Synthesis and Characterization of a 3D H-Bonded Supramolecular Complex with Chiral Channels Encapsulating 1D Left-Handed Helical Water Chains

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A chiral Cu^{II} dinuclear complex $[Cu_2(L\text{-shis})_2]\cdot 4H_2O$ (H_2shis = *N*-salicylidenylhistidine) has been synthesized. The dinuclear units are assembled into a 3D hydrogen-bonded supramolecular structure with 1D chiral channels through hydrogen bonds between imidazole N–H groups and carboxylate oxygen atoms. 1D left-handed helical water chains in an AABB fashion, anchored through weak hydrogen-bonding interactions with the host complex, are embodied in the chiral channels. X-ray powder diffraction shows the porous structure is destroyed when the lattice water molecules are removed thermally from the channels.

Introduction

Metal-organic frameworks containing channels or pores with various sizes and shapes have attracted much attention because of their potential applications in catalysis, separation and gas sorption and storage.[1–3] Chiral porous materials have great advantages over achiral ones in enantioselective separation and catalysis.[4] A direct and effective method for such materials is to ultilize enantioselective ligands.[5–7] Therein, using natural amino acids as chiral precursors is a simple and practical alternative.[8–10] Moreover, amino acids can afford different kinds of hydrogen bonds, which has an important effect on the structures of metal-organic materials.[11–13] Our interest has been focused on the employment of natural amino acids for synthesizing chiral ligands to direct the assembly of chiral metal-organic porous materials.

One-dimensional (1D) chain arrangement of water molecules has attracted much interest due to its occurrence in many fundamental biological processes which depend on the unique properties of water chains.[14–16] Such water chains could model the biological systems for transport of water or ions across membrane proteins with aquapores, and several examples of 1D water chains anchored by organic compounds or complexes have been reported.[17–22] Chakravarty described an unprecedented 1D helical chain of water in a dicopper(II) complex with a helical porous supramolecular structure-[20] and Vittal reported a staircase-like helical coordination polymeric architecture of a nickel(II) complex that hosts a 1D helical chain of lattice water molecules in a helical pore.[21] In these two cases, the 1D helical water chains are anchored by helical host complexes through weak hydrogen-bonding interactions and exhibit an alternate arrangement of two water molecules in the chains. While trying to construct chiral porous materials using a simple Schiff-base ligand derived from L-histidine, we obtained complex $[Cu_2(L\text{-shis})_2]\cdot 4H_2O$ (**1**) (H_2shis = *N*-salicylidenylhistidine), in which lattice water molecules are well ordered and arrayed in an AABB fashion to form 1D left-handed helical water chains encapsulated in the channels of the H-bonded supramolecular complex.

Results and Discussion

Complex **1** was obtained by the reaction of $Cu(NO_3)_2\cdot 3H_2O$ and a mixture of L-histidine and salicylaldehyde in basic ethanol/aqueous solution. The single-crystal X-ray analysis reveals that complex **1** crystallizes in the chiral space group $C222_1$ and consists of the neutral dinuclear unit $[Cu_2(L\text{-shis})_2]$ and four lattice water molecules, as shown in Figure 1. Cu1 is in a four-coordinate environment in which the shis anion as a tridentate ligand chelates Cu1 through the phenolato oxygen atom O3, the nitrogen atom N1 and the carboxylate oxygen atom O1, and the remaining site is occupied by an imidazole nitrogen atom N3A (A: $x, -y, 1-z$) from another shis ligand. Two Cu^{II} centers are connected by imidazole "arms" from two shis ligands to form a boat-shaped dinuclear unit. There exist H-bond donors (imidazole N–H groups) and acceptors (carboxylate oxygen atoms) on the top and bottom rims of each dinuclear unit, respectively, and this makes it a good building block for a hydrogen-bonded network. In fact, four such dimers are linked through hydrogen bonds [N2···O2B =

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2.699(5) Å, B: $x + 1/2, 1/2 - y, 1 - z$] to give a large cycle containing eight Cu^{II} centers. The eight-membered rings are further linked to each other through the same hydrogen bonds, generating a two-dimensional supramolecular grid layer.

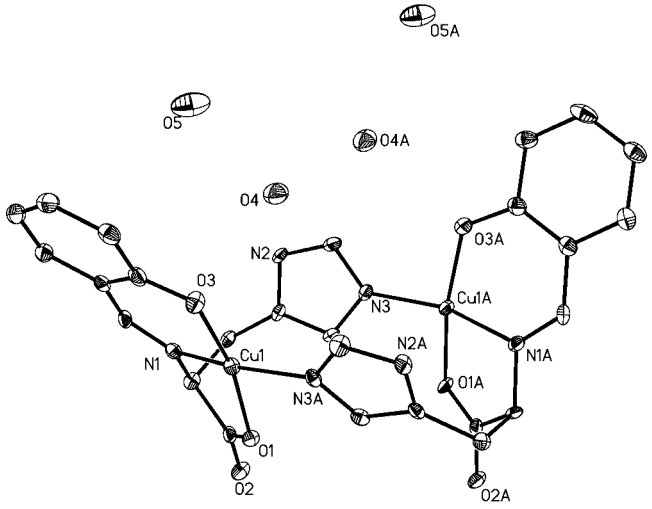

Figure 1. ORTEP view of the dinuclear complex. Selected bond lengths [Å] and angles [°]: Cu1–O1, 1.960(3); Cu1–N1, 1.922(4); Cu1–O3, 1.908(3); Cu1–N3A, 1.959(3); O3–Cu1–N1, 93.29(15); O3–Cu1–O1, 167.32(13); N1–Cu1–N3A, 162.34(13). Symmetry code: A: $x, -y, 1 - z$.

The asymmetric unit contains two water molecules which are bonded to each other through hydrogen bonding [O4···O5 = 2.813(5) Å]. The dinuclear unit anchors one water molecule through hydrogen bonding [O4···O3 = 2.983(5) Å] between coordinated phenolato oxygen atom O3 and atom O4 of water molecules. Atoms O4 and O4A (A: $x, -y, 1 - z$) of anchored water molecules are bonded to each other through hydrogen bonding [O4···O4A = 2.821(7) Å, A: $x, -y, 1 - z$]. Another water molecule is also anchored by a dinuclear unit of another asymmetric unit through hydrogen bonding [O5···O2H = 2.943(5) Å, H: $1 + x, y, z$] between uncoordinated carboxylate oxygen atom O2 and atom O5 of a water molecule. Thus, H-bonded O5–O4–O4A–O5A tetramers are filled with the grids of the 2D layer. Interestingly, the O5 atoms are also bonded to the same water molecules in symmetry through hydrogen bonds [O5···O5C = 2.869(8) Å, C: $3 - x, y, 3/2 - z$] which connect the 2D layers into a 3D structure with 1D chiral channels along the *c*-axis. Moreover, 1D helical water chains with a pitch of 16.9 Å along the *c*-axis are formed in the chiral channels, in which two water molecules are arranged by an AABB fashion (Figure 2). Such weak interactions upon the chiral host induce a homochiral left-handed helicity of water chains (Figure 3). In a sense, the formation of the helical water chain depends on the chemical information and structure of the dinuclear unit which anchors O4 and O4A within an H-bonded distance. Moreover, the H-bonded acceptors in **1** (phenolato and carboxylate oxygen atoms) are in favorable positions for anchoring different water molecules into an extended array.

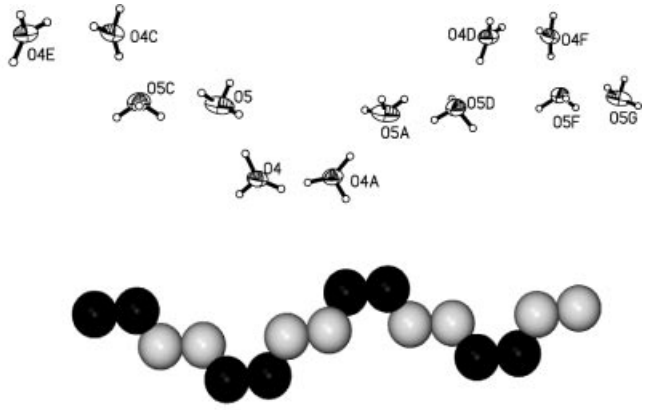

Figure 2. ORTEP view of the helical water chain along the *c*-axis (top) and view of the left-handed helix (bottom) containing water O4 (black) and water O5 (grey) in an AABB fashion. Symmetry codes: A: $x, -y, 1 - z$; C: $3 - x, y, 3/2 - z$; D: $3 - x, -y, z - 1/2$; E: $3 - x, -y, 1/2 + z$; F: $3 - x, y, 1/2 - z$; G: $x, y, z - 1$.

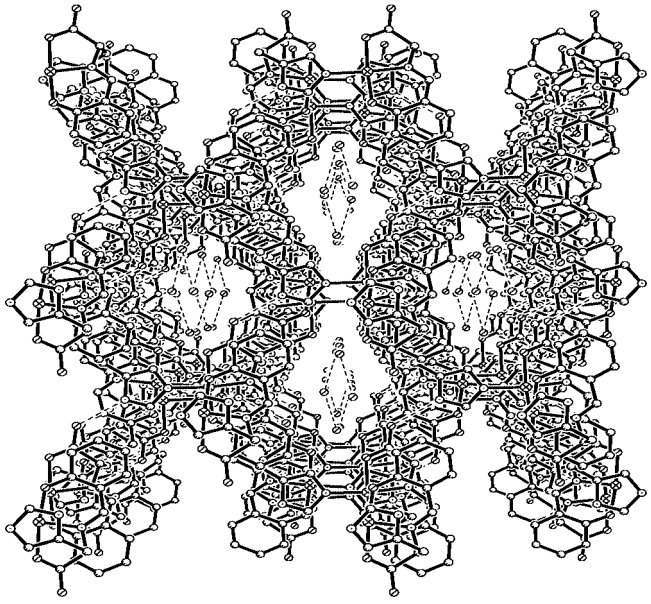

Figure 3. Helical water chains in the 1D channels of the host structure.

The thermogravimetric analysis (TGA) of **1** shows a weight loss of 10.4% in the temperature range 30–150 °C, which agrees with the calculated value (10.1%) for the loss of two water molecules per asymmetric unit. The DSC measurement at 20–150 °C at a rate of 5 °C·min^{-1} shows a single endothermal peak centered at 56.2 °C. The enthalpy per water molecule is ca. 16 kJ·mol^{-1}, which is similar to that observed in another infinite water chain.[19]

To investigate the influence of water molecules on the porous structure, we heated complex **1** at 150 °C for 2 h to remove water molecules (taking a cue from TGA). The elemental analysis of the dehydrated sample is consistent with the formula [Cu_2(L-shis)$_2$]. However, X-ray powder diffraction shows the porous structure of the host complex has been destroyed after the helical water chains being removed (Figure S3). It agrees well with interactions among the 2D

layers by weak hydrogen bonds between water molecules [O5···O5C = 2.869(8) Å, C: 3 – *x*, *y*, 3/2 – *z*]. When the water molecules are removed, the 2D layers are no longer as well ordered as in $[Cu_2(L\text{-shis})_2]\cdot 4H_2O$.

Conclusions

In conclusion, we have observed left-handed helical water chains in the chiral channels of the H-bonded chiral 3D supramolecular structure based on the dinuclear Cu^{II} complex of a Schiff base derived from L-histidine. The crystal structure of **1** exemplifies a synthetic host model anchoring the homochiral helical water chains in which water molecules are arranged in an AABB fashion.

Experimental Section

General Remarks: All reagents were analytical grade and used without further purification. The IR spectra as KBr disks were recorded with a Magna 750 FT-IR spectrophotometer. C, H, N elemental analyses were carried out with an Elementary Vario ELIII elemental analyzer. Thermogravimetric analysis was performed with a NETZSCH STA 449C instrument. The DSC curve was obtained with a NETZSCH DTA 404PC analyzer at a scan rate of 5 °C·min^{-1}. X-ray powder diffraction was performed with a Rigaku DMAX2500PC diffractometer.

Synthesis of Complex 1: To an aqueous solution (20 mL) of L-histidine (0.155 g, 1 mmol) and NaOH (0.040 g, 1 mmol), salicylaldehyde (0.122 g, 1 mmol) in ethanol (10 mL) was added slowly. The solution was stirred for 30 min and then $Cu(NO_3)_2\cdot 3H_2O$ (0.240 g, 1 mmol) in water (10 mL) was added. After stirring for 1 h, the filtered solution was allowed to stand in air for several days, and blue crystals were obtained in a yield of 60% (210 mg). $C_{26}H_{30}Cu_2N_6O_{10}$ (713.65): calcd. C 43.72, H 4.24, N 11.77; found C 43.47, H 4.38, N 11.55. IR (KBr): $\tilde{\nu}$ = 3416 br. [ν(OH)], 3151 m [ν(NH)], 1637 s [ν_{as}(COO)], 1603 s [ν(C=N)], 1369 m [ν_s(COO)] cm^{-1}.

X-ray Structure Determination: Single-crystal data were collected with a Rigaku Mercury-CCD diffractometer at 130 K, using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELXTL program package.[23] Crystal data: orthorhombic, space group $C222_1$ (no. 20), a = 11.8642(10), b = 14.6000(13), c = 16.9029(17) Å, V = 2927.9(5) Å^3, Z = 4, D_c = 1.619 g/cm^3, 9341 reflections collected, 2583 unique (R_{int} = 0.0468). Final *GooF* = 1.125, $R1$ = 0.0388, $wR2$ = 0.0860, R indices based on 2392 reflections with $I > 2\sigma(I)$ (refinement on F^2). Absolute structure parameter 0.038(19).[24] All non-hydrogen atoms were refined anisotropically and the organic hydrogen atoms were generated geometrically. The hydrogen atoms of water molecules are disordered. Full-occupancy hydrogen atoms H4B, H5B, and half-occupancy hydrogen atoms H4A, H4C, H5A, H5C were located by difference maps and constrained to ride on their parent O atoms in a trigonal arrangement. CCDC-268811 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): TGA and DSC curves of **1** (Figures S1 and S2); XRD patterns of **1** and the dehydrated product (Figure S3).

Acknowledgments

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[1] a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; b) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469–472.
[2] a) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* **2004**,*43*, 2334–2375; b) R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, K. Kindo, Y. Mita, A. Matsuo, M. Kobayashi, H. C. Chang, T. C. Ozawa, M. Suzuki, M. Sakata, M. Takata, *Science* **2002**, *298*, 2358–2361.
[3] a) S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148–1150; b) L. Pan, K. M. Adams, H. E. Hernandez, X. Wang, C. Zheng, Y. Hattori, K. Kaneko, *J. Am. Chem. Soc.* **2003**, *125*, 3062–3067.
[4] a) B. Kesanli, W. Lin, *Coord. Chem. Rev.* **2003**, *246*, 305–326; b) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986.
[5] R.-G. Xiong, X.-Z. You, B. F. Abrahams, Z. Xue, C.-M. Che, *Angew. Chem. Int. Ed.* **2001**, *40*, 4422–4425.
[6] O. R. Evans, H. L. Ngo, W. Lin, *J. Am. Chem. Soc.* **2001**, *123*, 10395–10396.
[7] Y. Cui, S. J. Li, W. Lin, *J. Am. Chem. Soc.* **2003**, *125*, 6014–6015.
[8] X. Shi, G.-S. Zhu, S.-L. Qiu, K.-L. Huang, J.-H. Yu, R.-R. Xu, *Angew. Chem. Int. Ed.* **2004**, *43*, 6482–6485.
[9] M. A. Alam, M. Nethaji, M. Ray, *Inorg. Chem.* **2005**, *44*, 1302–1308.
[10] J. D. Ranford, J. J. Vittal, D. Wu, X. Yang, *Angew. Chem. Int. Ed.* **1999**, *38*, 3498–3501.
[11] a) N. Ohata, H. Masuda, O. Yamauchi, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 531–532; b) N. Ohata, H. Masuda, O. Yamauchi, *Inorg. Chim. Acta* **2000**, *300*, 749–761; c) N. Ohata, H. Masuda, O. Yamauchi, *Inorg. Chim. Acta* **1999**, *286*, 37–45.
[12] T. Moriuchi, M. Nishiyama, K. Yoshida, T. Ishikawa, T. Hirao, *Org. Lett.* **2001**, *3*, 1459–1461.
[13] M. A. Alam, M. Nethaji, M. Ray, *Angew. Chem. Int. Ed.* **2003**, *42*, 1940–1942.
[14] S. Cukierman, *Biophys. J.* **2000**, *78*, 1825–1834.
[15] K. M. Jude, S. K. Wright, C. Tu, D. N. Silverman, R. E. Viola, D. W. Christianson, *Biochemistry* **2002**, *41*, 2485–2491.
[16] H. Kandori, *Biochim. Biophys. Acta* **2000**, *1460*, 177–191.
[17] R. Ludwig, *Angew. Chem. Int. Ed.* **2003**, *42*, 258–260.
[18] S. Pal, N. B. Sankaran, A. Samanta, *Angew. Chem. Int. Ed.* **2003**, *42*, 1741–1743.
[19] L. E. Cheruzel, M. S. Pometun, M. R. Cecil, M. S. Mashuta, R. J. Wittebort, R. M. Buchanan, *Angew. Chem. Int. Ed.* **2003**, *42*, 5452–5455.
[20] A. Mukherjee, M. K. Saha, M. Nethaji, A. R. Chakravarty, *Chem. Commun.* **2004**, 716–717.
[21] B. Sreenivasulu, J. J. Vittal, *Angew. Chem. Int. Ed.* **2004**, *43*, 5769–5772.
[22] a) L. Infantes, J. Chisholm, S. Motherwell, *CrystEngComm* **2003**, *5*, 480–486; b) L. Infantes, S. Motherwell, *CrystEngComm* **2002**, *4*, 454–461.
[23] G. M. Sheldrick, Bruker *SHELSTL-PC*, University of Göttingen, Germany, **1997**.
[24] H. D. Flack, *Acta Crystallogr.* **1983**, *A39*, 876–881.

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