Single-crystal-to-single-crystal transformation involving release of bridging water molecules and conversion of chain helicity in a chiral three-dimensional metal-organic framework†

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An unprecedented release of the bridging aqua molecules and conversion of chain helicity within a 3-D chiral cadmium(II) dicarboxylate coordination polymer was observed in a unique and drastic single-crystal-to-single-crystal transformation of dehydration.

Metal-organic Frameworks (MOFs) are kinds of potentially useful molecular materials that can exhibit flexibilities induced by chemical and physical stimului.[1] In particular, such flexibilities include conformational changes of ligands and coordination spheres, inter-layer/network shifting, and most drastically, coordination-bond cleavage and formation. In this context, single-crystal-to-single-crystal (SC–SC) transformations of MOFs have attracted considerable attention in recent years since these processes can directly and accurately investigate the relationship between the structures and properties involved.[2] However, the SC–SC transformations are still a challenge since crystals can hardly retain single crystallinity after a drastic solid-state rearrangement of atoms. A number of SC–SC transformations of MOFs have been reported, such as guest desorption–resorption, guest exchange, ligand exchange and thermally induced rearrangement reactions.[1,3–6] The known drastic SC–SC transformations associated with coordination bond cleavages and formations usually involve the loss of terminal aqua ligands, and/or coordination bonds of metal ions, such as d^{10} metals, that are relatively labile and/or flexible in adopting different coordination numbers and geometries.[1b,d,5b,6b,c] So far more drastic SC–SC transformation involving loss of bridging ligands has not been observed.

In addition, chiral MOFs are of great interest due to their potential applications in second-order nonlinear optical materials, chiral separation and asymmetric heterogeneous catalysts.[7–9] Such chiral MOFs can be usually achieved by using chiral ligands, and occasionally, by achiral ligands upon spontaneous resolution.[10] The achiral ligand approach may furnish MOFs with chiral helical chains, which is more attractive since achiral ligands are usually much facile.[11,12]

As a flexible and multidentate ligand,[13] bis(carboxymethylmercapto)-1,3,4-thiadiazole acid (H_2bct) can be expected to assemble metal ions into a MOF that may have helical chains and even chiral structure. Actually, we have successfully isolated a new three-dimensional (3-D) chiral MOF by a solvothermal reaction, namely [Cd(μ-OH_2)(bct)] (**1**). Being established by single-crystal X-ray diffraction, the crystals of **1** are a mechanical and racemic mixture of chiral crystals of **1**·mpm and **1**·pmp, in which mpm and pmp denote the helicity along *a*-, *b*- and *c*-axes, respectively. More interestingly, both **1**·mpm and **1**·pmp exhibit an unprecedented, drastic SC–SC transformations upon heating at 180 °C under vacuum into dehydrated **2**·pmm and **2**·mpp, respectively, both formulated as [Cd(bct)] (**2**). All the four compounds crystallize in the same orthorhombic space group $P2_12_12_1$.‡ Since the transformations of **1**·mpm to **2**·pmm and **1**·pmp to **2**·mpp are virtually identical, herein we only describe that from **1**·mpm to **2**·pmm.

As shown in Fig. 1a, the Cd^{II} ion in **1**·mpm adopts a slightly distorted octahedral CdO_5N coordination geometry [Cd–N, 2.3477(2) Å, Cd–O(carboxy), 2.2276(2)–2.2977(2) Å, Cd–O-(aqua), 2.3954(2) Å] where the longest Cd–O bonds belong to the bridging aqua ligands. The MOF consists of three types of 2_1 helices along *a*-, *b*- and *c*-axes, respectively. Among them, the first (*M*) left-handed one (along the *a*-axis) is bridged by the μ-aqua bridges between the metal ions with a pitch of 5.1461(6) Å (Fig. 2a), the second (*P*) right-handed one (along the *b*-axis) is bridged by the bct ligand using a carboxylate end and a nitrogen donor of the 1,3,4-thiadiazole group with a pitch of 10.196(1) Å (Fig. 2b), the third (*M*) left-handed one (along the *c*-axis) is bridged by the bct ligand using both carboxylate ends with a pitch of 20.941(2) Å due to the longer size of the bct ligand (Fig. 2c). Interestingly, the third type of helical chains are further interlinked by the *syn–anti* carboxylate bridges into 2-D undulating layers parallel to the *ac* plane (Fig. 2c and Fig. S1a in ESI†), which are further connected by the μ-aqua bridges and ligations of the 1,3,4-thiadiazole nitrogen atoms into the final condensed 3-D network (Fig. 3a).

It is notable that around the significantly longer Cd–O-(aqua) bond, an uncoordinated carboxylate oxygen (O2e, $e = -x - 1/2, -y + 1, z + 1/2$) and an *anti*-carboxylate oxygen atom (O4) are located in the close vicinity of the Cd^{II} ion [Cd1···O2e, 5.8783(5) Å and Cd1···O4, 3.1459(3) Å] (Fig. 1a), thus providing a favourable condition for a topochemical reaction. Actually, a thermogravimetric analysis (TGA) on a polycrystalline sample of **1** in air showed an

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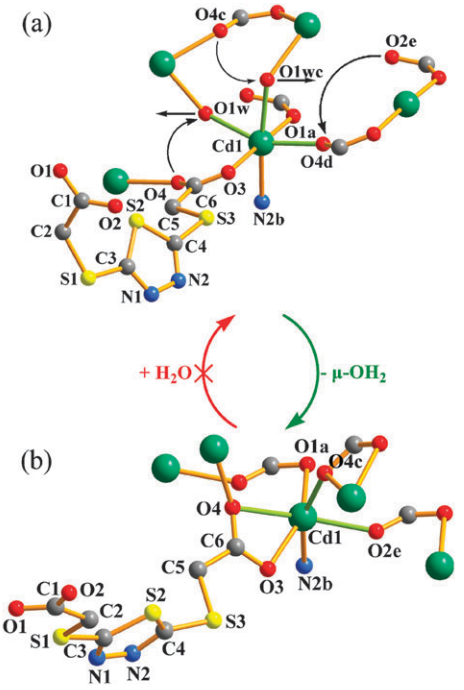

Fig. 1 The coordination environments in **1**·mpm (a) and **2**·pmm. (b) Some bct ligands are partially simplified for clarity, while the lime Cd–O bonds are possibly cleaved (a) and re-formed (b) ones during the transformation. Symmetry codes for **1**·mpm: a, $-x + 1/2, -y + 1, z + 1/2$; b, $x - 1/2, -y + 1/2, -z$; c, $x - 1/2, -y + 3/2, -z$; d, $x - 1, y, z$; e, $-x - 1/2, -y + 1, z + 1/2$. For **2**·pmm: a, $-x - 3/2, -y, z + 1/2$; b, $x + 1/2, -y + 1/2, -z$; c, $x + 1/2, -y - 1/2, -z$; e, $-x - 1/2, -y, z + 1/2$.

initial weight loss of 4.7% from 172 to 223 °C corresponding to the removal of one water molecule per formula unit (calcd. 4.6%), giving rise into a new phase that was stable up to 253 °C, followed by another weight loss corresponding to the collapse of the framework above 253 °C (Fig. S2 in ESI†). Meanwhile, powder X-ray diffraction (PXRD) patterns also indicated that **1** could be transformed at ≥ 180 °C under vacuum into a new phase (Fig. S4 in ESI†). In addition, a differential scanning calorimetry measurement on **1** indicated an abrupt endothermic peak at the transition temperature ($T_{\text{peak}} = 208$ °C and $\Delta H \approx 62.7$ kJ·mol^{-1}) (Fig. S3 in ESI†), corresponding to the loss of bridging aqua ligands, which is also in agreement with the TGA and PXRD results.

Based on the above observations, we heated a piece of single crystal of **1**·mpm at 180 °C for 30 min under vacuum, furnishing a new phase, or **2**·pmm. Although the single-crystal was cracked during heating, a smaller piece of single-crystal of dehydrated **2**·pmm suitable for the single-crystal diffraction was obtained (Fig. S5 in ESI†). Similarly, a single crystal of dehydrated **2**·mpp could also be transformed from a piece of single crystal of **1**·pmp. Meanwhile, bulk crystals of both **1**·mpm and **1**·pmp could also be transformed into crystalline **2**·pmm and **2**·mpp, respectively. However, single-crystals of **2** cannot be converted back to single-crystals of **1** after exposure in air for a few days.

The crystal structure of **2**·pmm features a 3-D network (Fig. 3b). However, the unit-cell volume decreases by 8.4%, owing to the release of water molecules and the structural change involved. Consequently, the crystals of **2**·pmm (2.487 g cm^{-3}) are denser than those of **1**·mpm (2.386 g cm^{-3}). In **2**·pmm, each metal ion is coordinated in a severely distorted

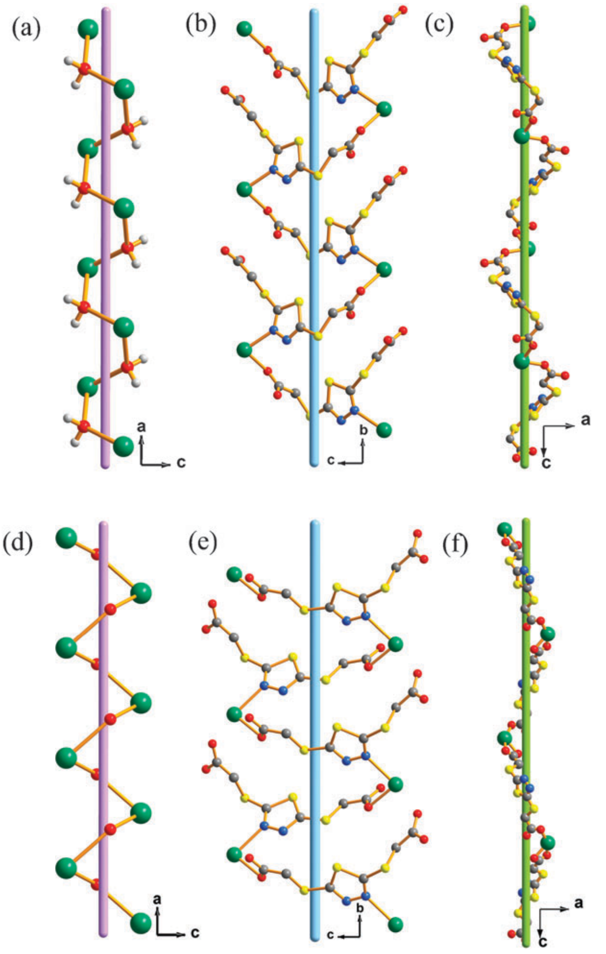

Fig. 2 The helices in **1**·mpm (a–c) and in **2**·pmm (d–f).

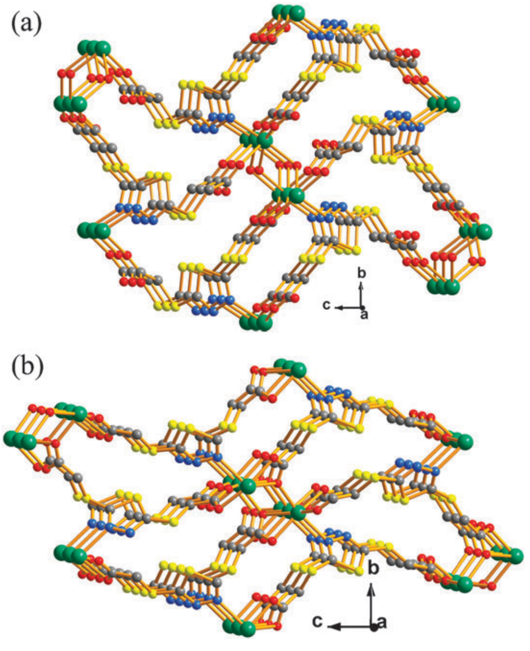

Fig. 3 The 3-D networks in **1**·mpm (a) and **2**·pmm (b).

triangular prism with five carboxylate oxygen atoms and one nitrogen atom from five different bct ligands [Cd–N, 2.467(1) Å, Cd–O, 2.256(1)–2.532(1) Å] (Fig. 1b), where the relevant Cd–O/N bond lengths are slightly longer in comparison to those in **1**·mpm, and the newly formed Cd–O4 bond length [2.532(1) Å] is the longest one. This fact is attributed to the flexibility of Cd^{II} in coordination. Meanwhile, the conformation of bct is slightly different, which may also be critical during the transformation. Being different but related to those in **1**, there are also three types of 2_1 helices in **2**·pmm: (*P*) right-handed [Cd–O] helices formed by the monoatomic [O(4)] carboxylate bridges between the metal ions with a pitch of 4.723(3) Å along the *a*-axis, (*M*) left-handed [Cd-bct] helices bridged by the bct ligand using a carboxylate end and a 1,3,4-thiadiazole nitrogen donor, and (*M*) left-handed [Cd-bct] helices bridged by both carboxylate ends, with a pitch of 8.316(6) Å and 25.62(2) Å, running along the *b*- and *c*-axes, respectively (Fig. 2d–f).

It is noteworthy that, although **2**·pmm retains chiral after the transformation, the helicities in **1**·mpm and **2**·pmm along the *a*- and *b*-axes are opposite (Fig. 2), which result from the cleavage and formation of Cd–O bonds and flexibility of the metal ion and ligand. Such a phenomenon has not been found in the literature. By superposition of the crystal structures of **1**·mpm and **2**·pmm, we find that the bond cleavage may involve three Cd–O bonds. Besides release of the μ-aqua molecule, the longest metal–carboxylate bond [Cd1–O4d, 2.2977(2) Å, $d = x - 1, y, z$] in **1**·mpm around each Cd^{II} ion may also be broken. Consequently, the neighbouring carboxylate O4, O4c ($c = x - 1/2, -y + 3/2, -z$) and O2e atoms ligate to the metal atom, resulting in changes in the coordination modes of two carboxylate ends during the transformation, one (with O1 and O2) from the monodentate mode to the *syn–anti* bridging one, while the other (with O3 and O4) from *syn–anti* bridging mode to chelating bridging one. Although such deduction represents a unique case among the known SC–SC transformations of MOFs, it is supported by the following reasons. Firstly, Cd^{II} ion is flexible in adopting different coordination geometries while Cd–O bonds are not very strong; secondly, the mercaptoethylene groups in bct are flexible; thirdly, "carboxylate shift" around metal centers has been proposed and observed for polynuclear systems.[14]

Preliminary Kurtz powder second harmonic generation (SHG) measurements on the racemic mixtures of **1** and **2** showed that they have SHG intensity of 0.5 and 1.0 *versus* that of technologically useful potassium dihydrogen phosphate (KDP), respectively, which confirm their acentric symmetries.[15]

In conclusion, a new 3-D chiral MOF has been synthesized by using a flexible dicarboxylate ligand, which exhibits an unprecedented, temperature-induced SC–SC transformation involving release of bridging aqua molecules and helicity conversion of the helical chains in two directions within the MOF.

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Notes and references

‡ Crystal data: Both **1** and **2** belong to the orthorhombic, space group $P2_12_12_1$ (No. 19) with $Z = 4$ at $T = 293$ K. For **1**·mpm: $a = 5.1461(6)$ Å, $b = 10.196(1)$ Å, $c = 20.941(2)$ Å, $V = 1098.8(2)$ Å^3, $\rho = 2.386$ g cm^{-3}, $\mu = 2.567$ mm^{-1}, final $R_1 = 0.0136$ for $I \geq 2\sigma(I)$, w$R_2 = 0.0362$ for all data, $S = 1.155$, Flack parameter = 0.01(2). For **1**·pmp: $a = 5.1436(6)$ Å, $b = 10.186(1)$ Å, $c = 20.945(3)$ Å, $V = 1097.4(2)$ Å^3, $\rho = 2.389$ g cm^{-3}, $\mu = 2.570$ mm^{-1}, final $R_1 = 0.0172$ for $I \geq 2\sigma(I)$, w$R_2 = 0.0401$ for all data, $S = 1.074$, Flack parameter = 0.00(2). For **2**·pmm: $a = 4.723(3)$ Å, $b = 8.316(6)$ Å, $c = 25.62(2)$ Å, $V = 1006.2(12)$ Å^3, $\rho = 2.487$ g cm^{-3}, $\mu = 2.789$ mm^{-1}, final $R_1 = 0.0580$ for $I \geq 2\sigma(I)$, w$R_2 = 0.1128$ for all data, $S = 1.077$, Flack parameter = 0.00(8). For **2**·mpp: $a = 4.716(2)$ Å, $b = 8.312(3)$ Å, $c = 25.56(1)$ Å, $V = 1001.8(7)$ Å^3, $\rho = 2.498$ g cm^{-3}, $\mu = 2.802$ mm^{-1}, final $R_1 = 0.0946$ for $I \geq 2\sigma(I)$, $wR_2 = 0.1896$ for all data, $S = 1.222$, Flack parameter = 0.16(15). CCDC 666519–666522. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717885a

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