Metal disordering Cu(II) supramolecular polymers constructed from a tripodal ligand possessing two different functional groups†

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Two novel coordination polymers with double-layer structures were constructed from a tripodal ligand TCMB (1,3,5-tris(carboxymethoxy)benzene) by controlling the solvent and diffusion velocity of the reaction systems. Both solvated isomers $[Cu_3(TCMB)_2(C_5H_5N)_3(H_2O)_3\cdot10H_2O]$ (**1**, *P6/m*, $a = b = 16.753(1)$, $c = 10.811(1)$ Å, $\alpha = \beta = 90.00°$, $\gamma = 120.00°$) and $[Cu_3(TCMB)_2(C_5H_5N)_3(H_2O)_3\cdot7.66H_2O\cdot DMF]$ (**2**. *P-3*, $a = b = 28.937(3)$, $c = 10.694(1)$ Å, $\alpha = \beta = 90.00°$, $\gamma = 120.00°$) exhibit peculiar metal disordering with fixed ligands due to the fact that the ligand can provide excessive potential coordinative sites with deficient metal centers available. Supramolecular isomerism induced by metal disordering was found for the first time.

Introduction

Recent years have witnessed the rapid development of supramolecular coordination solids which may have potential applications in many areas including gas storage, molecular sieves, ion-exchange, catalysis, magnetism and optoelectronics, and exhibit intriguing architectures and topologies, such as molecular grids, bricks, herringbones, ladders, rings, boxes, diamondoids, honeycombs.[1–4] In particular, exploring highly symmetrical multi-topic ligands and suitable metal ions to construct such frameworks is of higher interest.[5] For this kind of ligands, various coordination modes can be adjusted to satisfy the requirements of assembly process and interesting structural motifs may result, including those easily expected and in some cases unpredicted. Furthermore, highly symmetrical building blocks may lead to novel frameworks with high symmetries and extreme beauty.[6] In addition, as one of the most important aspects of supra-molecular chemistry and crystal engineering, supramolecular isomerism has received more and more attentions. Examples induced by variations like temperature, solvent, conformation of the ligand, *etc.*, have been well established.[7] Their design, however, is of a great challenge and remains less explored up to now.

Meanwhile, disordering structures known in inorganic and organic materials may result in novel physical properties such as ion conductivity, semiconductivity, magnetism, *etc.*[8] As for inorganic–organic hybrid compounds, disordered anions and guest solvent molecules have been observed in some examples.[9]

Central metal-disordering, however, has less been exploited so far.[10,11] Though metal centers of the SUBs $Zn_4O(CO_2)_4$ in very limited examples have been mentioned half-occupied with the disordering of the carboxylate ligands at the same time,[11] disordering of the metal centers with the fixed ligands has never been reported to our best knowledge, especially for supramolecular isomerism.

We are interested in constructing coordination polymers with novel topologies from highly symmetrical multi-topic units and have synthesized the inorganic fullerene-like molecules and 1-D or 2-D coordination polymers based on highly symmetrical $[Cp^*Fe(\eta^5\text{-}P_5).]$[12] More recently, a new tripodal ligand, 1,3,5-tris(carboxymethoxy)benzene (TCMB)[13] attracted our attention because of the additional OCH_2 groups which could not only provide more coordination sites except for the carboxylate groups but may also tune the structures and properties of the complexes in comparison with other well-investigated tripodal ligands. Herein, two novel supramolecular isomeric complexes $[Cu_3(TCMB)_2(C_5H_5N)_3(H_2O)_3\cdot10H_2O]$ (**1**) and $[Cu_3(TCMB)_2(C_5H_5N)_3(H_2O)_3\cdot7.66H_2O\cdot DMF]$ (**2**) were reported with unprecedented metal disordering structures based on this ligand.

Experimental

The TCMB ligand was prepared according to previous literature.[14] Commercially available reagents were used as received without further purification. Elemental analyses (C, H, N) were carried out with a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a VECTOR 22 spectrometer. Thermal analyses were performed on a TGA V5.1A Dupont 2100 instrument from room temperature to 700 °C with a heating rate of 10 °C min^{-1} under flowing nitrogen, and the data are consistent with the structures. Magnetic susceptibility of polycrystalline powders was measured in the temperature range of 1.8 to 300 K with applied magnetic field of 0.2 T using a SQUID magnetometer.

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† Electronic supplementary information (ESI) available: Selected bond lengths (Å) and angles (°) of **1** and **2** (Table S1), 3-D network of **1** (Fig. S1), 3-D network of **2** (Fig. S2), TGA of **1** and **2** (Fig. S3). See DOI: 10.1039/b616315g

Synthesis of complex 1

In a typical synthesis, a small beaker with a stoichiometric 2 : 3 solution of TCMB (0.5 mmol, 0.150 g) and $Cu(NO_3)_2 \cdot 6H_2O$ (0.75 mmol, 0.180 g) in DMF (10 ml) was placed in a large cylindrical jar containing 3mL pyridine, which was then sealed and left to stand. Large, blue–green, hexagonal crystals were separated several months later. Yields: 70 mg (22.28% based on TCMB). Elemental analysis (%) calcd for $C_{26}H_{39.33}Cu_2N_2O_{20.67}$: C 37.28; H 4.73; N 3.34; Cu 15.17; found: C 37.38; H 4.52; N 3.56; Cu 15.02. IR: $v = 3424(br,s)$, 3106(m), 1607(s), 1483(w), 1428(m), 1318(m), 1178(s), 1121(w), 1086(m), 829(w), 698(w) cm^{-1}.

Synthesis of complex 2

$Cu(NO_3)_2 \cdot 6H_2O$ (0.75 mmol, 0.180 g) were dissolved in H_2O (5 ml) at the bottom of a tube, the mixture of TCMB (0.5 mmol, 0.150 g) and pyridine (0.1 ml) in DMF (5 ml) were layered carefully. Large, blue–green, hexagonal crystals were grown along the wall of the tube several weeks later. Yields: 58 mg (18.02% based on TCMB). Elemental analysis (%) calcd for $C_{42}H_{61.33}Cu_3N_4O_{29.67}$: C 39.18; H 4.80; N 4.35; Cu 14.81; found: C 39.27; H 5.01; N 4.47; Cu 14.98. IR: $v = 3427(br,s)$, 1610(s), 1482(w), 1423(m), 1385(w), 1322(w), 1177(m), 1086(w), 697(w) cm^{-1}.

X-Ray crystallography

Data were measured on a Bruker SMART Apex2 diffractometer for **1** at 298 K and **2** at 153 K using graphite-monochromated Mo Kα radiation, respectively. Data reduction was performed with the Bruker SAINT package. The structures were solved with direct methods and refined with full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs, respectively.[15] Most metal centers in the complexes were statistically disordered. The site occupancy factors were given to 0.5 for Cu(1) atom in complex **1** and for Cu(2)–Cu(5) in complex **2** those sit on a general position. The coordinates of the non-hydrogen atoms were refined anisotropically, and the positions of the H-atoms were generated geometrically. Structure refinement details for the two pseudo-polymorphs are shown in Table 1. Figures are obtained using Olex program package.[16] CCDC reference numbers 609779–609780. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616315g
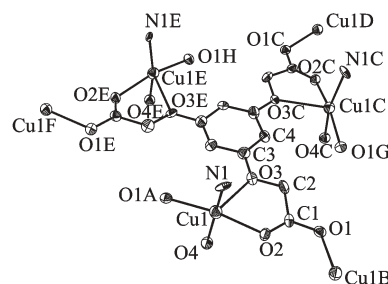
Results and discussion

Syntheses of the complexes

Different reaction systems are employed to obtain the complexes. It took several months for complex **1** to grow with gas diffusion of the pyridine molecules, while solution diffusion between DMF and water changes the reaction process and results in complex **2**. The presence of considerable amount of water in the reaction may have large influence on the assembly process—increasing the reaction velocity and decreasing the solubility of the resulting coordination polymer—and thus facilitates the crystallization of the products.

Structural descriptions

X-Ray diffraction reveals that complex **1** crystallized in hexagonal crystal system, space group $P6/m$. The local coordination environment of Cu1 can be described as a distorted square pyramid with two carboxylate oxygen atoms from separate ligands and nitrogen atom of pyridine as well as oxygen atom of water molecule in the square plane, one ether oxygen atom occupying the apical position (Fig. 1). The average Cu–O and Cu–N distances in the plane are 2.051(2) and 1.959(4) Å, respectively. The axial Cu1–O3 distance 2.412(2) Å is much longer, as resulted from Jahn–Teller effect, and the deviation of the Cu(II) center toward the apical oxygen atom from the mean coordination plane O1A–O4–O2–N1 is 0.092 Å.

The fascinating feature of the complex is disordered arrangements of the half-occupied metal centers and the fixed organic ligands. The whole structure can be roughly viewed as organic layers of the TCMB anions separated by disordered water and pyridine molecules alternately and the positions of Cu(II) ions are subject to the orientations of pyridine molecules. In order to interpret the structure clearly, fixed positions of the metal centers are supposed as illustrated in Fig. 2a. In this situation, each TCMB ligand coordinates to

Table 1 Crystallographic data and structure refinement details for the two pseudo-polymorphs

Complex	1	2
Emprical formula	$C_{26}H_{39.33}Cu_2N_2O_{20.67}$	$C_{42}H_{61.33}Cu_3N_4O_{29.67}$
Formula mass	837.67	1287.57
Space group	$P6/m$	P-3
$a = b$/Å	16.753 (1)	28.937(3)
c/Å	10.811 (1)	10.694(1)
$\alpha = \beta/°$	90.00	90.00
$\gamma/°$	120.00	120.00
$V/Å^3$	2627.8(4)	7754.9(1)
Z	3	6
D_{calcd}/g cm^{-3}	1.588	1.654
T/K	298	153
μ/mm^{-1}	1.301	1.323
Goodness of fit on F^2	1.163	1.022
R1, $wR2^a$ $[I > 2\sigma(I)]$	0.0599; 0.1223	0.0619; 0.1439
R1, $wR2^a$ [all data]	0.0925; 0.1322	0.0925; 0.1525

^{a} R1 $= \sum||Fo| - |Fc||/|Fo|$, wR2 $= [\sum w(\sum Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$.

Fig. 1 ORTEP plot (thermal ellipsoids set at the 30% probability) of the asymmetric unit along with some symmetry related atoms completing coordination environment of the metal centers in **1**. All the metal sites are half-occupied. Disordered pyridine molecule is represented only by N1 atom. Solvent molecules and hydrogen atoms are omitted for clarity. Symmetry codes: A: $1 + y$, $1 - x + y$, $-z$; B: $x - y$, $-1 + x$, $-z$; C: $1 - x + y$, $1 - x$, $+z$; D: $+y$, $1 - x + y$, $-z$; E: $1 - y$, $x - y$, $+z$; F: $2 - x$, $1 - x$, $-z$.; G: $1 - x$, $-y$, $+z$; H: $+x - y$, $+x$, $+z$.
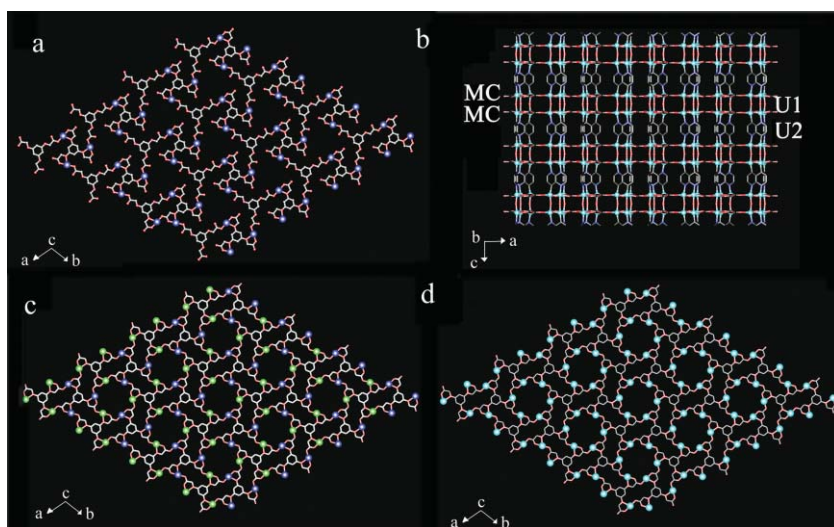
Fig. 2 (a) View of single MC (metal-carboxylate) layer along the *c* axis, assuming the metal centers are fixed. (b) A perspective view of **1** down the *b* axis, indicating the alternating MC and U (units) layers (U1 and U2 represent disordered water and pyridine molecules, respectively). (c) Two adjacent layers of **1** viewed down the *c* axis. Oxford blue and green balls represent the metal ions fully-occupied in different layers, respectively. (d) Statistical representation of **1** viewed down the *c* axis, with sky blue balls representing half-occupied Cu(II) ions. All the hydrogen atoms and the solvent molecules have been omitted for clarity.

three metal centers by C_3 rotation symmetry with two kinds of coordination modes (structures **I** and **II**, Scheme 1), in which one is chelating of the ether oxygen atoms and carboxylate oxygen atoms imposing the neighboring metal–metal separation around the aromatic ring of *ca.* 7.923(8) Å; and the other is monodentate of the carboxylate oxygen atoms with the long
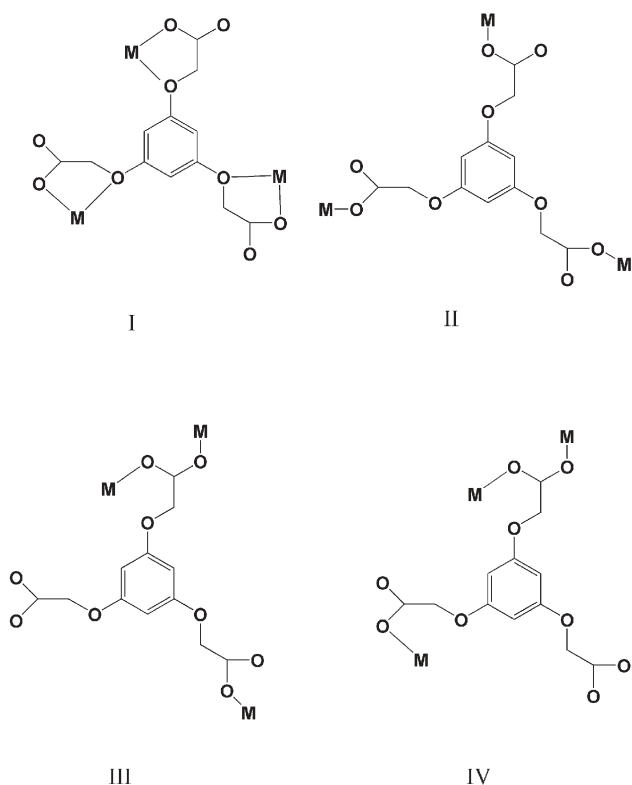

Scheme 1 Structures **I–IV**.

metal–metal distance of *ca.* 13.737(4) Å. This connectivity affords screw propeller-shaped 63-membered macrocycles sharing the edges closely, leading to metal–carboxylate (MC) layer along the *ab* plane. All the atoms in the layer exhibit a good planarity, which is rare even for rigid BTC ligand. Water and pyridine molecules coordinate to metal atoms lying perpendicular to the layer. As a result, alternating U1-MC-U2-MC layers (U1 and U2 represent the water and pyridine units, respectively) along the *c* axis are formed (Fig. 2b), more diverse than general single and double layer structures.[17] And strictly parallel aromatic rings of the TCMB ligands in each MC layer are involved in π–π stacking interactions with the adjacent layer with the face-to-face separation of 3.756 Å by water layers and 7.055 Å by pyridine layers, respectively.

Interestingly, the water molecules and the pyridine molecules are disordered and statistically distributed in two positions with the nitrogen atom bonded to copper centers. Consequently, the metal centers are also disordered and their arrangements in adjacent layers are relative to each other. That is, when the metal centers are observed in one layer, the opposite metal sites of neighboring layers should be vacant (Fig. 2c). In fact, the metal centers can occupy the open sites randomly according to pyridine molecules and the resulting structure should be statistical with all metal sites half-occupied (Fig. 2d). Furthermore, significant C–H⋯O interactions between the aromatic ring and the carboxylate groups of neighboring ligands are observed with C⋯O distance and C–H⋯O angle of 3.313(3) Å and 165.47°, respectively (Fig. 3). Even if all the vacancies in one layer are occupied by the metal centers at one time and the adjacent layers consist of the organic anions, the whole structure may still be stable. Except for the uncertain coordinative bonds, such intermolecular contacts, together with weak stacking interactions above should be considered as important forces for stabilizing this novel double layer structure.
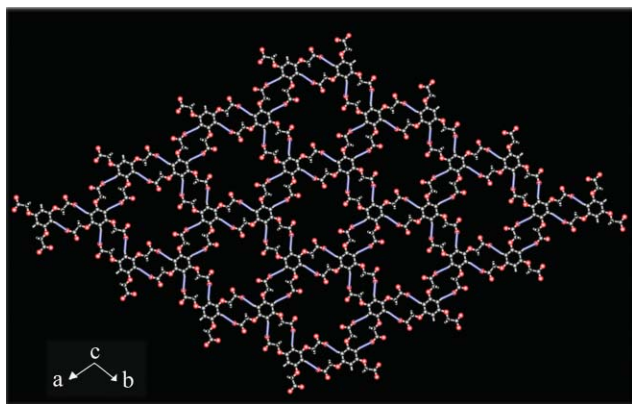
Fig. 3 View of C–H···O interactions (represented by blue sticks) among the organic ligands in one layer in **1**. The metal centers and the solvent molecules are omitted for clarity.

Remarkably, whatever arrangements the copper atoms are assumed, the stacking of the whole network results in two different kinds of hydrophilic channels running parallel to the *c* axis (Fig. 2d). The hexagonal ones are composed of the copper centers and the bridging carboxylate groups with the effective void size of the ring of 10.279(2) Å in diameter based on the distance of the opposite copper atoms. While the parallelogrammic ones are comparably small with dimensions of 7.163(9) × 3.690(4) Å based on the distances of nearest atoms in the diagonals. These channels surround each other, just like beautiful snowflakes. Moreover, a large amount of disordered water molecules involved in strong hydrogen bonds are hosted in these channels (Fig. 4), and the total solvent-accessible volume of the channels in the unit cell is 608.2 Å^3, which accounts for 23.1% of the total cell volume as calculated by PLATON.[18]

Slight change in the reactions afforded complex **2**, which possesses different but interrelated structure with complex **1**. **2** crystallized in trigonal space group, a comparably lower symmetric crystal system. As shown in Fig. 5, the metal centers also show disordered square pyramidal coordination geometry, and the ligands coordinate to the metal centers with C_1 symmetry instead of C_3 rotational symmetry. While out of the
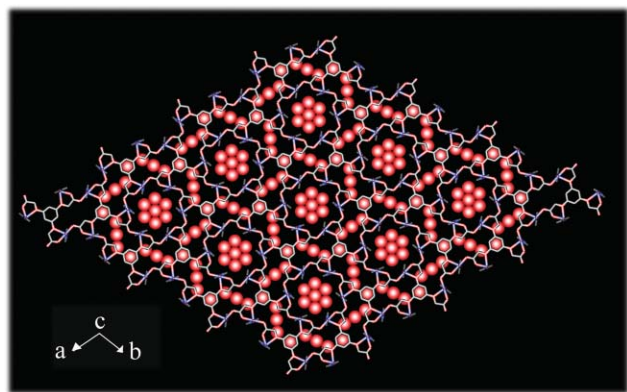
Fig. 4 Three-dimensional network of **1** viewed down the *c* axis, showing space-filling of the solvent molecules. (Red, oxygen.) Hydrogen atoms are omitted for clarity.
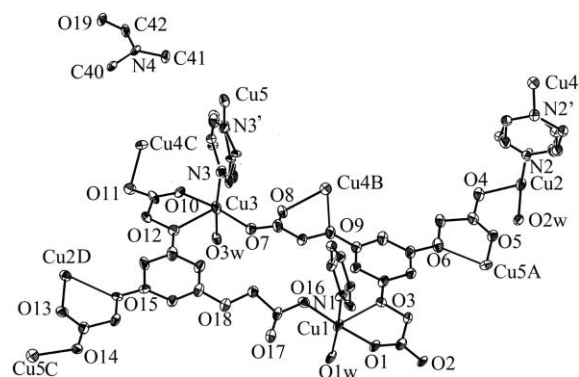

Fig. 5 ORTEP plot (thermal ellipsoids set at the 30% probability) of the asymmetric unit along with some symmetry related atoms completing coordination environment of the metal centers in **2**. Disordered solvent molecules and hydrogen atoms are omitted for clarity. Symmetry codes: A: $1 + y$, $1 - x + y$, $1 - z$; B: $2 - x$, $1 - y$, $1 - z$; C: $+x - y$, $-1 + x$, $1 - z$; D: $1 - x + y$, $1 - x$, $+z$.

five metal sites, four are still disordered with the occupancy of 50%, and only Cu1 coordinated to the fixed pyridine molecules is fully occupied. Consequently, the whole structure also depends on the arrangement of the metal centers and several potential arrangements of the metal centers may exist, significantly diverse than those in complex **1**.

One prediction is shown in Fig. 6a, Cu2 and Cu5 atoms are assumed to exist except for Cu1. In this situation, the ligands can adopt two kinds of coordination modes (structures **III** and **IV**, Scheme 1), which only involve two carboxylate groups of each ligand. Six carboxylate groups of different ligands bridge six metal centers (three Cu2 and three Cu5) alternately in *syn–anti* mode to form a hexamer structure with an 18-membered ring. These hexamers are connected further with each other through Cu1 atoms bridged by the monodentate carboxylate groups. Accordingly, except for screw propeller-shaped 63-membered macrocycles (A) similar to complex **1**, two other kinds of macrocycles are formed: one contains the Cu$_6$(CO2)$_6$ of the hexameric unit (B), the other involves only six OCH$_2$COOH groups linked by the C–H···O weak interactions between the aromatic rings and the uncoordinated carboxylate groups (C). The whole MC layers are thus formed by these macrocycles sharing the edges.

Fig. 6b illustrates the second probable arrangement containing the metal centers of Cu1, Cu3 and Cu4. In this situation, two other coordination modes (structures **V** and **VI**, Scheme 2) of the ligands are found. Though similar Cu$_6$(CO$_2$)$_6$ hexamers with three Cu3 and three Cu4 atoms are formed *via* the *syn–anti* carboxylate groups, they are not connected but extended into nonamers by coordinating to three Cu1 atoms through the monodenate carboxylate oxygen atoms. C–H···O weak interactions connect these discrete units into 2-D layer.
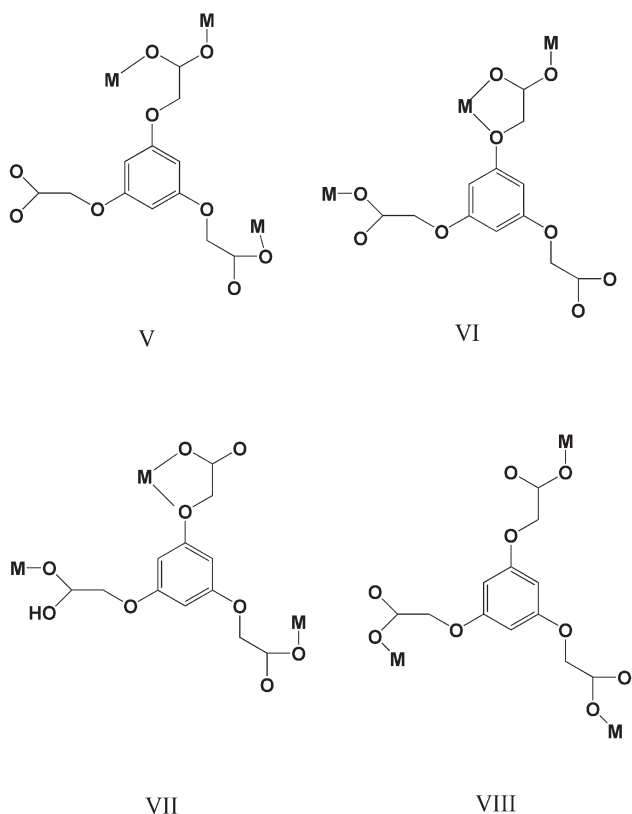
The third potential arrangement of the metal centers deals with Cu1, Cu2 and Cu3 (Fig. 6c), which also composes of nanomers *via* weak C–H···O interactions. In contrast to the second situation, metal centers in each nanomer are arranged in such a way that three metal centers (Cu2) are situated inside in a triangular array while six (three Cu1 and three Cu3) outside in a hexagonal one. All the carboxylate groups of the
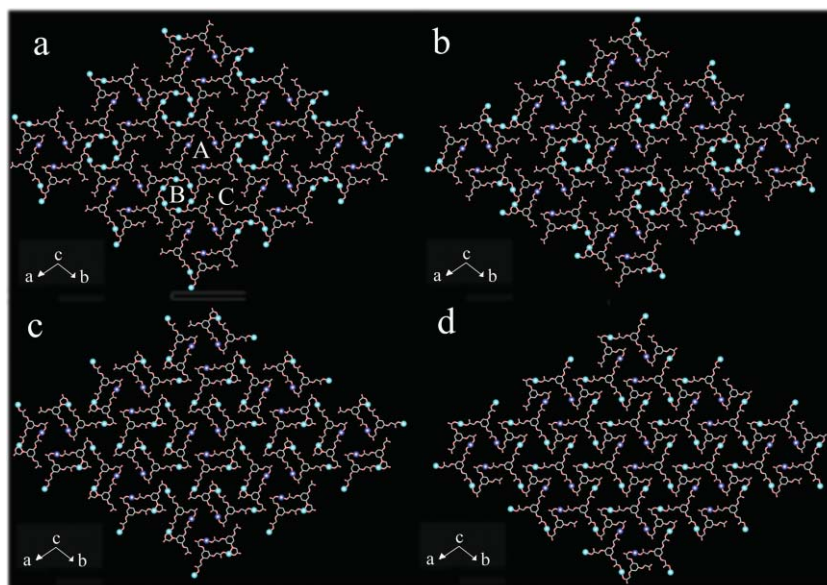
Fig. 6 The potential arrangement of the metal centers in one layer of complex **2** along the *c* axis, with Oxford blue and sky blue balls representing fully and half-occupied Cu(II) ions, respectively. Solvent molecules are omitted for clarity. Except for Cu1 centers, (a) Cu2 and Cu5; (b) Cu3 and Cu5; (c) Cu2 and Cu3; (d) Cu4 and Cu5 are shown, respectively.

ligand are involved in the coordination and two other kinds of coordination modes are adopted (structures **VII** and **VIII**, Scheme 2).

The fourth arrangement with Cu1, Cu4 and Cu5 described in Fig. 6d is fascinatingly uniform with that of complex **1**, and detailed structures were omitted.

Similarly, the adjacent layers are also relative to each other depending on the orientation of the nitrogen atoms of the pyridine molecules. For clarity, the neighboring layer corresponding to the first situation is shown in Fig. 7.

In fact, no fixed arrangement of the metal centers can be confirmed, and the resulting structure we obtained is statistical of all the situations above (Fig. 8). Anyway, this structure is different from that of complex **1** in that there are present significant sites without metal centers. Although similar U_1-MC-U_2-MC layers are also formed, the aromatic rings along the *c* axis are slightly offset and separated by water and pyridine molecules with different interlayer distances of 4.075 and 6.641 Å, respectively. Another important difference between the two complexes is the solvent molecules in the lattices. Apart from disordered water molecules, fixed DMF molecules are situated (Fig. 9), which may be considered as a

Scheme 2 Structures **V**–**VIII**.
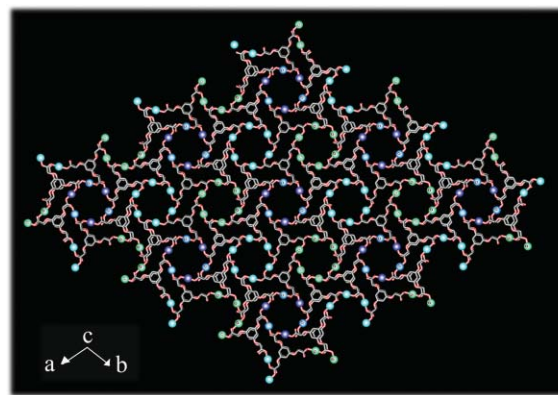
Fig. 7 Arrangement of adjacent layers in **2** consistent with the situation in Fig. 6a. Oxford blue and sky blue balls represent metal centers in one layer, and light blue and light green balls in adjacent layer.
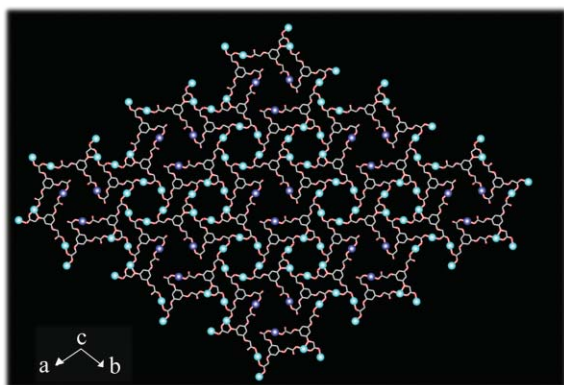
Fig. 8 View of the structure of **2** along the *c* axis, with Oxford blue and sky blue balls representing fully- and half-occupied Cu(II) ions, respectively.

factor influencing the degrees of the metal disordering and may be important to understand the difference of the complexes. To some extent, the presence of the DMF molecules may reduce the symmetry of the whole framework. In addition, the total solvent-accessible volume of the channel in the unit cell calculated by PLATON[18] is 1771.2 Å^3, about 22.8% of the total cell volume. Importantly, without considering the solvent molecules, the two complexes can be reviewed as supramolecular isomers caused by disordering metal centers, which was observed for the first time.

Structurally, in both complexes the ether oxygen atoms can provide new coordination sites with almost the same coordination ability with the carboxylate groups, very different from the reported unsaturated metal centers (UMCs), in which carboxylate groups can coordinate to the metal centers selectively.[19] Thus, the disordering of the metal atoms can be qualitatively understood: excessive potential coordinative sites *versus* deficient metal centers. Certainly, because of space hindrance, the pyridine molecules with terminal coordination could play another important role.

Thermal behavior and magnetic properties

The TGA results for the two complexes are complicated, revealing a few stage processes (see ESI).† For complex **1**,
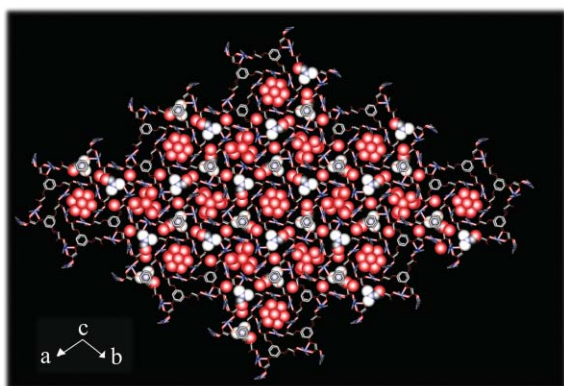
Fig. 9 Three-dimensional network of **2** viewed down the *c* axis, showing space-filling of the solvent molecules. (Red, oxygen; gray, carbon; blue, nitrogen) Hydrogen atoms are omitted for clarity.

three steps are found: the first stage involves a 8.05% loss between 40 and 80 °C, which is attributed to the loss of $5.5H_2O$ per unit (calculated 7.88%), and the second loss weight of 6.52% occurs between 100 and 160 °C, suggesting the release of some guest molecules of $4.5H_2O$ (calculated 6.45%). Loss of the water and pyridine ligands was found between 220 and 280 °C, indicating the decomposition of the whole structure. Similar loss stages were observed for complex **2**, the first loss of 6.64% between 40 and 70 °C was assigned to 4.66 guest water molecules (calculated 6.52%), and the second loss of 9.75% between 100 and 180 °C corresponds to the weight of one DMF and other three water molecules (calculated 9.86%). The whole structure began to decompose until all the coordinated water and pyridine molecules were removed between 210 and 280 °C.

Temperature-dependent magnetic susceptibility measurements on polycrystalline samples of **1** and **2** indicate that both complexes exhibit very weak ferromagnetic coupling between copper centers. As shown in Fig. 10, the value of $\chi_m T$ at room temperature of **1** is equal to 1.27 cm^3 mol^{-1} K (1.36 cm^3 mol^{-1} K for **2**), corresponding to three isolated Cu^{II} ions. Upon cooling, the value remains constant until the temperature is about 5 K, and then increases gradually, reaching 1.40 cm^3 mol^{-1} K (1.43 cm^3 mol^{-1} K for **2**) at 1.8 K, indicative of weak ferromagnetic behavior. The magnetization
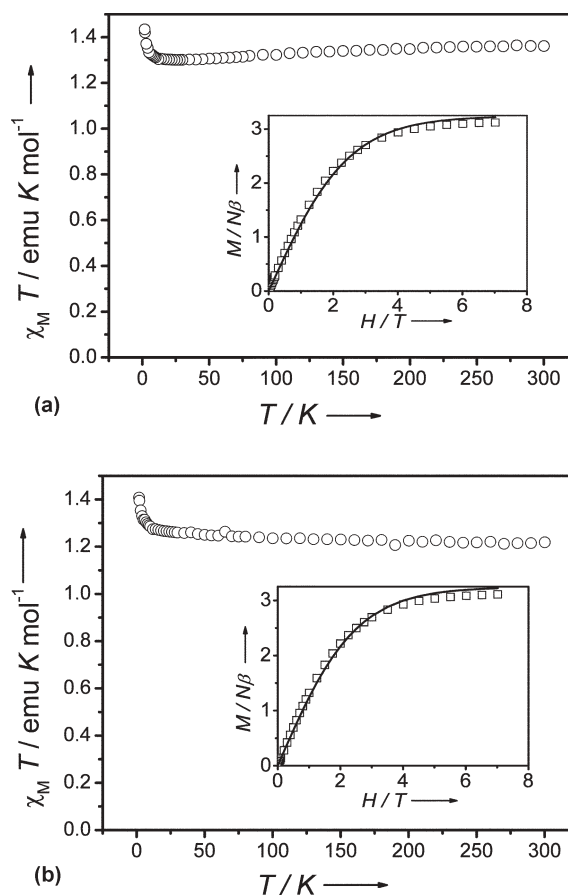
Fig. 10 Temperature dependence of the magnetization of **1** (a) and **2** (b) in the form of $\chi_M(T)$ (○). The inserts show the plots of the magnetization at 1.8 K (the solid lines represent best fits based on Brillouin function with *s* = 3/2.

data at 1.8 K for both complexes are depicted as an M versus H plot and the curves are well consistent with the Brillouin function for three magnetically noninteracting Cu^{II} centers, with $g = 2.10$ and $S = 3/2$, suggesting magnetic saturation of the complexes, which further confirms disordering of the metal centers. An inspection of the structures allows us to account for the observed magnetic properties. Two kinds of magnetic exchange pathways could be observed due to the disordered metal centers. Firstly, chelating of ether oxygen and carboxylate oxygen atoms of the TCMB ligand bridges the three copper ions in the m-phenylene arrangement, leading to possible ferromagnetic coupling according to spin-polarization mechanism.[20] Secondly, the superexchange of carboxylate groups in a *syn–anti* conformation may induce ferromagnetic interactions between the metal centers.[21] Apparently, the long distance of the Cu–O bond as well as the disordering of the paramagnetic ions should be responsible for the largely reduced coupling compared with similar linkages.

Conclusions

In summary, from a tripodal ligand TCMB with two different functional groups, we have successfully synthesized two novel supramolecular isomeric complexes with different degrees of metal disordering in the whole structure. Our investigation demonstrates that the additional ether oxygen atoms can provide new coordination sites competing with the terminal carboxylate groups, leading to interesting metal disordering structures with excessive coordination sites of the ligands in comparison with deficient metal centers. The introduction of new functional groups to highly symmetrical ligands can lead to novel frameworks with unusual structures and properties. We are now extending our work in this field and further investigations are ongoing.

Acknowledgements

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