Angew. Chem. **1992**, *104*, 799; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 787; d) F. Canales, M. C. Gimeno, A. Laguna, P. G. Jones, *J. Am. Chem. Soc.* **1996**, *118*, 4839; e) S. Canales, O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, F. Mendizabal, *Organometallics* **2000**, *19*, 4985.

[5] D. Fenske, T. Langetepe, M. M. Kappes, O. Hampe, P. Weis, *Angew. Chem.* **2000**, *112*, 1925; *Angew. Chem. Int. Ed.* **2000**, *39*, 1857.

[6] **1**: Elemental analysis calcd (found) for $[Au_6\{Ph_2PN(CH_3C_6H_4)PPh_2\}_3S_2](ClO_4)_2\cdot 2CH_2Cl_2$: C 37.52 (37.49), H 2.82 (2.52), N 1.38 (1.34). Positive-ion FAB-MS: ion cluster at m/z 2772 $[M - ClO_4]^+$; positive-ion ESI-MS: ion cluster at m/z 2772 $[M - ClO_4]^+$, m/z 1336 $[M - 2ClO_4]^{2+}$; negative-ion ESI-MS: ion cluster at m/z 99 $[ClO_4]^-$; ^1H NMR (500 MHz, $[D_6]$acetone, 298 K): $\delta = 2.02$ (s, 9H, CH_3), 6.16 (d, 6H, $J = 8.3$ Hz, *o*-H of NAr), 6.61 (d, 6H, $J = 8.3$ Hz, *m*-H of NAr), 7.28–7.31 (m, 24H, PPh_2), 7.43–7.46 (m, 18H, PPh_2), 7.65–7.74 (m, 18H, PPh_2); $^{31}P\{^1H\}$ NMR (202 MHz, $[D_6]$acetone, 298 K): $\delta = 82.7$.

[7] Crystal data for **1**: $C_{93}H_{81}Au_6Cl_2N_3O_8P_6S_2$, $M_r = 2871.25$, cubic, space group $I2_13$ (No. 199), $a = 36.465(4)$ Å, $V = 48487(9)$ Å^3, $Z = 12$, $\rho_{calcd} = 1.180$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 5.576$ mm^{-1}, $F(000) = 16248$, $T = 301$ K. 43580 reflections measured, of which 8604 were unique ($R_{int} = 0.1570$) and were used in all calculations. Final $R = 0.0842$ (for observed data with $I > 2\sigma(I)$). 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-155449. 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).

[8] B.-C. Tzeng, C.-K. Chan, K.-K. Cheung, C.-M. Che, S.-M. Peng, *Chem. Commun.* **1997**, 135.

[9] L. Hao, M. A. Mansour, R. J. Lachicotte, H. J. Gysling, R. Eisenberg, *Inorg. Chem.* **2000**, *39*, 5520.

[10] J. M. Forward, D. Bohmann, J. P. Fackler, Jr., R. J. Staples, *Inorg. Chem.* **1995**, *34*, 6330.

[11] a) A. Vogler, H. Kunkely, *J. Am. Chem. Soc.* **1986**, *108*, 7211; b) K. R. Kyle, C. K. Ryu, J. A. DiBenedetto, P. C. Ford, *J. Am. Chem. Soc.* **1991**, *113*, 2954; c) P. C. Ford, E. Cariati, J. Bourassa, *Chem. Rev.* **1999**, *99*, 3625.

First Diastereomerically Controlled Aggregation of L-Cysteinato Cobalt(III) Octahedra, Assisted by Silver(I) Ions

Takumi Konno,* Takashi Yoshimura, Kazumi Aoki, Ken-ichi Okamoto, and Masakazu Hirotsu

During the past decade considerable progress has been made in the design and creation of supramolecular systems.[1] While the majority of supramolecular species have been constructed from organic ligands and metal ions by spontaneous self-assembly, our strategy is to use metal thiolate complexes as building blocks which can aggregate by forming S-bridged structures with a variety of metal ions.[2] In particular, we are interested in the aggregation of tris(chelate)-type octahedral complexes with simple bidentate *N,S*-thiolate ligands such as 2-aminoethanethiolate (aet = $NH_2CH_2CH_2S^-$) and L-cysteinate (L-cys = $NH_2CH(COO^-)CH_2S^-$), with the aim of creating chiral supramolecular architectures.[3] To date, a number of chiral aggregates based on the octahedral $[M(aet)_3]$ unit (M = Co^{III}, Rh^{III}, Ir^{III}) with three thiolate donors, such as trinuclear $[Co^{III}\{M(aet)_3\}_2]^{3+}$,[4] pentanuclear $[Ag^I_3\{M(aet)_3\}_2]^{3+}$,[5] and octanuclear $[Zn^{II}_4O\{M(aet)_3\}_4]^{6+}$,[6] as well as analogous aggregates based on the $[M(\text{L-cys-}N,S)_3]^{3-}$ unit, have been prepared, and their unique stereochemical, spectroscopic, and redox properties have been extensively studied. In contrast, the aggregation of octahedral complex units with a single thiolate donor has been studied far less; only a few trinuclear and tetranuclear species such as $[Co(aet)(en)_2]^{2+}$ or $[Co(SCH_2COO)(en)_2]^+$ (en = $NH_2CH_2CH_2NH_2$) have been reported.[7]

To expand the range of chiral supramolecular architectures based on octahedral complex units with thiolate donors, it is desirable to find the key factors that control their aggregation by studying the fundamental $[Co^{III}(\text{thiolato-}S)(\text{amine-}N)_5]$ system. We therefore started by investigating the aggregation of $[Co(aet)(en)_2]^{2+}$ and $[Co(\text{L-cys-}N,S)(en)_2]^+$ assisted by metal ions. Recently, we found that the reaction of racemic $[Co(aet)(en)_2]^{2+}$ with $AgNO_3$ in a 1:1 ratio gives an S-bridged $Co^{III}Ag^I$ coordination polymer having a one-dimensional infinite zigzag chain structure, namely, $\{[Ag\{Co(aet)(en)_2\}](NO_3)_3\}_\infty$.[8] Interestingly, the chain structure discriminated the chiral configuration (Λ or Δ) of $[Co(aet)(en)_2]^{2+}$ to give exclusively the enantiomeric $(\Lambda\text{-}Co^{III}Ag^I)_\infty$ and $(\Delta\text{-}Co^{III}Ag^I)_\infty$ chains, which separate from one another as homochiral crystals. Given this result, we expected that similar $(Co^{III}Ag^I)_\infty$ chiral chain structures would be formed on using the Λ_L or Δ_L diastereomer of $[Co(\text{L-cys-}N,S)(en)_2]^+$ instead of racemic $[Co(aet)(en)_2]^{2+}$. Indeed, we found that the reactions of Λ_L- or Δ_L-$[Co(\text{L-cys-}N,S)(en)_2]^+$ with $AgNO_3$ lead to the formation of fascinating chiral supramolecular structures, which are markedly dependent on whether the Λ_L or Δ_L diastereomer is used (Scheme 1).

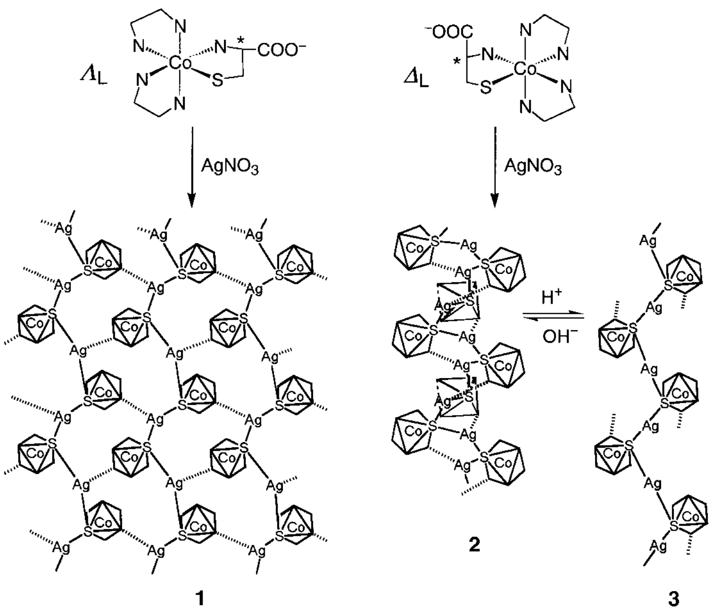
Treatment of a dark brown aqueous solution of Λ_L-$[Co(\text{L-cys-}N,S)(en)_2](ClO_4)$[9] with $AgNO_3$ in a 1:1 ratio at room temperature gave a dark red solution, from which red plate crystals of **1** were isolated by adding an aqueous solution of $NaNO_3$. The electronic absorption spectrum of **1** in water is characterized by an intense S-to-Co charge-transfer (CT) band at 288 nm and a first d–d absorption band at 497 nm. The disappearance of a distinct shoulder at ca. 560 nm in the first d–d band of the starting material Λ_L-$[Co(\text{L-cys-}N,S)(en)_2]^+$ is indicative of coordination of the thiolate S atom to an Ag^I ion.[7b, 8] Plasma emission spectral analysis indicated that **1** contains Co and Ag atoms in a 1:1 ratio, and the elemental analysis was consistent with the 1:1 stoichiometry of $[Co(\text{L-cys})(en)_2](NO_3)\cdot AgNO_3$.

The crystal structure of **1**, determined by X-ray analysis, revealed the presence of an asymmetric unit consisting of one octahedral Λ_L-$[Co(\text{L-cys-}N,S)(en)_2]^+$ unit and one Ag^I ion

---

[*] Prof. T. Konno, Dr. T. Yoshimura, K. Aoki, Dr. M. Hirotsu
Department of Chemistry, Faculty of Engineering
Gunma University
Kiryu, Gunma 376-8515 (Japan)
Fax: (+81)277-30-1263
E-mail: konno@ch.wani.osaka-u.ac.jp

Prof. K. Okamoto
Department of Chemistry
University of Tsukuba
Tsukuba, Ibaraki 305-8571 (Japan)



Scheme 1. Synthesis of **1**, **2**, and **3**.

(Figure 1 a), besides two nitrate anions.[10] In the complex cation of **1**, the thiolate S atom of each octahedral Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ unit is bound to two Ag$^\mathrm{I}$ ions to form a one-dimensional zigzag $(\mathrm{Co^{III}Ag^{I}})_\infty$ chain structure (Co–S 2.263(3), Ag–S 2.501(3) and 2.511(3) Å). This chain structure resembles that found in $\{[\mathrm{Ag}\{\mathrm{Co(aet)(en)_2}\}](\mathrm{NO_3})_3\}_\infty$ (Co–S 2.287(2), Ag–S 2.532(2) and 2.546(2) Å).[8] However, the S-Ag-S angle in **1** deviates significantly from 180° (149.62(7)8°); in contrast the S-Ag-S angle in $\{[\mathrm{Ag}\{\mathrm{Co(aet)(en)_2}\}](\mathrm{NO_3})_3\}_\infty$ is 173.14(6)°. A detailed inspection of the extended structure of **1** revealed that the COO$^-$ group of each Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ unit, which adopts an equatorial orientation, chelates an Ag$^\mathrm{I}$ ion of the adjacent zigzag chain (Ag–O2 2.490(8), Ag–O1 2.598(1) Å; O1-Ag-O2 51.1(3)°). Thus, the $(\mathrm{Co^{III}Ag^{I}})_\infty$ chains are connected with one another by Ag–O bonds to form a two-dimensional extended sheetlike structure composed of cyclic $\mathrm{Co_3^{III}Ag_3^{I}}$ units (Figure 2).

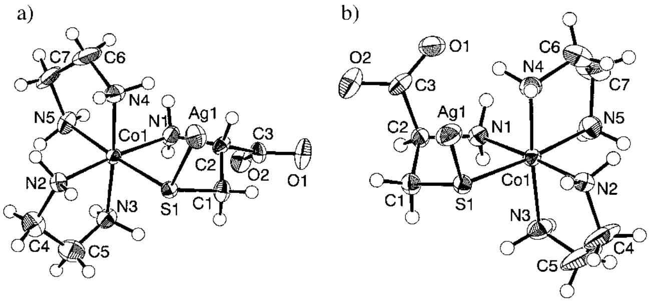


Figure 1. ORTEP plots of the complex cations (asymmetric units) of **1** (a) and **2** (b).

A similar 1:1 reaction of the Δ_L diastereomer of [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ with AgNO$_3$ produced dark red prismatic crystals of **2**. While the absorption spectrum of **2** in water is very similar to that of **1**, its CD spectral feature is significantly different, especially in the d–d absorption band region, and this reflects a difference in configuration at the Co$^\mathrm{III}$ ion. Along with the elemental and plasma emission spectral analyses, which were in good agreement with the formula for the 1:1 adduct Δ_L-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}](NO$_3$)$_2$, the structure of **2** was established by X-ray analysis.[10] As shown in Figure 3, the complex cation of **2** is a one-dimensional helical coordination polymer consisting of asymmetric Δ_L-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}]$^{2+}$ units. The thiolate S atom of each octahedral Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ unit is bound to two Ag$^\mathrm{I}$ ions to form an infinite $(\mathrm{Co^{III}Ag^{I}})_\infty$ chain (Co–S 2.251(2), Ag–S 2.550(2) and 2.553(2) Å), as in the case of **1**. However,

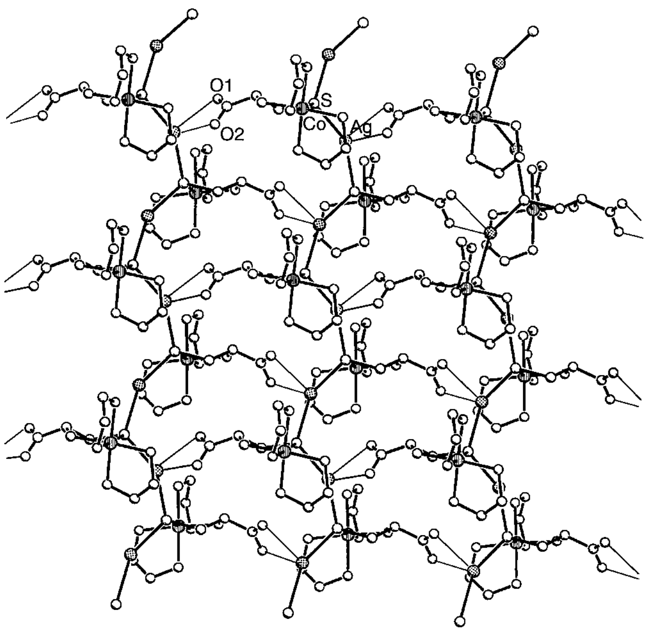


Figure 2. View of the complex cation of **1**. Hydrogen atoms are omitted for clarity.

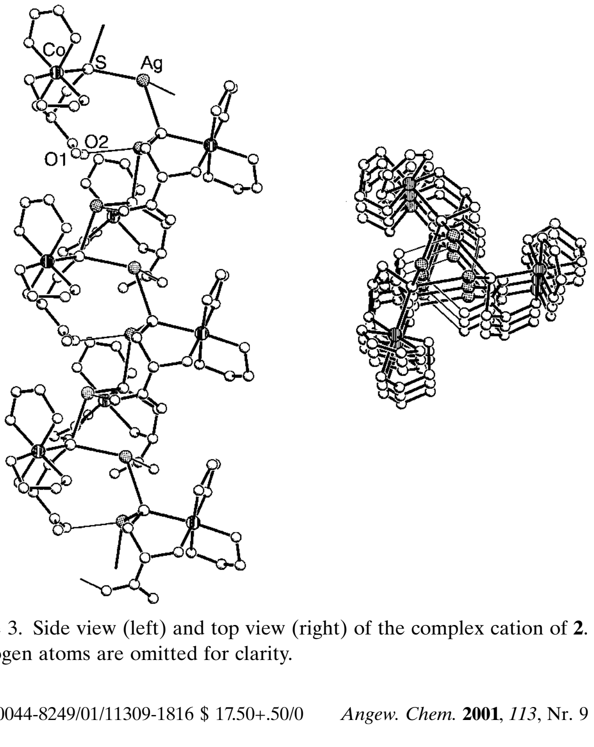


Figure 3. Side view (left) and top view (right) of the complex cation of **2**. Hydrogen atoms are omitted for clarity.

each Ag^I ion is weakly coordinated by the COO^- group of the Δ_L-[Co(L-cys-*N,S*)(en)$_2$]$^+$ unit attached to the same chain (Ag–O2 2.539(6) Å), besides the two S atoms of two different Δ_L-[Co(L-cys-*N,S*)(en)$_2$]$^+$ units, so that the chain forms a left-handed helical structure around the crystallographic 3_2 screw axis. In contrast to **1**, the COO^- group of the Δ_L-[Co(L-cys-*N,S*)(en)$_2$]$^+$ unit in **2** adopts an axial orientation (Figure 1b), which is responsible for the remarkable difference in aggregation of the octahedral [Co(L-cys-*N,S*)(en)$_2$]$^+$ units with Ag^I ions.

Besides their different structures, **1** and **2** exhibited different reactivity toward acid. The addition of HNO_3 to an aqueous solution of **2** produced pink microcrystalline needles of **3**, while treatment of **1** with HNO_3 in water resulted in its recrystallization. Aggregate **3** could also be prepared directly by the 1:1 reaction of Δ_L-[Co(L-Hcys-*N,S*)(en)$_2$](ClO$_4$)$_2$ with $AgNO_3$ in water followed by addition of HNO_3. The IR spectrum of **3** exhibits a relatively sharp COO stretching band at 1732 cm^{-1}, as opposed to the broad COO stretching band centered at 1598 cm^{-1} for **2**. This IR band of **3** is characteristic of a COOH group,[11] and elemental and plasma emission spectral analyses were in good agreement with the formula for the protonated 1:1 adduct Δ_L-[Ag{Co(L-Hcys)(en)$_2$}](NO$_3$)$_3$. In the solid-state absorption spectrum (Nujol paste), **3** shows a first d–d absorption band at nearly the same position (502 nm) as **2** (499 nm). Since the $Co^{III}Ag^ICo^{III}$ trinuclear complex having μ_2-thiolate donors, Δ_L,Δ_L-[Ag{Co(L-cys)(en)$_2$}$_2$]$^{3+}$,[12] exhibits the first d–d absorption band at shorter wavelength of 488 nm, we believe that the S atom of each Co^{III} complex unit in **3** is bound to two Ag^I ions in a μ_3-thiolate mode, as in **2**. However, the protonated COOH group of each Co^{III} unit would not coordinate to bridging Ag^I ion in a $(Co^{III}Ag^I)_\infty$ chain structure. Hence we assume that **3** has a one-dimensional zigzag chain structure like that found in {[Ag{Co(aet)(en)$_2$}](NO$_3$)$_3$}$_\infty$,[8] rather than a helical structure, as in **2**.[13] Interestingly, when an aqueous solution of **3** was neutralized with NaOH, red prismatic crystals of **2** were regenerated. This result obviously indicates that **3** reverts to the helical structure of **2** on changing the pH of the solution (Scheme 1).

In summary, the facile reactions of Δ_L- or Δ_L-[Co(L-cys-*N,S*)(en)$_2$]$^+$ with $AgNO_3$ gave the unique $Co^{III}Ag^I$ coordination polymers **1** and **2**, respectively. While **1** has a two-dimensional sheetlike structure, **2** forms one-dimensional left-handed helices.[14] Compound **2** undergoes reversible conversion to **3**, which is assumed to have a one-dimensional zigzag structure that retains the Δ_L configuration of the Co^{III} complex unit. Although a variety of helical coordination polymers have been prepared from organic ligands and metal ions,[15] only one report has appeared on the interconversion of the helical and nonhelical chain structures.[15k] Furthermore, **2** is a rare example of heterometallic helix in which left-handed helicity is predetermined by the chiral configuration of the L-cys ligand in Δ_L-[Co(L-cys-*N,S*)(en)$_2$]$^+$. The polymeric structures in **1** and **2** are comparable with the secondary structures of proteins: the β-sheet and α-helix, respectively. Finally, the present results demonstrate that the construction of highly organized chiral molecular architectures can be achieved by the introduction of simple L-cys ligands with free COO^- groups in an octahedral complex unit, and that their overall topology is controlled by the diastereomerism of the complex unit and conditions of reaction with Ag^I ions.

Experimental Section

1: An aqueous solution of $AgNO_3$ (0.09 g, 0.53 mmol) was added to a dark brown solution of Δ_L-[Co(L-cys-*N,S*)(en)$_2$](ClO$_4$)[9] (0.20 g, 0.50 mmol) in water (90 mL), and the mixture was stirred at room temperature for 30 min. After addition of an aqueous solution of $NaNO_3$ (0.50 g), the dark red reaction solution was stored at 4 °C for 1 d. The resulting red crystalline product was collected by filtration and recrystallized from water by adding a saturated aqueous solution of $NaNO_3$. Yield: 0.23 g (83 %); elemental analysis calcd for $[Ag\{Co(C_3H_5NO_2S)(C_2H_8N_2)_2\}](NO_3)_2\cdot H_2O$: C 15.34, H 4.23, N 17.89; found: C 15.34, H 4.28, N 17.87; UV/Vis (H_2O): $\sigma_{max}/10^3$ ($\lg\varepsilon$) = 20.13 (2.28), 28.6 (3.1, sh), 34.75 cm^{-1} (4.12 M^{-1}cm^{-1}); CD (H_2O): $\sigma_{ext}/10^3$ ($\Delta\varepsilon$) = 18.47 (+2.13), 21.11 (−0.45), 24.22 (+1.06), 29.04 (−1.08), 35.11 (−9.71), 41.91 cm^{-1} (−5.75 M^{-1}cm^{-1}).

2: An aqueous solution of $AgNO_3$ (0.07 g, 0.41 mmol) was added to a dark red solution containing Δ_L-[Co(L-Hcys-*N,S*)(en)$_2$](ClO$_4$)$_2\cdot H_2O$[9] (0.20 g, 0.38 mmol) in water (20 mL) and a 0.25 M aqueous solution of NaOH (1.5 mL), and the mixture was stirred at room temperature for 40 min. After addition of an aqueous solution of $NaNO_3$ (0.33 g), the dark red reaction solution was allowed to stand at room temperature for 3 d. The resulting red prismatic crystals were collected by filtration. Yield: 0.19 g (85 %); elemental analysis calcd for $[Ag\{Co(C_3H_5NO_2S)(C_2H_8N_2)_2\}](NO_3)_2\cdot \frac{8}{3}H_2O$: C 14.54, H 4.59, N 16.96; found: C 14.46, H 4.43, N 16.68; UV/Vis (H_2O): $\sigma_{max}/10^3$ ($\lg\varepsilon$) = 20.00 (2.16), 28.3 (2.4, sh), 34.84 cm^{-1} (4.04 M^{-1}cm^{-1}); CD (H_2O): $\sigma_{ext}/10^3$ ($\Delta\varepsilon$) = 19.47 (−2.81), 24.66 (+2.59), 34.66 (−13.9), 47.51 cm^{-1} (20.3 M^{-1}cm^{-1}).

3: An aqueous solution of $AgNO_3$ (0.07 g, 0.41 mmol) was added to a dark brown solution of Δ_L-[Co(L-Hcys-*N,S*)(en)$_2$](ClO$_4$)$_2\cdot H_2O$[9] (0.20 g, 0.38 mmol) in water (20 mL), and the mixture was stirred at room temperature for 40 min. After addition of a 1.0 M aqueous solution of HNO_3 (4 mL), the dark red reaction solution was allowed to stand at room temperature for 3 h. The resulting pink microcrystalline needles were collected by filtration. Yield: 0.18 g (74 %); elemental analysis calcd for $[Ag\{Co(C_3H_6NO_2S)(C_2H_8N_2)_2\}](NO_3)_3\cdot 2.5\,H_2O$: C 13.17, H 4.26, N 17.56; found: C 13.21, H 4.29, N 17.40; UV/Vis (H_2O): $\sigma_{max}/10^3$ ($\lg\varepsilon$) = 19.98 (2.17), 28.3 (2.4, sh), 34.84 cm^{-1} (4.07 M^{-1}cm^{-1}); CD (H_2O): $\sigma_{ext}/10^3$ ($\Delta\varepsilon$) = 19.46 (−2.93), 24.66 (+2.70), 34.36 (−19.6), 46.95 cm^{-1} (17.2 M^{-1}cm^{-1}). This complex was also prepared by adding a 1.0 M aqueous solution of HNO_3 (1 mL) to a solution of **2** (0.09 g) in water (15 mL), and allowing the mixture to stand at 4 °C for 1 d. Yield: 0.08 g (81 %). When an acidic solution of $\mathbf{3}\cdot 2.5\,H_2O$ (0.20 g) in water (20 mL) was neutralized with a 0.25 M aqueous solution of NaOH, and the mixture was kept at 4 °C for one week, red prismatic crystals of **2** formed. Yield: 0.12 g (66 %).

Received: December 4, 2000 [Z16212]

---

[1] a) J. M. Lehn, *Supramolecular 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**, 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; j) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853; k) G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483.

[2] a) T. Konno, K. Yonenobu, J. Hidaka, K. Okamoto, *Inorg. Chem.* **1994**, *33*, 861; b) K. Tokuda, K. Okamoto, T. Konno, *Inorg. Chem.* **2000**, *39*, 333; c) T. Konno, M. Hattori, T. Yoshimura, M. Hirotsu, *Chem. Lett.* **2000**, 852.

[3] T. Konno, Y. Chikamoto, K. Okamoto, T. Yamaguchi, T. Ito, M. Hirotsu, *Angew. Chem.* **2000**, *112*, 4264; *Angew. Chem. Int. Ed.* **2000**, *39*, 4098.

[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) M. J. Heeg, E. L. Blinn, E. Deutsch, *Inorg. Chem.* **1985**, *24*, 1118; d) T. Konno, S. Aizawa, K. Okamoto, J. Hidaka, *Chem. Lett.* **1985**, 1017; e) K. Okamoto, S. Aizawa, T. Konno, E. Einaga, J. Hidaka, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3859; f) T. Konno, S. Aizawa, K. Okamoto, J. Hidaka, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 792; g) T. Konno, K. Namamura, K. Okamoto, J. Hidaka, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2582.

[5] a) T. Konno, K. Okamoto, *Inorg. Chem.* **1997**, *36*, 1403; b) 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) 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.

[8] T. Konno, K. Tokuda, K. Okamoto, M. Hirotsu, *Chem. Lett.* **2000**, 1258.

[9] H. C. Freeman, C. J. Moore, W. G. Jackson, A. M. Sargeson, *Inorg. Chem.* **1978**, *17*, 3513.

[10] Crystal structure analysis: General: Rigaku AFC7S diffractometer, $T = 23\,^{\circ}\mathrm{C}$, $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). The structures were solved by direct methods (SIR92 for **1** and SHELXS-86 for **2**) and refined by full-matrix least-squares methods on F^2 by using SHELXL-93. Hydrogen atoms, except for those of water molecules, were placed at calculated positions but were not refined. The absolute structures for **1** and **2** were determined on the basis of the known *R* configuration of the asymmetric carbon atom in the L-cys ligand and were confirmed by the Flack parameters (−0.10(6) for **1** and 0.03(3) for **2**). **1**: $C_7H_{23}AgCoN_7O_9S$, crystal dimensions $0.10 \times 0.15 \times 0.15$ mm, orthorhombic, space group $P2_12_12_1$, $a = 8.037(4)$, $b = 8.056(3)$, $c = 26.648(6)$ Å, $V = 1725.4(9)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 2.110\ \mathrm{g\,cm^{-3}}$, $\mu = 22.75\ \mathrm{cm^{-1}}$, $\omega/2\theta$ scan mode, $2\theta_{\max} = 55.0$, 2298 reflections collected, 2296 independent reflections, 1815 observed reflections ($F > 4\sigma(F)$), 235 parameters, empirical absorption corrections based on ψ scans, max./min. transmission 0.992/0.882, $R_1 = 0.054$ ($F > 4\sigma(F)$), $wR_2 = 0.155$ (all data), residual electron density 3.04/−1.24 e Å^{-3} (peaks larger than 1.0 e Å^{-3} were found in the vicinity of heavy atoms). **2**: $C_7H_{26.33}AgCoN_7O_{10.67}S$, crystal dimensions $0.13 \times 0.14 \times 0.60$ mm, trigonal, space group $R3$, $a = 24.115(3)$, $c = 8.417(3)$ Å, $V = 4238(1)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.812\ \mathrm{g\,cm^{-3}}$, $\mu = 18.63\ \mathrm{cm^{-1}}$, $\omega/2\theta$ scan mode, $2\theta_{\max} = 55.0$, 2398 reflections collected, 2170 independent reflections, 2076 observed reflections ($F > 4\sigma(F)$), 268 parameters, empirical absorption corrections based on ψ scans, max./min. transmission 0.997/0.916, $R_1 = 0.038$ ($F > 4\sigma(F)$), $wR_2 = 0.116$ (all data), residual electron density 0.84/−0.70 e Å^{-3}. 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-153429 (**1**) and CCDC-153430 (**2**). 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] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, **1997**.

[12] The 2:1 reaction of Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$](ClO$_4$) with AgClO$_4$ in water gave the 2:1 adduct Λ_L,Λ_L-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$](ClO$_4$)$_3 \cdot 4\,H_2O$ (**4**). X-ray analysis demonstrated that in the complex cation of **4**, the central Ag^{I} ion is coordinated by two thiolate S atoms of two octahedral Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units to form an S-bridged Co^{III}Ag^{I}Co^{III} trinuclear structure (Ag−S 2.393(1), Co−S 2.263(1) Å; S-Ag-S 172.39(6)°). The corresponding 2:1 adduct Δ_L,Δ_L-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$](ClO$_4$)$_3 \cdot 4\,H_2O$ (**5**) was prepared by using Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2 \cdot H_2O$ instead of Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$](ClO$_4$). It was confirmed that **5** also has an S-bridged Co^{III}Ag^{I}Co^{III} trinuclear structure, from its elemental and plasma emission spectral analyses, electronic absorption and CD spectra, and molar conductivity in water (303 Ω cm^2 mol^{-1}), which is in good agreement with that of **4** (307 Ω cm^2 mol^{-1}).

[13] In agreement with this assumption, a noticeable difference was observed in the solid-state CD spectra (Nujol paste) of **2** and **3**, though their CD spectra in water are essentially identical; **2** exhibits a major negative CD band at 521 nm in the solid state, while the corresponding negative band of **3** appears at much longer wavelength of 551 nm.

[14] As indicated by one of the referees, the solid-state structures of **1** and **2** would not be retained in solution; conversion to monomers and/or oligomers would result from cleavage of Ag−S and Ag−O bonds. This is suggested by the fact that the CD spectra of **1** and **2** in water are very similar to those of **4** and **5**, respectively.

[15] a) T. Suzuki, H. Kotsuki, K. Isobe, N. Moriya, Y. Nakagawa, M. Ochi, *Inorg. Chem.* **1995**, *34*, 530; b) S. R. Batten, B. F. Hoskins, R. Robson, *Angew. Chem.* **1997**, *109*, 652; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 636; c) C. A. Hester, R. G. Baughman, H. L. Collier, *Polyhedron* **1997**, *16*, 2893; d) L. Carlucci, G. Ciani, D. W. V. Gudenberg, D. M. Proserpio, *Inorg. Chem.* **1997**, *36*, 3812; e) C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton, A. H. White, *Angew. Chem.* **1998**, *110*, 970; *Angew. Chem. Int. Ed.* **1998**, *37*, 920; f) M.-L. Tong, X.-M. Chen, B.-H. Ye, S. W. Ng, *Inorg. Chem.* **1998**, *37*, 5278; g) K. R. Reddy, M. V. Rajasekharan, J.-P. Tuchagues, *Inorg. Chem.* **1998**, *37*, 5978; h) R. Bau, *J. Am. Chem. Soc.* **1998**, *120*, 9380; i) K. Biradha, C. Seward, M. J. Zaworotko, *Angew. Chem.* **1999**, *111*, 584; *Angew. Chem. Int. Ed.* **1999**, *38*, 492; j) H. Kumagai, K. Inoue, *Angew. Chem.* **1999**, *111*, 1694; *Angew. Chem. Int. Ed.* **1999**, *38*, 1601; k) T. Ezuhara, K. Endo, Y. Aoyama, *J. Am. Chem. Soc.* **1999**, *121*, 3279; l) O. Mamula, A. V. Zelewsky, T. Bark, G. Bernardinelli, *Angew. Chem.* **1999**, *111*, 3129; *Angew. Chem. Int. Ed.* **1999**, *38*, 2945; m) M. C. Hong, W. P. Su, R. Cao, M. Fujita, J. X. Lu, *Chem. Eur. J.* **2000**, *6*, 427; n) Y. Zhang, J. Li, J. Chen, Q. Su, W. Deng, M. Nishiura, T. Imamoto, X. Wu, Q. Wang, *Inorg. Chem.* **2000**, *39*, 2330; o) W. W. Ellis, M. Schmitz, A. A. Arif, P. J. Stang, *Inorg. Chem.* **2000**, *39*, 2547; p) E. Colacio, M. Ghazi, R. Kiveskas, J. M. Moreno, *Inorg. Chem.* **2000**, *39*, 2882; q) S. Sailaja, M. V. Rajasekharan, *Inorg. Chem.* **2000**, *39*, 4586.

Diiron Azadithiolates as Models for the Iron-Only Hydrogenase Active Site: Synthesis, Structure, and Stereoelectronics[**]

Joshua D. Lawrence, Hongxiang Li,
Thomas B. Rauchfuss,[*] Marc Bénard,[*] and
Marie-Madeleine Rohmer

The active site of the Fe-only hydrogenases (FeH's)[1, 2] resemble archetypal [$Fe_2(SR)_2(CO)_6$] derivatives first reported by Reihlen in 1928[3] and feature four unusual ligands: CO, CN$^-$, [$(RS)_3Fe_4S_4(SR)$], and a unique organic dithiolate cofactor. Recent work has suggested that this dithiolate is

---

[*] Prof. Dr. T. B. Rauchfuss, J. D. Lawrence, Dr. H. Li
School of Chemical Sciences
University of Illinois
Urbana, IL 61801 (USA)
Fax: (+1) 217-333-2685
E-mail: rauchfuz@uiuc.edu

Dr. M. Bénard, Dr. M.-M. Rohmer
Laboratoire de Chemie Quantique, UMR 7551, CNRS and
Université Louis Pasteur
67000 Strasbourg (France)
Fax: (+33) 3-88-61-20-85
E-mail: benard@quantix.u-strasbg.fr

[**] This research was supported by the NIH and the Centre Universitaire et Régional de Ressources Informatiques of ULP and CNRS.

0044-8249/01/11309-1818 $ 17.50+.50/0