Metallohelice: Effects of Hydrogen Bond Interactions on Helical Morphology

Yugen Zhang,* Li Jianmin,*† Masayoshi Nishiura,†† Wei Deng,† and Tsuneo Imamoto††
Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China
†*Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China*
††*Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho, Inage-ku, Chiba 263-8522*

(Received August 23, 1999; CL-990728)

An interesting chiral metallohelical complex $[Cd(C_4H_4O_4)(SC(NH_2)_2)_2]_n$ (**I**) is spontaneous assembled. The formation is driven by multiple intramolecular hydrogen bond interactions to form the helical structure and by multiple intermolecular hydrogen bond interactions to form chiral supramolecular arrays.

The design and synthesis of molecules that can organize into specific supramolecular assemblies in the solid state is an area of considerable interest,[1] since it may lead to new materials with desirable chemical and physical properties. The helix is a dominant motif in biomolecules, it is also expected to play key roles in advanced materials.[2] Much recent interests has been focused on helical polynuclear metal complexes and coordination polymers.[3-5] We are particularly interested in using the no intrinsic chirality metal ligands to form chiral solid state supramolecular assemblies,[6] synthesizing chiral metallohelices which use weak interactions (hydrogen bonds, π-stacking etc.) as the predominant forces that determined secondary and third structure.[7] In this letter we report an interesting example of spontaneous assembly of infinite metallohelical complex. This formation is driven by multiple intramolecular hydrogen bond interactions to form helical structure and by multiple intermolecular hydrogen bond interactions to form chiral supramolecular arrays.

Complexes (**I**) was prepared by mixing of aqueous solutions of $CdSO_4$, succinic acid and thiourea in the ratio of 1:1:2. The pH value of the solution was controlled at 5~6. Needle like crystals suitable for an X-ray analysis were isolated in several days.[8] X-Ray analysis reveals that complex **I** possesses a right-handed (*P*, clockwise)[4a,6a] chiral single helical structure (Figure 1).[9] It is assembled by Cd(II) ion, succinate dianion and thiourea. The helix has a long pitch 12.99 Å and small average radius 1.99 Å.[10] Here, metal ligands have no intrinsic chirality, the chiral helix formed without any unsymmetry inducing factor. The helical sense shows the effect of weak interaction: multiple intramolecular hydrogen bond interactions. It is known that the four carbon atoms chain of succinato group is unfavorable forming bent half-circle conformation which is needed in ideal helical structure. Here, the intramolecular hydrogen bonds, N_3---O_3, 2.950 Å, 155.71° and N_1---O_4, 2.875 Å, 150.43°, led the carbon chain of succinato ligand turn around (torsion angle of the four carbon atoms is 71.8(4)°) to form this helical structure.

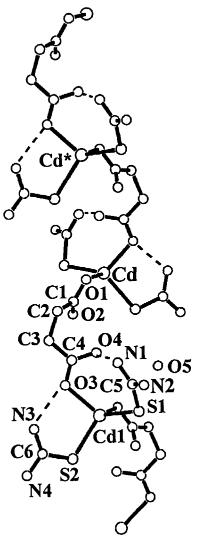

Figure 1. Molecular structure of **I**, the intramolecular hydrogen bonds is given in dash line. Selected bond lengths (Å): Cd-Sl 2.5118(9), Cd-S2 2.5051(9), Cd-O1 2.256(2), Cd-O4 2.248(3).

Here, in the structure of **I**, all metallohelices within the lattice have the same helical chirality. Crystallization from the solution should produce enantiomeric crystals in equal numbers. The lattice architecture provides insights into the observed chiral resolution. The lattice contains ordered arrays of metallohelices in the *b,c* plane. Each metallohelix is positioned at the center of hexagon composed of six surrounding metallohelices; between neighboring helices there are 16 sets of intermolecular hydrogen

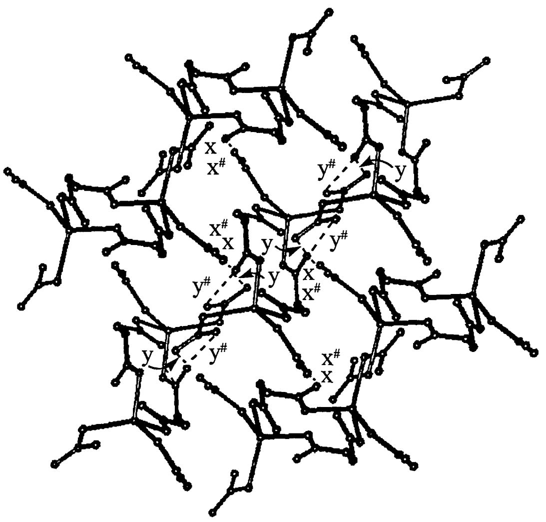

Figure 2. A portion of the crystal lattice for **I** (view of *b,c* plane). Each metallohelix is positioned at the center of hexagon composed of six surrounding metallohelices and linked by intermolecular hydrogen bonds. Selected intermolecular hydrogen bond lengths (Å) and angles (°): x, 2.867, 147.89; x#, 2.921, 142.36; y 2.915, 147.63; y# 3.018, 140.99. Hydrogens and the water molecule are removed for clarity.

bond interactions observed in one turn.[11] Four of these hydrogen bond interactions are unique by symmetry, which in **I** are 2.867, 2.921, 2.915, and 3.018 Å with corresponding ∠D-H-A angles of 147.89°, 142.36°, 147.63°, and 140.99° (Figure 2). The clustering of inter-molecular hydrogen bonds within an array undoubtedly contributes to the stabilization of this supramolecular assembly of metallohelices.[7,12] However, the water molecule (O_5) is also involved in the inter-molecular hydrogen bonds (N4-O5, 2.943 Å, 158.18°; O5-O3, 2.987 Å, 154.20°) which also contribute to this stabilization effect. This type of stabilization necessitates the nearly perfect alignment of helices within an array which is only possible if individual metallohelices are of the same helicity. Thus the assembly of the arrays during crystallization appears to be enantioselective for one helicity.

These results demonstrate how weak inter- and intramolecular hydrogen bond interactions can be used to assemble metal-based chiral supramolecular species. We are investigating currently how these weak interactions affect the assembly of supramolecular species.

We thank the National Nature Science Foundation for financial support.

References and Notes

1 a) G. D. Desiraju, "Crystal Engineering: The design of Organic Solids," Elsevier, New York (1989). b) J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, **29**, 1304 (1990). c) M. J. Zaworotko, *Chem. Soc. Rev.*, **23**, 283 (1994).

2 a) L. Zelikovich, J. Libman, and A. Shanzer, *Nature*, **374**, 790 (1995). b) J. C. Nelson, J. G. Saven, J. S. Moore, and P. G. Wolynes, *Science*, **277**, 1793 (1997). c) R. Oda, I. Huc, M. Schmutz, S. J. Candau, and F. C. Mackintosh, *Nature*, **399**, 566 (1999).

3 a) G. M. Whitesides, J. P. Mathias, and C. T. Seto, *Science*, **254**, 1312 (1991). b) G. P. Dado and S. H. Gellman, *J. Am. Chem. Soc.*, **116**, 1054 (1994). c) Y. Hamuro, S. J. Geib, and A. D. Hamilton, *J. Am. Chem. Soc.*, **118**, 7529 (1996).

4 a) C. Piguet, G. Bernardinelli, and G. Hopfgartner, *Chem. Rev.*, **97**, 2005 (1997). b) D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, **35**, 1154 (1996). c) D. S. Lawrence, T. Jiang, and M. Levett, *Chem. Rev.*, **95**, 2229 (1995). d) A. E. Rowan and R. J. M. Nolte, *Angew. Chem., Int. Ed.*, **37**, 63 (1998).

5 a) N. Ohata, H. Masuda, and O. Yamauchi, *Angew. Chem., Int. Ed. Engl.*, **35**, 531 (1996). b) T. W. Bell and H. Jousselin, *Nature*, **367**, 441 (1994). c) M. Albrecht and M. Schneidet, *Chem. Commun.*, **1998**, 137. d) N. Yoshida, H. Oshio, and T. Ito, *Chem. Commun.*, **1998**, 63.

6 a) T. Ezuhara, K. Endo, and Y. Aoyama, *J. Am. Chem. Soc.*, **121**, 3279 (1999). b) Y. Zhang, S. Wang, G. D. Enright, and S. R. Breeze, *J. Am. Chem. Soc.*, **120**, 9398 (1998). c) W. Lin, O. R. Evans, R. Xiong, and Z. Wang, *J. Am. Chem. Soc.*, **120**, 13272 (1998). d) O. J. Gelling, F. Van Bolhuis, and B. L. Feringa, *J. Chem. Soc., Chem. Commun.*, **1991**, 917. e) H. Koshima and T. Matsuura, *J. Synth. Org. Chem. Jpn.*, **56**, 268 (1998).

7 a) T. Kawamoto, O. Prakash, R. Ostrander, A. L. Rheingold, and A. S. Borovik, *Inorg. Chem.*, **34**, 4292 (1995). b) T. Kawamoto, B. S. Hammes, B. Haggerty, G. P. A. Yap, A. L. Rheingold, and A. S. Borovik, *J. Am. Chem. Soc.*, **118**, 285 (1996). c) Y. Zhang, J. Li, M. Nishiura, T. Imamoto, manuscript in preparation.

8 Anal. Found: C, 18.02; H, 3.56; N, 14.12%. Calcd for $C_6H_{14}N_4O_5S_2Cd$: C, 18.06; H, 3.51; N, 14.04%.

9 Crystal Data for I: , M = 398.73, orthorhombic, $P2_12_12_1$, a = 13.419(2), b = 7.8294(7), c = 12.989(3) Å, V = 1364.6(3) Å^3, $F(000)$ = 792, Z = 4, Dc = 1.941 g/cm^3, T = 173 K, μ(Mo-Kα) = 19.26 cm^{-1}, λ(Mo-Ka) = 0.71070 Å. A crystal of approximate dimensions 0.30 × 0.30 × 0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-II imaging plate area detector with graphite monochromated Mo-Kα radiation. Scattering factors were taken from Cromer and Waber. A total of 2318 reflections were collected, of which 2292 had $I > 3\sigma(I)$ with 163 parameters. The data were corrected for Lorentz-polarization effects. The structure was solved by direct methods (SIR-92) and refined by full-matrix least-squares. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but their positions were not refined. All calculations were performed using teXsan crystallographic software package of Molecular Structure Corporation. Final R = 0.027, wR = 0.038, goodness of fit = 1.00.

10 Typical α-helix in protein: pitch 5.4 Å, av. radius 2.3 Å.

11 The Cd-Cd distances observed in the helix is 7.928 Å and between the neighboring helices are 7.048, 7.497, 7.767 Å.

12 a) S. K. Burley and G. A. Petsko, *Adv. Protein Chem.*, 39, 125 (1988). b) C. A. Hunter, *Chem. Soc. Rev.*, **1994**, 101. c) J. C. Nelson, J. G. Saven, J. S. Moore, and P. G. Wolynes, *Science*, **277**, 1793 (1997). d) B. Honig and F. E. Cohen, *Folding Design*, **1**, R17 (1996).