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Spontaneously Resolved Chiral Three-Fold Interpenetrating Diamondoidlike Cu(II) Coordination Polymers with Temperature-Driven Crystal-to-Crystal Transformation

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The chiral 3-fold interpenetrating diamondoidlike Cu(II)-containing coordination polymer [Cu(2,5-bis(4-pyridyl)-1,3,4-oxadiazole)$_2$(H_2O)](ClO_4)$_2$]$_n$ (**1a**) is reported. It undergoes a temperature-driven reversible single-crystal-to-single-crystal structural transformation between room- (293 K, **1a**) and low-temperature (150 K, **1b**) forms.

The design and syntheses of organic−inorganic coordination polymers with novel topologies and structural motifs is of current interest in the field of coordination chemistry.[1−3] Over the past decades, different classes of polymeric compounds fitting this general description have been successfully designed and synthesized. Some of them exhibit encouraging potential applications, including nonlinear optics, catalysis and separation, magnetism and molecular recognition, and so on.[3] Among different types of net-assembled polymeric frameworks reported so far, interpenetrating chiral networks are of particular interest in relation to the topological types of three-dimensional nets postulated by Wells.[4] On the other hand, the solid-state structural transformation of metal−organic frameworks is also an interesting phenomenon attracting increasing attention and which may prove to possess important applications. For instance, structural transitions upon removal and exchange of guest molecules from metal−organic frameworks have been well documented.[5] We and others have been developing coordination polymers generated from oxadiazole bridging organic ligands such as 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (**L1**) and inorganic salts. Arising from the bent shape of the oxadiazole-containing ligand together with the coordination preferences of transition metals, new types of coordination polymers, some with open channels, have been obtained.[6] In this communication, we report the spontaneous resolution of a novel chiral 3-fold interpenetrating three-dimensional Cu(II)-containing coordination polymer, namely [Cu(**L1**)$_2$(H_2O)](ClO_4)$_2$]$_n$(solvate) (**1a**), which shows a reversible single-crystal-to-single-crystal reversible structural transformation between room (293 K, **1a**) and low temperature (150 K, **1b**) (Figure 1).

The reaction[7] of $Cu(ClO_4)_2 \cdot 6H_2O$ with **L1** in a 1:2 ratio in a CH_2Cl_2/CH_3OH mixed solvent system afforded **1a** as deep blue crystals in 90% yield. In this reaction system, the product does not depend on the ligand-to-metal reactant ratio. At room temperature (RT), compound **1a** crystallizes[8] in the

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(1) (a) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638. (b) Zaworotko, M. J.; Moulton, B. *Chem. Rev.* **2001**, *101*, 1629. (c) Batten, S.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.

(2) (a) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703. (b) Fujita, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469. (c) Losier, T. P.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2779.

(3) (a) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Lin, W.; Evans, O. R.; Xiong, R.-G.; Wang, Z. *J. Am. Chem. Soc.* **1998**, *120*, 13272. (c) Garder, G. B.; Venkataraman, D.; Moore, J. S.; Lee, S. *Nature* 1995, *374*, 792. (d) Kahn, O.; Pei, Y.; Verdguer, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1998**, *110*, 782. (e) Su, C.-Y.; Goforth, A. M.; Smith, M. D.; Pellechia, P. J.; zur Loye, H.-C. *J. Am. Chem. Soc.* **2004**, *126*, 3576.

(4) Well, F. *Further Studies of Three-dimensional Nets*; ACA Monograph No. 8; American Crystallographic Association: Buffalo, NY, 1979.

(5) Suh, M. P.; Ko, J. W.; Choi, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 10976 and references therein.

(6) (a) Dong, Y.-B.; Cheng, J.-Y.; Wang, H.-Y.; Huang, R.-Q.; Tang, B.; Smith, M. D.; zur Loye, H.-C. *Chem. Mater.* **2003**, *15*, 2593. (b) Dong, Y.-B.; Ma, J.-P.; Huang, R.-Q.; Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2003**, *42*, 294. (c) Du, M.; Guo, Y.-M.; Chen, S.-T.; Bu, X.-H.; Batten, S. R.; Ribas, J.; Kitagawa, S. *Inorg. Chem.* **2004**, *43*, 1287.

(7) Preparation of [Cu(**L1**)$_2$(H_2O)](ClO_4)$_2$ (**1a**). A solution of $Cu(ClO_4) \cdot 6H_2O$ (37.5 mg, 0.1 mmol) in MeOH was layered onto a solution of **L1** (44.8 mg, 0.2 mmol) in CH_2Cl_2 (9 mL). The solutions were left for about one month at room temperature, and deep-blue crystals were obtained. Yield, 90% (based on $Cu(ClO_4) \cdot 6H_2O$). IR (KBr, cm^{-1}): 3500(s), 3130(w), 1626(s), 1572(s), 1540(s), 1488(s), 1435(s), 1335(m), 1280(w), 1222(w), 1145(s), 1119(vs), 1089(vs), 842(s), 728(m), 710(m). Anal. Calcd for $C_{24}H_{22}Cl_2CuN_8O_{12}$ C, 38.45; H, 2.94; N, 14.95. Found: C, 38.30; H, 2.73; N, 14.72.

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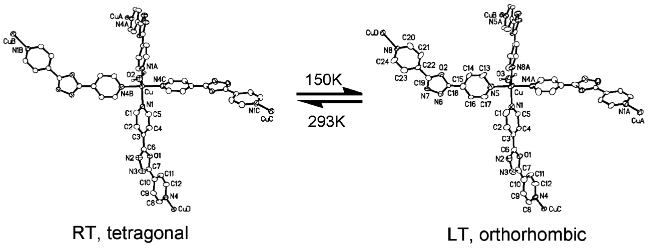

Figure 1. Displacement ellipsoid plot of the Cu(II) environments of the RT tetragonal and LT orthorhombic forms, showing the atom labeling scheme. Note the two nonequivalent ligands in the LT form. Ellipsoids drawn at the 20% and 30% probability levels for the RT and LT forms, respectively. Selected bond distances (Å): RT form: Cu−N1(N1A) = 2.012(2), Cu−N4B(N4C) = 2.032(2), Cu−O2 = 2.216(2). LT form: Cu−N1 = 2.031(7), Cu−N8A = 2.019(6), Cu−N5 = 2.026(7), Cu−N4A = 2.036(7), Cu−O3 = 2.175(5).

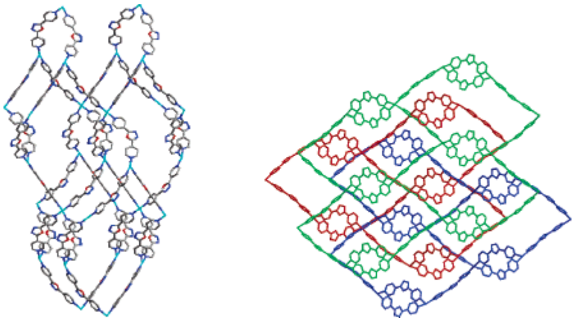

Figure 2. Diamondoidlike framework (left) and its 3-fold interpenetrating network (right, in different colors) in **1a**.

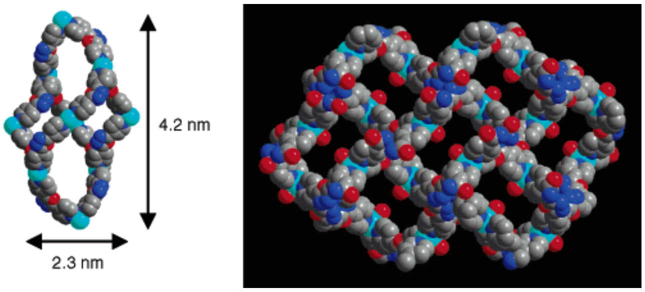

Figure 3. Adamantoid cavity formed in individual framework (left) and rectangular channels formed along the [110] direction (right) in **1a**, ClO_4^- counterions are omitted for clarity.

chiral tetragonal space group $P4_12_12$, an enantiomorphous space group confirmed on the basis of the absolute structure (Flack) parameter of 0.04(1) refined from the X-ray data. As shown in Figure 1, each Cu(II) center lies in a square pyramidal coordination environment of four basal N-donors from one crystallographically independent **L1** ligand and its three symmetry equivalents and one axial O-donor from a coordinated water molecule. The Cu(II) center and the coordinated water molecule are located on a crystallographic 2-fold axis of rotation along the [110] direction. Bond distances around Cu(II) are unremarkable (Figure 1). In the solid state (Figure 2), Cu(II) centers are linked by bent **L1** ligands into a three-dimensional adamantoid arrangement, leaving huge cavities inside the frameworks. When viewed down the crystallographic *a*, *c*, and [110] directions, big rhombic, rectangular, or elliptical channels could be found (Supporting Information). However, these channels of an individual diamondoid framework (4.2 × 2.3 nm^2) are partially filled up by two interpenetrated symmetry-equivalent frameworks, leaving the only rectangular channels along the crystallographic *c* axis with the dimension of 8 × 18 $Å^2$ (Figure 3), in which the badly disordered ClO_4^- anions and solvent molecules (crystallographically unidentified) are located (Supporting Information). The TGA trace of **1a** indicates that, after solvent guest removal, the framework of the compound is stable up to 225 °C.

The most important feature of the crystal of **1a** is that it undergoes a reversible single-crystal-to-single-crystal structural transformation driven by temperature. When crystals of **1a** were cooled from room temperature to 150 K, a reduction in crystal symmetry from tetragonal to orthorhombic was observed, commencing near 170 K and complete by ca. 160 K. The transformation results in only a slight unit cell change, indicated in the diffraction data by the breaking of the equivalence of the tetragonal *a* and *b* axes. Some degradation of crystal quality was indicated by the broadening of the diffraction maxima and disappearance of intense high-angle diffraction; however, the change was conclusively established through a complete X-ray single-crystal analysis at 150 K. The transformation results in degeneration of the 4_1 symmetry axis into a 2_1 axis and adoption of the chiral orthorhombic space group $P2_12_12_1$. The low-temperature crystal is twinned to emulate its former tetragonal symmetry.[8] This unusual structural transformation from tetragonal **1a** to orthorhombic **1b** was verified by the ADDSYM routine in PLATON[9] and the successful refinements. The structure determination reveals that at low temperature (LT) the square pyramidal $\{CuN_4O\}$ coordination environment persists largely unchanged with only slightly different bond distances and angles (Figure 1 and Supporting Information). There are now two crystallographi-

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(8) All intensity data measurements performed with Bruker SMART APEX CCD diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å). Data reduction: SAINT-PLUS Version 6.22, absorption corrections not applied. Structure solution (direct methods), full-matrix least-squares refinement (F^2) and Fourier calculations performed with SHELXTL Version 6.14. All programs obtained from Bruker AXS, Madison, WI. Crystal data **1a** (RT form): $[Cu(\mathbf{L1})_2(H_2O)](ClO_4)_2$·unknown solvate: $M_r = 748.94$, deep-blue block, tetragonal, $P4_12_12$, $a = 16.4355(6)$, $c = 13.9077(6)$ Å, $V = 3756.8(3)$ $Å^3$, $Z = 4$. Final R indices [$I > 2\sigma(I)$] R1 = 0.0291, wR2 = 0.0746. Disordered solvent and ClO_4^- anions could not be modeled successfully and were removed from the reflection data with SQUEEZE[9] (solvent/anion-accessible void volume = 1770.6 $Å^3$, 47.1% total unit cell volume). Crystal data **1b** (LT form): $[Cu(\mathbf{L1})_2(H_2O)](ClO_4)_2$·unknown solvate: $M_r = 748.94$, deep-blue block, orthorhombic, $P2_12_12_1$, $a = 13.7327(14)$, $b = 16.4189(16)$, $c = 16.5975(16)$ Å, $V = 3742.3(6)$ $Å^3$, $Z = 4$. Final R indices [$I > 2\sigma(I)$] R1 = 0.0633, wR2 = 0.1625. Orthorhombic cell axes permuted (*abc*(ortho) = *cab*(tetrag)) to conform to conventional orthorhombic cell $a < b < c$. Disordered solvent and one ClO_4^- anion could not be modeled successfully and were removed from the reflection data with SQUEEZE[9] (solvent/anion-accessible void volume = 1753.1 $Å^3$, 46.8% total unit cell volume). Crystal refined as pseudo-tetragonal twin, with twin matrix (by rows) [1 0 0/0 0 1/0 1 0], and refined major twin fraction = 0.75(2). Refinement truncated at $2\theta_{max} = 45°$ due to lack of appreciable high-angle scattering. Crystal data **1a′** (the data were obtained after **1b** was warmed again to room temperature): $[Cu(\mathbf{L1})_2(H_2O)](ClO_4)_2$·unknown solvate: $M_r = 748.94$, deep-blue block, tetragonal, $P4_12_12$, $a = 16.403(2)$, $c = 13.905(3)$ Å, $V = 3741.6(10)$ $Å^3$, $Z = 4$. Final R indices [$I > 2\sigma(I)$] R1 = 0.0710, wR2 = 0.1689.

(9) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; University of Utrecht: Utrecht, The Netherlands, 1998.

cally independent L1 ligands. At 150 K, the thermal motion is lessened to the extent that a highly restrained three-component disorder model for one of the two ClO_4^- anions could be refined. The ClO_4^- anion is located near the vacant Cu(II) coordination site, with the closest Cu−O distance being >3 Å. Compared to **1a**, an almost identical polymeric pattern with 3-fold interpenetrating three-dimensional cationic framework was found (Figure S4). The structural transformation is apparently a mild shift in ligand arrangement, perhaps promoted by partial anion/solvent motion within the cavities, which causes a breakdown of the crystallographically imposed 4-fold symmetry. When the temperature was warmed again to RT (293 K), the tetragonal RT structure of **1a** was restored, as evidenced by X-ray single-crystal analysis.[8]

As we know, there are several ways to access chiral systems, such as starting with achiral building blocks to construct chiral structures,[10] using chiral organic ligands incorporating metal ions into supramolecular arrays or coordination polymers, or forming helical chains.[11] To date, numerous chiral metal−organic polymeric compounds are obtained on the basis of the above strategies; however, the chiral three-dimensional porous networks, especially those constructed from symmetrical ligands, are still quite unusual.[12] To the best of our knowledge, compound **1a** is the first chiral 3-fold interpenetrating three-dimensional network showing a single-crystal-to-single-crystal transformation in the solid state driven by temperature, although some robust metal−organic compounds which are able to retain their frameworks and single-crystallinity upon removal and exchange of the guest molecules were reported. [6c,13]

Compound **1a** is photoluminescent in the solid state.[14] **1a** exhibits one fluorescence emission maximum at 373 nm upon photoexcitation at 213 nm. Compared to the fluorescence signal of the free **L1** ligand (358 nm), this emission peak is slightly red-shifted. We thus believe that the luminescence of **1a** originates from ligand-centered $n-\pi^*$ or $\pi-\pi^*$ process (Figure S6). A circular dichroism (CD) spectrum of **1a** was recorded on the single crystals. It is noteworthy that CD spectra of two kinds of single crystals with opposite handedness are mirror images of each other, which indicates their enantiomeric nature (Supporting Information). The spectra exhibit an obvious Cotton effect, indicating that spontaneous resolution took place during the course of crystallization, which provides potential utility as chiroptical materials.[15]

In summary, we have shown that the achiral bent 2,5-bis-(4-pyridyl)-1,3,4-oxadiazole ligand could be used as a spacer to synthesize a chiral metal−organic framework. The new chiral polymeric complex $[Cu(2,5\text{-bis}(4\text{-pyridyl})\text{-}1,3,4\text{-oxadiazole})_2(H_2O)](ClO_4)_2]_n$ (**1a**) exhibits an interesting temperature-controlled phase-transformation phenomenon. We believe such completely stereospecific self-assembly of uncoordinated heteroatoms containing organic spacers and inorganic metal ions without any chiral auxiliary in self-assembly would offer a very useful tool for chiroptical and chiral recognition applications. Current efforts toward the preparation of new chiral polymeric systems such as **1a** containing other transition metals based on this type of ligand are underway.

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Supporting Information Available: Crystallographic data of **1a**−**b** and X-ray Structure Determination (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) (a) Ezuhara, T.; Endo, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3279. (b) Biradha, K.; Seward, C.; Zaworotko, M. J. *Angew. Chem.* **1999**, *111*, 584. (b) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511 and references therein.

(11) (a) Pschirer, N. G.; Ciurtin, D. M.; Smith, M. D.; Bunz, U. H. F.; zur Loye, H.-C. *Angew. Chem., Int. Ed*. **2002**, *41*, 583. (b) Fragoso, A.; Kahn, M. L.; Casineiras, A.; Sutter, J. P.; Kahn, O.; Cao, R. *Chem. Commun.* **2000**, 1547. (c) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzato, S. *Chem. Commun.* **2000**, 1319.

(12) A chiral heteromeric diamondoid-net with the bent ligand, see: Sasa, M.; Tanaka, K.; Bu, X.-H.; Shiro, M.; Shionoya, M. *J. Am. Chem. Soc.* **2001**, *123*, 10750. For examples of 2-fold three-dimensional racemate diamondoid net with the bent ligand, see ref 6c.

(13) (a) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (b) Biradha, K.; Hongo, Y.; Fujita, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3843. (c) Kepert, C. J.; Rosseinsky, M. J. *Chem. Commun.* **1999**, 375.

(14) (a) Ciurtin, D. M.; Pschirer, N. G.; Smith, M. D.; Bunz, U. H. F.; zur Loye, H.-C. *Chem. Mater.* **2001**, *13*, 2743.

(15) Cui, Y.; Lee, S.-L.; Lin, W. *J. Am. Chem. Soc.* **2003**, *125*, 6014.