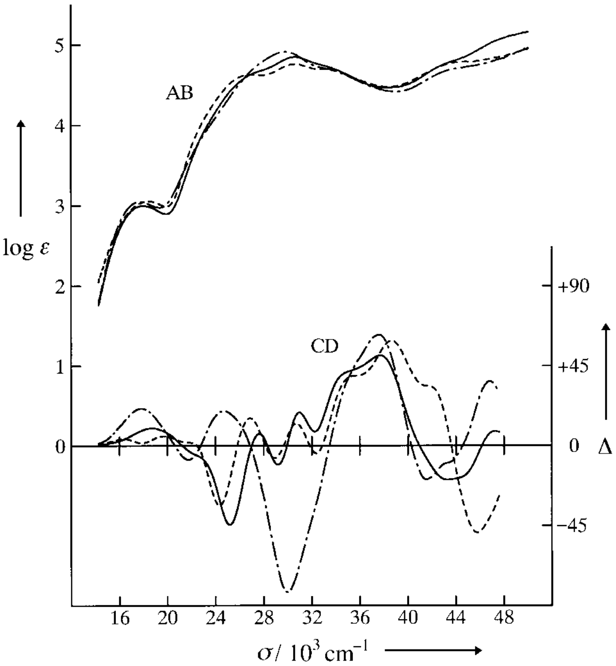


Figure 2. Electronic absorption (AB) and CD spectra of $(+)^{\mathrm{CD}}_{260}$-$(\Lambda)_2$-$[\mathbf{1}]^{2+}$ × 2 (•–•–), $(+)^{\mathrm{CD}}_{260}$-$(\Lambda)_4$-$[\mathbf{2}]^{6+}$ (–––), and $(+)^{\mathrm{CD}}_{260}$-$(\Lambda)_4$-$[\mathbf{3}]^{6+}$ (——) in H_2O.

meric salts. The overall CD spectral behavior of $(+)^{\mathrm{CD}}_{260}$-$[\mathbf{1}]^{2+}$ in water (Figure 2) resembles that of the $(\Lambda)_2$ isomer of the related sulfur-bridged $\mathrm{Co^{III}Pd^{II}Co^{III}}$ trinuclear complex $[\mathrm{Pd\{Co(aet)_2(en)\}_2}]^{4+}$, in which the central $\mathrm{Pd^{II}}$ ion is coordinated by four thiolato sulfur atoms from two terminal C_2-*cis*(*S*)-$[\mathrm{Co(aet)_2(en)}]^{+}$ units.[3d] This suggests that the $(+)^{\mathrm{CD}}_{260}$ isomer of $[\mathbf{1}]^{2+}$ has the $(\Lambda)_2$ configuration. When $(+)^{\mathrm{CD}}_{260}$-$(\Lambda)_2$-$[\mathbf{1}]^{2+}$ was used as the starting complex, instead of the racemate of $[\mathbf{1}]^{2+}$, only the $(+)^{\mathrm{CD}}_{260}$ isomer of $[\mathbf{2}]^{6+}$ was formed. Thus, the $(+)^{\mathrm{CD}}_{260}$ isomer of $[\mathbf{2}]^{6+}$ is assigned to the $(\Lambda)_4$ isomer, while the $(-)^{\mathrm{CD}}_{260}$ isomer to the $(\Delta)_4$ one. Contrary to the agreement in the absorption spectra between $[\mathbf{2}]^{6+}$ and two moles of $[\mathbf{1}]^{2+}$, the CD spectrum of $(+)^{\mathrm{CD}}_{260}$-$(\Lambda)_4$-$[\mathbf{2}]^{6+}$ differs markedly from that of two moles of $(+)^{\mathrm{CD}}_{260}$-$(\Lambda)_2$-$[\mathbf{1}]^{2+}$, especially in the region around $24-32\times10^3\,\mathrm{cm^{-1}}$ (Figure 2). If $[\mathbf{2}]^{6+}$ dissociated in solution, its CD spectrum would be identical to two moles of $[\mathbf{1}]^{2+}$; the difference in the CD spectra suggests that $[\mathbf{2}]^{6+}$ remains intact in solution. The four thiolato sulfur atoms in $[\mathbf{2}]^{6+}$, which became asymmetric by binding with $\mathrm{Au^I}$ ions, besides their skew cyclic structure, seem to contribute significantly to the CD spectrum.

Treatment of $[\mathbf{1}](\mathrm{NO_3})_2\cdot1.5\,\mathrm{H_2O}$ with $\mathrm{AgNO_3}$ in a ratio of 1:1 in water also produced a dark brown aqueous solution, from which dark green-brown microcrystals ($[\mathbf{3}](\mathrm{NO_3})_6\cdot9\,\mathrm{H_2O}$) were isolated. The plasma emission analysis indicated that $[\mathbf{3}]^{6+}$ contains Co, Pd, and Ag atoms in a 2:1:1 ratio and the elemental analysis is consistent with the formula of $[\mathrm{Ag_2\{Pd[Co(aet)_3]_2\}_2}](\mathrm{NO_3})_6\cdot9\,\mathrm{H_2O}$. An X-ray structural analysis of $[\mathbf{3}](\mathrm{NO_3})_6\cdot9\,\mathrm{H_2O}$[9] demonstrated that the complex cation $[\mathbf{3}]^{6+}$ has a sulfur-bridged $\mathrm{Co^{III}_4Pd^{II}_2Ag^{I}_2}$ octanuclear structure, in which four *mer*(*S*)-$[\mathrm{Co(aet)_3}]$ units are linked by two $\mathrm{Pd^{II}}$ and two $\mathrm{Ag^I}$ atoms in a cyclic form. The overall structure of $[\mathbf{3}]^{6+}$ is similar to that of $[\mathbf{2}]^{6+}$. In particular, the bond distances and angles around the Co and Pd atoms in $[\mathbf{3}]^{6+}$ (average lengths [Å] Co–S = 2.266(3) and Pd–S = 2.324(3)) coincide well with those found in $[\mathbf{2}]^{6+}$. However, the S-Ag-S angles (average 168.28°) in $[\mathbf{3}]^{6+}$ deviate considerably from 180° and, furthermore, the average Ag–S distance of 2.373(3) Å) in $[\mathbf{3}]^{6+}$ is about 0.09 Å longer than the average Au–S distance in $[\mathbf{2}]^{6+}$. When an aqueous solution of $[\mathbf{3}](\mathrm{NO_3})_6$ was treated with $[\mathrm{AuCl\{S(CH_2CH_2OH)_2\}}]$ at room temperature, $\mathrm{Ag^I}$ atoms in $[\mathbf{3}]^{6+}$ were replaced by $\mathrm{Au^I}$ atoms to produce $[\mathbf{2}]^{6+}$. These results imply that the $\mathrm{Co^{III}_4Pd^{II}_2Ag^{I}_2}$ octanuclear metallacycle in $[\mathbf{3}]^{6+}$ is more flexible than the $\mathrm{Co^{III}_4Pd^{II}_2Ag^{I}_2}$ metallacycle in $[\mathbf{2}]^{6+}$. The stereochemical behavior of $[\mathbf{3}]^{6+}$ is the same as that of $[\mathbf{2}]^{6+}$, forming only a pair of enantiomers, $(\Delta)_4(R)_{12}$ and $(\Lambda)_4(S)_{12}$. While $[\mathbf{3}]^{6+}$ could not be resolved by column chromatography (SP-Sephadex C-25) because of the adsorption in the column, the optically active isomer of $[\mathbf{3}]^{6+}$ was obtained by fractional crystallization of its diastereomeric salts of $[\mathrm{Sb_2}((R,R)\text{-tartrate})_2]^{2-}$. As shown in Figure 2, not only the absorption spectrum but also the CD spectrum of $(+)^{\mathrm{CD}}_{260}$-$(\Lambda)_4$-$[\mathbf{3}]^{6+}$ are very similar to that of $(+)^{\mathrm{CD}}_{260}$-$(\Lambda)_4$-$[\mathbf{2}]^{6+}$. Moreover, the ^{13}C NMR spectrum $[\mathbf{3}]^{6+}$ exhibits six methylene carbon signals, as does $[\mathbf{2}]^{6+}$. Accordingly, it is reasonable to assume that the sulfur-bridged $\mathrm{Co^{III}_4Pd^{II}_2Ag^{I}_2}$ cyclic structure of $[\mathbf{3}]^{6+}$, observed in crystal, is also retained in solution.

In summary, the reaction of *fac*(*S*)-$[\mathrm{Co(aet)_3}]$ with $\mathrm{Pd^{II}}$ in water under mild conditions gives a sulfur-bridged $\mathrm{Co^{III}Pd^{II}}$-$\mathrm{Co^{III}}$ trinuclear complex $[\mathrm{Pd\{Co(aet)_3\}_2}]^{2+}$, $[\mathbf{1}]^{2+}$. This result indicates that *fac*(*S*)-$[\mathrm{Co(aet)_3}]$ readily isomerizes to adopt a *mer*(*S*) geometry. Complex $[\mathbf{1}]^{2+}$ was found to function as a bidentate trinuclear-metalloligand toward linear $\mathrm{Au^I}$ and $\mathrm{Ag^I}$ ions, forming unprecedented octanuclear metallacycles, $[\mathrm{M^I_2\{Pd^{II}[Co^{III}(aet)_3]_2\}_2}]^{6+}$ (M = Au, Ag). These cyclic structures are fairly stable in solution and discriminate the absolute configurations of the $\mathrm{Co^{III}}$ and bridging sulfur chiral centers. Thus, optically active metallacycles with a total of 16 chiral centers are available. Finally, the present results demonstrate that a variety chiral molecular assemblages consisting of metal ions with different oxidation states and coordination geometries can be constructed by the controlled design of sulfur-bridged polynuclear structures with nonbridging thiolato sulfur atoms.

Experimental Section

$[\mathbf{1}]\mathrm{Cl_2}\cdot5\,\mathrm{H_2O}$ and $[\mathbf{1}](\mathrm{NO_3})_2\cdot1.5\,\mathrm{H_2O}$: To a stirred dark-blue suspension of *fac*(*S*)-$[\mathrm{Co(aet)_3}]$ (1.0 g, 3.5 mmol) in water (150 mL) was added $\mathrm{Na_2[PdCl_4]}$ (0.52 g, 1.8 mmol) and the mixture was stirred at 30 °C for 6 h. After removal of unreacted *fac*(*S*)-$[\mathrm{Co(aet)_3}]$ by filtration, a saturated NaCl aqueous solution (25 mL) was added to the filtrate, followed by storage at 4 °C for 1 day. The resulting dark-green powder was collected by filtration and recrystallized from water by adding a saturated NaCl aqueous solution. The nitrate salt of $[\mathbf{1}]^{2+}$ was obtained by using a saturated $\mathrm{NaNO_3}$ aqueous solution instead of a saturated NaCl aqueous solution. Yield for $[\mathbf{1}]\mathrm{Cl_2}\cdot5\,\mathrm{H_2O}$: 0.94 g (64 %); Yield for $[\mathbf{1}](\mathrm{NO_3})_2\cdot1.5\,\mathrm{H_2O}$: 1.00 g (69 %); elemental analysis for $[\mathrm{Pd\{Co(C_6H_{18}N_3S_3)_3\}_2}]\mathrm{Cl_2}\cdot5\,\mathrm{H_2O}$: calcd: C 17.16, H 5.28, N 10.01; found: C 17.44, H 5.34, N 10.09; for $[\mathrm{Pd\{Co(C_6H_{18}N_3S_3)_3\}_2}](\mathrm{NO_3})_2\cdot1.5\,\mathrm{H_2O}$: calcd: C 17.32, H 4.72, N 13.47; found: C 17.34, H 4.79, N 13.76; ^{13}C NMR (500 MHz, $\mathrm{D_2O}$, sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS)): 31.45, 34.05, 36.17 ($\mathrm{CH_2S}$), 51.86, 56.09, 57.48 ($\mathrm{CH_2N}$); UV/Vis ($\mathrm{H_2O}$): $\sigma_{\mathrm{max}}/10^3$ ($\log\varepsilon$) = 17.68 (2.75), 22.3 (3.4 sh), 29.59 (4.61), 33.5 (4.4 sh), 44.13 $\mathrm{cm^{-1}}$ (4.4 $\mathrm{M^{-1}\,cm^{-1}}$ sh).

[**2**]$Cl_6 \cdot 16\,H_2O$: To a solution of Na[$AuCl_4$] (0.10 g, 0.28 mmol) in water (2 mL) was added 2,2′-thiodiethanol (0.16 mL). The resulting colorless solution was added to a solution of [**1**]$Cl_2 \cdot 5\,H_2O$ (0.20 g, 0.24 mmol) in water (40 mL). The mixture was stirred at RT for 30 min, followed by addition of several drops of a saturated NaCl aqueous solution. The reaction solution was allowed to stand at RT for 5 days, which gave dark green-brown microcrystals. Yield: 0.22 g (82 %); elemental analysis for $[Au_2\{Pd[Co(C_6H_{18}N_3S_3)_3]_2\}_2]Cl_6 \cdot 16\,H_2O$: calcd C 12.77, H 4.64, N 7.45; found: C 12.71, H 4.69, N 7.43; ^{13}C NMR (500 MHz, D_2O, DSS): $\delta = 34.86$, 35.55, 40.40 (CH_2S), 48.44, 56.00, 57.22 (CH_2N); UV/Vis (H_2O): $\sigma_{max}/10^3$ ($\log\varepsilon$) = 18.36 (3.05), 26.91 (4.63), 30.56 (4.76), 33.6 (4.7 sh), 43.6 cm^{-1} (4.8 $\mathrm{M}^{-1}\,cm^{-1}$ sh).

[**3**]$(NO_3)_6 \cdot 9\,H_2O$: To a solution of [**1**]$(NO_3)_2 \cdot 1.5\,H_2O$ (0.20 g, 0.24 mmol) in water (40 mL), $AgNO_3$ (0.04 g, 0.24 mmol) was added. The mixture was stirred at RT for 30 min, followed by addition of several drops of a saturated aqueous $NaNO_3$. The reaction solution was allowed to stand at RT for 5 days, which gave dark green-brown microcrystals. Yield: 0.20 g (80 %); elemental analysis for $[Ag_2\{Pd[Co(C_6H_{18}N_3S_3)_3]_2\}_2](NO_3)_6 \cdot 9\,H_2O$: calcd: C 13.65, H 4.29, N 11.94; found: C 13.44, H 4.28, N 11.71; ^{13}C NMR (500 MHz, D_2O, DSS): $\delta = 33.03$, 35.21, 39.27 (CH_2S), 50.02, 55.98, 57.25 (CH_2N); UV/Vis (H_2O): $\sigma_{max}/10^3$ ($\log\varepsilon$) = 17.82 (3.00), 27.1 (4.6 sh), 30.56 (4.85), 33.8 (4.7 sh), 43.7 cm^{-1} (4.8 $\mathrm{M}^{-1}\,cm^{-1}$ sh).

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[1] a) J. M. Lehn, *Supermolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**; b) P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502; c) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005; d) M. Fujita, *Chem. Soc. Rev.* **1998**, *27*, 417; e) C. J. Jones, *Chem. Soc. Rev.* **1998**, *27*, 289; f) B. Olenyuk, A. Fechtenkötter, P. J. Stang, *J. Chem. Soc. Dalton Trans.* **1998**, *11*, 1707; g) D. L. Caulder, K. N. Raymond, *J. Chem. Soc. Dalton Trans.* **1999**, 1185; h) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117; i) J. A. R. Navarro, B. Lippert, *Coord. Chem. Rev.* **1999**, *185–186*, 653.

[2] a) R. H. Lane, N. S. Pantaleo, J. K. Farr, W. M. Coney, M. G. Newton, *J. Am. Chem. Soc.* **1978**, *100*, 1610; b) M. J. Heeg, R. C. Elder, E. Deutsch, *Inorg. Chem.* **1979**, *18*, 2036; c) M. J. Heeg, R. C. Elder, E. Deutsch, *Inorg. Chem.* **1980**, *19*, 554.

[3] a) T. Konno, K. Okamoto, J. Hidaka, *Inorg. Chem.* **1992**, *31*, 160; b) T. Konno, J. Hidaka, K. Okamoto, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1353; c) T. Konno, K. Okamoto, *Chem. Lett.* **1996**, 975; d) T. Konno, T. Machida, K. Okamoto, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 175; e) T. Konno, N. Matsuno, K. Okamoto, M. Hirotsu, *Chem. Lett.* **1999**, 1243.

[4] a) D. H. Busch, D. C. Jicha, *Inorg. Chem.* **1962**, *1*, 884; b) G. R. Brubaker, B. E. Douglas, *Inorg. Chem.* **1967**, *6*, 1562; c) R. E. DeSimone, T. Ontko, L. Wardman, E. L. Blinn, *Inorg. Chem.* **1975**, *14*, 1313; d) M. J. Heeg, E. L. Blinn, E. Deutsch, *Inorg. Chem.* **1985**, *24*, 1118; e) T. Konno, K. Okamoto, J. Hidaka, *Acta Crystallogr. Sect. C* **1993**, *49*, 222; f) T. Konno, K. Namamura, K. Okamoto, J. Hidaka, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2582; g) T. Konno, K. Okamoto, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 610.

[5] a) K. Okamoto, T. Konno, Y. Kageyama, J. Hidaka, *Chem. Lett.* **1992**, 1105; b) K. Okamoto, Y. Kageyama, T. Konno, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2573; c) T. Konno, K. Okamoto, *Inorg. Chem.* **1997**, *36*, 1403; d) T. Konno, K. Tokuda, T. Suzuki, K. Okamoto, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1049.

[6] a) T. Konno, K. Okamoto, J. Hidaka, *Inorg. Chem.* **1991**, *30*, 2253; b) T. Konno, T. Nagashio, K. Okamoto, J. Hidaka, *Inorg. Chem.* **1992**, *31*, 1160; c) K. Okamoto, T. Konno, J. Hidaka, *J. Chem. Soc. Dalton Trans.* **1994**, 533; d) T. Konno, K. Okamoto, J. Hidaka, *Inorg. Chem.* **1994**, *33*, 538.

[7] a) T. Konno, S. Aizawa, K. Okamoto, J. Hidaka, *Chem. Lett.* **1985**, 1017; b) K. Okamoto, S. Aizawa, T. Konno, E. Einaga, J. Hidaka, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3859; c) S. Aizawa, K. Okamoto, E. Einaga, J. Hidaka, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1601; d) T. Konno, K. Okamoto, J. Hidaka, *Inorg. Chem.* **1992**, *31*, 3875; e) T. Konno, K. Okamoto, J. Hidaka, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 101; f) T. Konno, C. Sasaki, K. Okamoto, *Chem. Lett.* **1996**, 977; g) K. Okamoto, C. Sasaki, Y. Yamada, T. Konno, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1685.

[8] B.-L. Chen, K.-F. Mok, S.-C. Ng, *J. Chem. Soc. Dalton Trans.* **1998**, 4035.

[9] Crystal structure analysis: General: Bruker CCD area detector, $T = 203$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), semiempirical absorption correction with SADABS. The structures were solved by direct methods (SIR 92) and refined with full-matrix least-squares procedures on F^2 using SHELXL-93. [**2**]$Cl_6 \cdot 16\,H_2O$: crystal size $0.10 \times 0.09 \times 0.08$ mm, orthorhombic, space group *Pbcn*, $a = 18.888(2)$, $b = 13.397(1)$, $c = 28.211(2)$ Å, $V = 7138.6(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.100\ g\,cm^{-3}$, $\mu = 61.40\ cm^{-1}$, ω scan mode, $2\theta_{max} = 55.18$, 7869 reflections collected, 7869 independent reflections, 5102 observed reflections ($F > 4\sigma(F)$), 352 parameters, semiempirical absorption correction with SADABS, max./min. transmission 0.647/0.547, R_1 ($F > 4\sigma(F)$) = 0.038, wR_2 (all data) = 0.133, residual electron density 2.22/−1.43 e Å^{-3} (the peaks larger than 1.0 e Å^{-3} were found in the vicinity of heavy atoms). Hydrogen atoms except those of water molecules were placed at calculated positions but were not refined. [**3**]$(NO_3)_6 \cdot 9\,H_2O$: crystal size $0.25 \times 0.13 \times 0.10$ mm, monoclinic, space group *Pn*, $a = 22.3703(4)$, $b = 13.9570(7)$, $c = 23.4220(4)$ Å, $\beta = 107.633(1)°$, $V = 6969.3(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.013\ g\,cm^{-3}$, $\mu = 24.23\ cm^{-1}$, ω scan mode, $2\theta_{max} = 55.28$, 22 370 reflections collected, 16 071 independent reflections, 13 955 observed reflections ($F > 4\sigma(F)$), 352 parameters, semiempirical absorption correction with SADABS, max./min. transmission 0.746/0.473, R_1 ($F > 4\sigma(F)$) = 0.042, wR_2 (all data) = 0.127, residual electron density 1.15/−0.83 e Å^{-3} (the peaks larger than 1.0 e Å^{-3} were found in the vicinity of heavy atoms and nitrate anions). The asymmetric unit contained two crystallographically independent, yet nearly identical, complex cations [**3**]$^{6+}$. Hydrogen atoms were not included in the calculations. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144580 ([**2**]$Cl_6 \cdot 16\,H_2O$) and -144581 ([**3**]$(NO_3)_6 \cdot 9\,H_2O$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Proton-Coupled Electron Transfer from Sulfur: A S-H/S-D Kinetic Isotope Effect of ≥ 31.1**

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There is an extensive redox chemistry of high oxidation state ruthenium(IV) oxo,[1] and osmium(VI) nitrido,[2] and osmium(IV–VI) hydrazido[3] complexes based on multiple electron/atom transfers such as O atom,[4] N^- ion,[3] and H^-

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