Inorg. Chem. **2007**, *46*, 1532–1534

Inorganic Chemistry
Communication

Deliberate Design of a 3D Homochiral Cu^{II}/L-met/Ag^{I} Coordination Network Based on the Distinct Soft–Hard Recognition Principle

Tzuoo-Tsair Luo,[†] Liang-Yu Hsu,[‡] Chan-Cheng Su,[‡] Chuen-Her Ueng,[‡] Tseng-Chang Tsai,[§] and Kuang-Lieh Lu*,[†]

Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan, Department of Chemistry, National Taiwan Normal University, Taipei 116, Taiwan, and Department of Applied Chemistry, National Kaohsiung University, Kaohsiung 811, Taiwan

Received November 10, 2006

A homochiral amino acid coordination network $[\{Ag_3Cu_3(\text{L-methioninato})_6(NO_3)_3(H_2O)_3\}\cdot 7H_2O]_n$, self-assembled from Cu^{II}, Ag^{I}, and L-methionine via a distinct soft–hard recognition process, shows interesting characteristics, in that it is constructed from 1D helical building blocks and contains homochiral channels in which 1D water chains are hosted. This result provides an effective and controllable strategy for the preparation of enantiopure heterometallic supramolecular structures that are relevant to biopolymers.

Molecular recognition based on noncovalent donor–acceptor interactions plays a critical role in a variety of biological processes. Such effects that follow basic chemical principles permit extremely complex biological functions to be manipulated and dominate the storage of large amounts of messages in living organisms.[1,2] Amazingly, using only essential building blocks such as amino acids, nucleobases, etc., biological systems are able to achieve perfect self-organization and carry out complicated vital functions.[2] However, many biological effects that are relevant to basic chemical principles still need to be better understood. Therefore, the self-assembly of supramolecular complexes from biological precursor molecules or their derivatives is one of the most interesting research topics.[3−9] In particular, the self-assembly of amino acid coordination networks has attracted considerable attention because of the unique properties induced by the amino acid ligands.[5,8,9] Relevant coordination networks with helical chains,[5a] helical channels,[8a] or water aggregates[9] have already been shown to be of critical importance and to have rudimentary in vivo significance.

Ligands based on amino acids offer multiple metal binding sites and various weak interactions with other interacting groups. Because of these complex interactions of amino acid functional groups, especially their zwitterion properties, the preparation of amino acid supramolecular structures becomes more unpredictable and difficult to control.[5e] Thus, the design of amino acid coordination networks has been a challenging issue in materials science and biochemistry.[10] As part of our ongoing efforts in the synthesis of functional crystalline materials,[11] herein we report on an effective strategy for the design and synthesis of a 3D homochiral heterobimetallic

---

* To whom correspondence should be addressed. E-mail: lu@chem.sinica.edu.tw.

[†] Academia Sinica.

[‡] National Taiwan Normal University.

[§] National Kaohsiung University.

(1) (a) Yashima, E.; Maeda, K.; Okamoto, Y. *Nature* **1999**, *399*, 449. (b) Langer, R.; Tirrell, D. A. *Nature* **2004**, *428*, 487.

(2) (a) Lehn, J. M. *Science* **2002**, *295*, 2400. (b) Desiraju, G. R. *Nature* **2001**, *412*, 397. (c) Reinhoudt, D. N.; Crego-Calama, M. *Science* **2002**, *295*, 2403. (d) Alper, J. *Science* **2002**, *295*, 2396.

(3) (a) Price, C.; Horrocks, B. R.; Mayeux, A.; Elsegood, M. R. J.; Clegg, W.; Houlton, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1047. (b) Garcia-Terán, J. P.; Castillo, O.; Luque, A.; Garcia-Couceiro, U.; Román, P.; Lezama, L. *Inorg. Chem.* **2004**, *43*, 4549.

(4) Gei*β*elmann, A.; Klüfers, P.; Kropfgans, C.; Mayer, P.; Piotrowski, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 924.

(5) (a) Anokhina, E. V.; Jacobson, A. J. *J. Am. Chem. Soc.* **2004**, *126*, 3044. (b) Zhang, J. J.; Sheng, T. L.; Hu, S. M.; Xia, S. Q.; Leibeling, G.; Meyer, F.; Fu, Z. Y.; Chen, L.; Fu, R. B.; Wu, X. T. *Chem.—Eur. J.* **2004**, *10*, 3963. (c) Noord, A. D. C.; Kampf, J. W.; Pecoraro, V. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 4667. (d) Gordon, L. E.; Harrison, W. T. A. *Inorg. Chem.* **2004**, *43*, 1808. (e) Yamauchi, O.; Odani, A.; Takani, M. *J. Chem. Soc., Dalton Trans.* **2002**, 3411. (f) Kremer, C.; Torres, J.; Dominguez, S.; Mederos, A. *Coord. Chem. Rev.* **2005**, *249*, 567. (g) An, H. Y.; Wang, E. B.; Xiao, D. R.; Li, Y. G.; Su, Z. M.; Xu, L. *Angew. Chem., Int. Ed.* **2006**, *45*, 904. (h) Anokhina, E. V.; Go, Y. B.; Lee, Y.; Vogt, T.; Jacobson, A. J. *J. Am. Chem. Soc.* **2006**, *128*, 9957. (i) Vaidhyanathan, R.; Bradshaw, D.; Rebilly, J. N.; Barrio, J. P.; Gould, J. A.; Berry, N. G.; Rosseinsky, M. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6495.

(6) Guillou, N.; Livage, C.; Drillon, M.; Férey, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 5314.

(7) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (b) Dai, L. X. *Angew. Chem., Int. Ed.* **2004**, *43*, 5726.

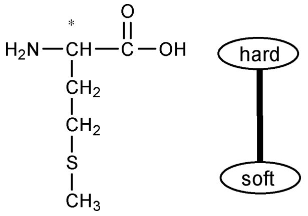
(8) (a) Shi, X.; Zhu, G.; Qiu, S.; Huang, K.; Yu, J.; Xu, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6482. (b) Imai, H.; Inoue, K.; Kikuchi, K.; Yoshida, Y.; Ito, M.; Sunahara, T.; Onaka, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 5617. (c) Ranford, J. D.; Vittal, J. J.; Wu, D.; Yang, X. *Angew. Chem., Int. Ed.* **1999**, *38*, 3498. (d) Ye, Q.; Li, Y. H.; Wu, Q.; Song, Y. M.; Wang, J. X.; Zhao, H.; Xiong, R. G.; Xue, Z. *Chem.—Eur. J.* **2005**, *11*, 988. (e) Niklas, N.; Hampel, F.; Alsfasser, R. *Chem. Commun.* **2003**, 1586. (f) Telfer, S. G.; Bernardinelli, G.; Williams, A. F. *Chem. Commun.* **2001**, 1498. (g) Qu, Z. R.; Zhao, H.; Wang, X. S.; Li, Y. H.; Song, Y. M.; Liu, Y. J.; Ye, Q.; Xiong, R. G.; Abrahams, B. F.; Xue, Z. L.; You, X. Z. *Inorg. Chem.* **2003**, *42*, 7710. (h) Alam, M. A.; Nethaji, M.; Ray, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1940.

(9) Sreenivasulu, B.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5769.

(10) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273.

10.1021/ic062132k CCC: $37.00

Chart 1. Chiral Soft−Hard Bifunctional Ligand of L-Methionine



amino acid coordination network that is self-assembled through a completely distinct soft−hard recognition process. This unique network shows interesting biomimetic characteristics, in that it is constructed from 1D helical building units and contains chiral channels and 1D water chains that are hosted in the helical channels.

Compound $[\{Ag_3Cu_3(\text{L-methioninato})_6(NO_3)_3(H_2O)_3\}\cdot 7H_2O]_n$ (**1**) was synthesized in high yield (62%) by a single-step self-assembly process from $Cu(NO_3)_2\cdot 3H_2O$, $AgNO_3$, and L-methionine in an ethanol/water diffusion system at ambient temperature. The synthetic strategy involved the use of an enantiopure ligand of L-methionine as a chiral building unit to build a coordination network. As shown in Chart 1, L-methionine can bind to metal centers through the hard amino and carboxylate group sites, with the thioether side-chain group serving as a soft site. If two different coordination centers of Cu^{II} and Ag^{I} cations can distinctly coordinate to L-methionine according to the hard−soft principle, a self-assembly process would occur, leading to the formation of the target structure. Although the soft−hard principle is a common concept in biology and chemistry, its specificity is not always higher than other complex interactions. To our knowledge, related coordination networks that are self-assembled via a distinct soft−hard recognition process have not yet been highlighted.[12] Interestingly, this deliberately proposed result has proven to be valid.

A single-crystal X-ray analysis reveals that compound **1** crystallizes in the chiral orthorhombic space group $P2_12_12_1$ and forms a 3D heterobimetallic coordination network.[13] Each Cu^{II} center is chelated by two L-methioninato ligands through the N and O atoms in a trans manner, producing two five-membered rings with the Cu^{II} ion located in the center of the equatorial N_2O_2 plane (Figure 1). An additional coordination with one μ-carboxylate O atom from a neighboring L-methioninato ligand gives rise to the apical bond, and the intermolecular connectivities generate a left-handed single-helical chain with a pseudo-4_1 screw axis (Figure 2). Furthermore, a nitrate O atom is weakly coordinated to the Cu2 center at an axial position. Thus, the Cu1 and Cu3 centers adopt square-pyramidal geometries, while the Cu2 center is octahedrally coordinated. Notably, the Cu_∞ helix is a rodlike building unit that is similar to the α-helix chain of a protein. In addition to the main chain of the rod, the side chains of the L-methioninato ligands extend outward in a helical array. The Cu−Cu translation is 5.3 Å per turn of the helix. The S atoms of the L-methioninato ligands are all bound to the Ag^{I} centers because of their soft preference. Each Ag^{I} center adopts a distorted tetrahedral coordination geometry. The three Ag atoms are linked by the μ^2-S atoms of the L-methioninato ligands to form a unique Ag-trimer unit (Figure S1 of the Supporting Information).

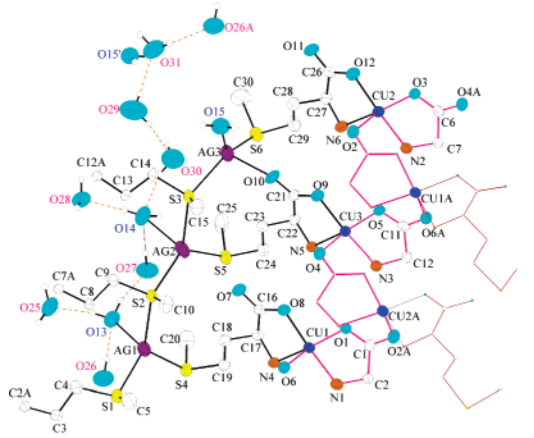


Figure 1. Cu_∞ helix (pink solid line), the hydrogen-bonded water chain (orange thin dashed line), and the local coordination environments of Cu^{II} and Ag^{I} in **1**. Nitrate anions and other H atoms have been omitted for clarity. (Selected fragments of L-methioninato are shown with arbitrary radii and thin bonds; other atoms are represented as 30% thermal ellipsoids.)

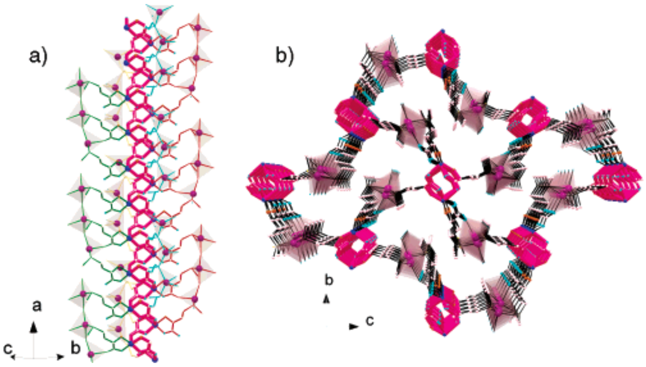


Figure 2. (a) Side view of the helical building block and the Ag-trimer units. (b) Top view of the framework of **1** along the *a* axis. (Water guest molecules and nitrate anions inside the channels have been omitted for clarity. Color codes are as in Figure 1.)

The infinite Cu_∞-helix chains in **1** are stacked in parallel and connected by the linkages of the L-methioninato ligands and the Ag-trimer units to give 1D helical channels (Figure 2b) in which three nitrate ions and seven water molecules per formula unit reside as guests. In order to realize the conformation of the helical channel, the arrangement of the Ag-trimer units with a winding-stair-like geometry is highlighted in Figure 3. The arrangement of the Ag-trimer units, which are connected through L-methioninato ligands and Cu atoms, generates a right-handed, hydrophilic helical channel. The Ag trimer−Ag trimer translation is 15.87 Å per turn of the helix. The twist rhombic chiral channel has dimensions

---

(11) (a) Luo, T. T.; Tsai, H. L.; Yang, S. L.; Liu, Y. H.; Yadav, R. D.; Su, C. C.; Ueng, C. H.; Lin, L. G.; Lu, K. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 6063. (b) Lu, Y. L.; Wu, J. Y.; Chan, M. C.; Huang, S. M.; Lin, C. S.; Chiu, T. W.; Liu, Y. H.; Wen, Y. S.; Ueng, C. H.; Chin, T. M.; Lu, K. L. *Inorg. Chem.* **2006**, *45*, 2430. (c) Liu, Y. H.; Wu, H. C.; Lin, H. M.; Hou, W. H.; Lu, K. L. *Chem. Commun.* **2003**, 60.

(12) (a) Gerrard, L. A.; Wood, P. T. *Chem. Commun.* **2000**, 2107. (b) Okada, T.; Tanaka, K.; Shiro, M.; Shionoya, M. *Chem. Commun.* **2005**, 1484.

(13) Crystal data for **1**: $C_{30}H_{80}Ag_3Cu_3N_9O_{31}S_6$, $M = 1769.62$, orthorhombic, space group $P2_12_12_1$, $a = 15.8730(1)$ Å, $b = 16.9061(1)$ Å, $c = 22.8297(2)$ Å, $V = 6126.36(8)$ Å^3, $Z = 4$, R1 = 0.0363, wR2 = 0.0786, GOF = 1.053.

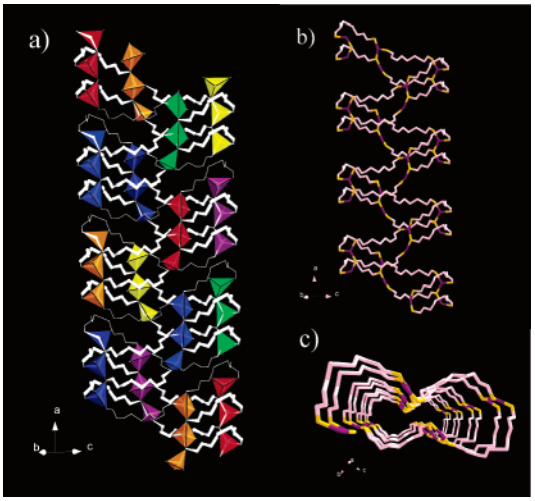


Figure 3. Simplified views of the right-handed helical channel of **1**: (a) side view, where the Ag tetrahedrons are represented as rainbow-like colors to show their helical sequence; (b) part of the white connections in part a; (c) top view of part b. Only the connections of the backbone atoms are shown for clarity.

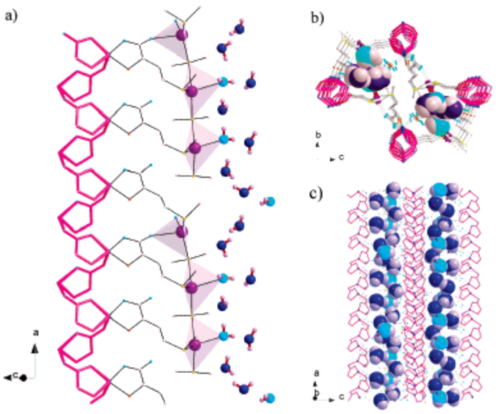


Figure 4. Hydrogen-bonded water chain in **1**: (a) water chain coordinated to the Ag-trimer units and propagating along its staircase-like environment; (b) top view of the water chains inside a helical channel; (c) side view of part b. Color codes are as in Figure 1.

of 11.84 × 22.17 Å (based on Ag···Ag distances; Figure 2b). Because the Ag trimer contains weakly coordinated water molecules, metal active sites directed toward the chiral channels might be formed upon the removal of water molecules. From further analysis of the framework, the helical description is one possible choice; another is to discard the longer Cu−O axial Jahn−Teller elongated bonds to obtain a 2D complex with undulated layers stacking along the *b* axis (Figures S2 and S3 of the Supporting Information).

Furthermore, an interesting observation was made that 1D water chains are hosted in the helical channels (Figure 4). Three Ag-coordinated water molecules and the other seven guest water molecules were all found to be strongly hydrogen-bonded together. The hydrogen-bond O···O distances within the water chain span the range 2.738(1)−2.872(7) Å (Table S1 of the Supporting Information). The water chains that propagate in a zigzag conformation along the [100] direction are anchored to the Ag-trimer units and help support the overall architecture. An ordered chain of water molecules inside a helical channel should be a biomimetic model for the behavior of water chains in biological pores.[14]

A thermogravimetric analysis (TGA) of **1** shows that guest water molecules are eliminated from the network (calcd 10.2%; found 10.2%) when the temperature is increased from room temperature to about 200 °C, after which decomposition of the compound occurs (Figure S6 of the Supporting Information). The powder X-ray diffraction (PXRD) study showed that compound **1** almost lost its crystallinity, even at 50 °C. After dehydration of **1** at 110 °C and rehydration at room temperature, the PXRD pattern showed that the peaks, after rehydration, correspond to those of the "as-synthesized" compound. The dehydration−rehydration cycle can be repeated many times (Figures S8−S10 of the Supporting Information). These results indicate that compound **1** is capable of undergoing a reversible crystal-to-amorphous-to-crystal transformation. This type of dynamic structural transformation remains one of the most interesting phenomena in crystal engineering,[15] particular for the cases of homochiral coordination polymers assembled from biological precursor molecules.

In conclusion, the design strategy for amino acid coordination frameworks based on the distinct soft−hard principle was demonstrated. Compound **1** contains five unique features: (1) a 3D homochiral heterobimetallic amino acid coordination network; (2) winding-stair-like-arranged Ag trimers as the building units for the assembly of the right-handed helical channels; (3) an infinite left-handed Cu_∞-helix chain analogous to the α-helix structure of a protein; (4) serving as a model of a 1D water chain in a biological pore; (5) having a reversible guest desorption−sorption property. Our results provide an effective and controllable route for the preparation of enantiopure heterometallic supramolecular structures that are relevant to biopolymers.

Acknowledgment. We thank Academia Sinica and the National Science Council, Taiwan, for financial support.

Supporting Information Available: Crystallographic details in CIF format for **1**, experimental section, additional pictures, selected bond lengths and angles, and TGA, differential scanning calorimetry, PXRD, and IR data. This material is available free of charge via the Internet at http://pubs.acs.org.

IC062132K

---

(14) (a) Sansom, M. S. P.; Biggin, P. C. *Nature* **2001**, *414*, 156. (b) Ludwig, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1808. (c) Mukherjee, A.; Saha, M. K.; Nethaji, M.; Chakravarty, A. R. *Chem. Commun.* **2004**, 716. (d) Neogi, S.; Bharadwaj, P. K. *Inorg. Chem.* **2005**, *44*, 816.

(15) Kitagawa, S.; Uemura, K. *Chem. Soc. Rev.* **2005**, *34*, 109.