

Eight coordination with bis(bidentate) bridging ligands: zeolitic topology versus square grid networks†

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The assembly of the asymmetric bis(bidentate) 2-pyrimidinecarboxylate ligand with Cd^{II} produces a metal–organic framework with the RHO zeolitic topology, while 5-(2'-pyrimidyl)tetrazolate with Cd^{II} leads to square grid networks.

Porous metal–organic frameworks (MOFs), as a new generation of crystalline porous materials, have attracted considerable attention for their fundamental significance and potential applications such as gas storage and separation, catalysis and sensors.^{1,2} In principle, the framework structure and the pore properties of MOFs can be engineered and tailored by the judicious selection of metal ions and organic ligands with various geometries and functionalities. An intriguing conceptual strategy towards highly porous MOFs is to replace the SiO₄/AlO₄ tetrahedral building units (TBUs) in inorganic zeolites with molecular TBUs consisting of metal ions and organic ligands. However, examples of such zeolitic MOFs (ZMOFs) are still rare,^{3–6} and their rational construction is a great synthetic challenge, because the default net (the naturally preferred high-symmetric net) for TBUs is the diamond net.^{1a} Very recently, a series of archetypical ZMOFs have been constructed from appropriate metal ions (Zn and Co) and imidazoles.⁴ In these materials, the formation of TBUs is facilitated by the preference of the metal ions for tetrahedral coordination, and the formation of zeolitic topologies is facilitated by the ability of the imidazole (im) bridge to make an M–im–M angle of about 145°, which corresponds to the average Si–O–Si angle observed in inorganic zeolites.^{4a,b} Our approach is to generate molecular TBUs from eight-coordinated metal ions as “tetrahedral” nodes and bis(bidentate) ligands as ditopic linkers. The simplest and most extensively studied bis(bidentate) ligand is oxalate (ox). A number of 3D oxalate frameworks with eight-coordinated metal ions (Cd^{II}, Zr^{IV}, Y^{III} and In^{III}) have been reported,^{7,8} but most of them have the default diamond topology,⁷ and no zeolitic topology has been identified. Only recently, a ZMOF was synthesized from eight-coordinated In^{III} and bis(bidentate) 4,5-imidazole-dicarboxylate (Himdc²⁻).⁵ In the present paper, we report the distinct MOFs constructed from eight-coordinated Cd^{II} and two different bis(bidentate) ligands, 2-pyrimidinecarboxylate (pymc) and 5-(2'-pyrimidyl)tetrazolate (pymtz). The com-

pounds are [Cd(pymc)₂]·7H₂O (**1**, RHO-type ZMOF) and [Cd(pymtz)₂] (**2**, square grid network).

Compound **1** was synthesized from the solvothermal reaction of CdCl₂ and 2-pyrimidinonitrile (pymCN) in aqueous ethanol (1 : 1),† which involved the *in situ* hydrolytic transformation of 2-pyrimidinonitrile into pymc. X-ray crystallographic analysis‡ revealed that compound **1** is a 3D MOF with the RHO zeolitic topology (Fig. 1). Each Cd^{II} ion resides on a crystallographic C₂ axis and is eight-coordinated by four pymc ligands, which are all bisected by crystallographic mirror planes and serve as bis(bidentate) bridges between Cd^{II} ions. The MN₄O₄ geometry is dodecahedral with the *mmmm* arrangement of ligands, that is, the four ligands span the four *m* edges that define the two perpendicular trapezoids characteristic of a dodecahedron.⁹ Such arrangement makes the four ligands radiate from the metal center in four noncoplanar directions, and hence dictates the [Cd(pymc)₄] units as TBUs. The resulting 3D framework exhibits the RHO zeolitic topology,¹⁰ which is featured by truncated cuboctahedral super-cages (α -cages) connected *via* octagonal prisms (D8R secondary building units, SBUs). The α -cage is constructed from twelve Cd₄(pymc)₄ squares (4-ring SBUs), eight Cd₆(pymc)₆ hexagons (6-ring SBUs), and six Cd₈(pymc)₈ octagons (8-ring SBUs). As a result of the expansion of the space between vertices (the Cd···Cd distances spanned by pymc are 6.19 and 6.33 Å, while the Si···Si distance spanned by a single O atom is about 3.0 Å in oxide zeolites), the cavity of the α -cage in **1** is much larger than those in the oxide counterparts. A sphere of 17.2 Å in diameter can fit into the cavity without touching the internal van der Waals surface of the cage. The surface apertures of the cage are also increased, with the free diameters of the 6- and 8-ring apertures being, respectively 6.57 and 10.26 Å. Therefore, the α -cavities are connected by 6-ring and D8R apertures to produce a single 3D systems of interconnecting open channels throughout the structure. This is distinct from the archetypal inorganic rho zeolite,⁷ which contains two non-interconnecting 3D channel systems because the 6-ring apertures are too small. Platon calculations¹¹ reveal that the solvent-accessible void volume in **1** is about 15 583 Å³ per unit cell (56.7% of the cell volume). The carboxylate oxygen atoms of the ligands are accessible on the internal surface, and a large number of heavily disordered water molecules are included in the cavities.

[Cd(pymtz)₂] (**2**) was synthesized from the solvothermal reaction of CdCl₂, pymCN and NaN₃†, which involved the *in situ* [2 + 3] cycloaddition of the nitrile with the azide ion. Two polymorphs of **2** could be obtained as pure phases,

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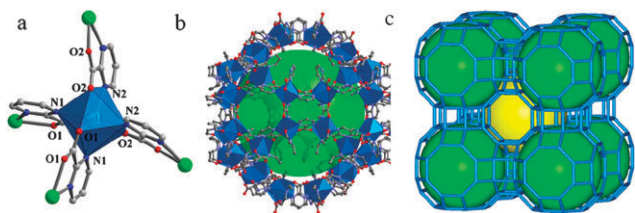


Fig. 1 Views of the structure of **1**, showing the coordination environments of Cd^{II} and pymc (a), the α -cage (b), and the RHO zeolitic topology (c).

dependent upon the solvents used. While the use of DMF as solvent led to **2- α** , the use of water generated **2- β** . This indicates the subtle structure-directing roles of the solvents,¹² although the solvents are absent in the final structures. The β form has been synthesized from CdCl₂ with Na(pymtz) in a recently published paper.¹³

The asymmetric unit of the α structure is only 1/8 of the formula, with Cd^{II} residing at the crystallographic D_{2d} position and pymtz having the C_{2v} symmetry. The MN₈ coordination geometry can be described as a highly distorted square prism with an $llll$ arrangement of the ligands, that is, four ligands parallel to the unique axis of the prism span the four lateral edges (Fig. 2a). The basal face of the prism consists of alternating N_{pym} and N_{tz} atoms from different ligands. With Cd–N_{pym} [2.831(2) Å] being much longer than Cd–N_{tz} [2.299(2) Å], the coordination polyhedron is severely distorted from the ideal square prism, and the distortion is mainly reflected by the folding of the base about the N_{pym}···N_{pym} diagonal, which divides the base into two triangular faces with a dihedral angle of 124.6° (Fig. 2b). Such coordination geometry is in striking contrast with the distorted square antiprismatic geometry in **2- β** .¹³ In the latter, four ligands around Cd^{II} are arranged in a pinwheel-like fashion and span the four lateral edges of the antiprism (Fig. 2d and e). Despite these differences, the $llll$ arrangement in both prismatic and antiprismatic geometries makes the ligands radiate from the metal center in four coplanar directions, and hence dictates the [Cd(pymtz)₄] units as square building units (SqBUs), which leads to 2D square grid networks (Fig. 2c and f).

Apparently, the framework topology strongly depends upon the geometric arrangement of the ligands around the metal ion. The asymmetry of the pymc ligand fits perfectly with the dodecahedral coordination and the RHO topology. A dodecahedron consists of two perpendicular trapezoids. With the dodecahedral $mmmm$ arrangement, the bulkier pym group and the smaller carboxylate group of pymc are put on the long and short edges of the trapezoids, respectively, and hence the interligand repulsion is minimized. The dodecahedral $mmmm$ arrangement is also observed in the diamond metal–oxalate frameworks with 8-coordinated metal ions,⁷ but the dodecahedrons are connected in different ways. While the symmetric ox ligands spanning opposite m edges link the MO₈ dodecahedrons into the infinite zigzag chains (Fig. 3a) characteristic of the diamond framework, the connection of the CdN₄O₄ dodecahedrons by the asymmetric pymc ligands spanning opposite m edges leads to the 8-ring SBUs (Fig. 3a) of the RHO framework. From Fig. 3a and 3b, it is obvious that the dodecahedral $mmmm$ arrangement of the asymmetric pymc

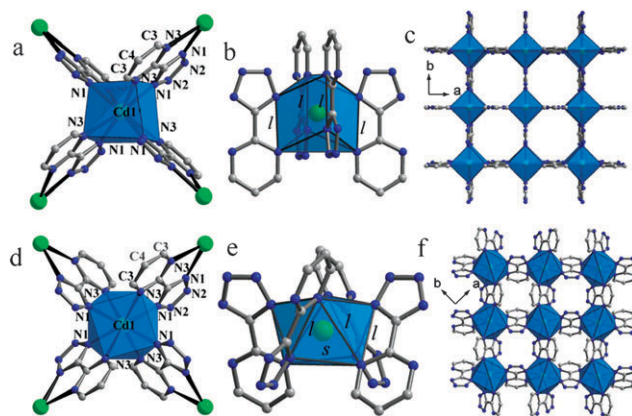


Fig. 2 Structures of **2- α** (a–c) and **2- β** (d–f), showing the coordination environments of Cd^{II} and pymc and the square grid networks.

ligands is incompatible with the zigzag chain: the formation of the zigzag chain requires that the carboxylate and pym groups of some ligands exchange positions, and such a chain would suffer from increased interligand repulsion.

The formation of the square grid networks in **2** can be justified as follows. The pymtz ligand is less asymmetric, and the replacement of the carboxylate groups by tetrazole rings in the above dodecahedral $mmmm$ arrangement would lead to significant interligand repulsion between the tetrazole groups. To relax the steric hindrance, the tetrazole groups move away from the unique axis of the polyhedron. In **2- α** , the relaxation followed by relative slipping of the ligands along the axis gives rise to the highly distorted square prism (Fig. 2b), while in **2- β** , the relaxation is accompanied by inclining of the ligands with respect to the axis, generating the square antiprismatic arrangement (Fig. 2e). The relationship of the three polyhedrons can be better understood as follows: the two perpendicular trapezoids in the dodecahedron are transformed into two perpendicular and relatively slipped rectangles in the distorted prism, or into two twisted and perpendicular (referring to the mean planes) tetragons in the antiprism. The square prismatic or antiprismatic $llll$ arrangement of the ligands is destined for the square grid network. Although the square grid net is

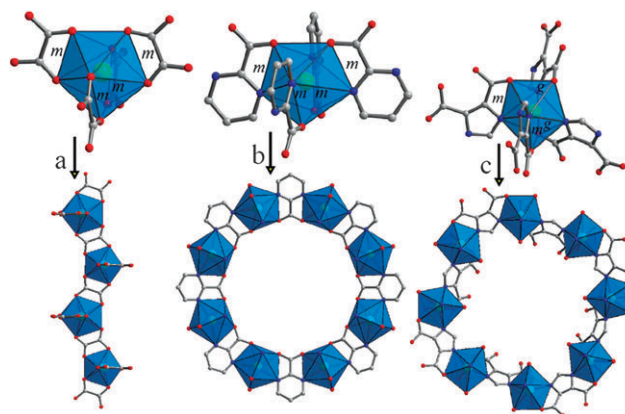


Fig. 3 (a) The $mmmm$ dodecahedral arrangement of ox leads to the zigzag chain in oxalates, (b) the same arrangement of pymc leads to the 8-ring SBUs in **1**, and (c) the $mmgg$ dodecahedral arrangement of Himdc leads to the 8-ring SBUs in [In(Himdc)₂][−].

among the most common topologies for extended coordination networks, examples based on eight-coordinated metal ions and bis(bidentate) linkers are rare. It is noted that square antiprismatic geometry has been observed in a few mixed Cd^{II}Zr^{IV} oxalates, but the ox ligands occupy four basal edges of the antiprism (*ssss* arrangement). Such arrangement defines [M(ox)₄] as a TBU, and leads to 3D homochiral networks with interconnected helical chains.⁸

The above analyses illustrate the great challenge of constructing ZMOFs. The previously known example of ZMOFs with eight-coordinated metal ions and bis(bidentate) bridges has an anionic RHO framework of formula [In(Himdc)₂]⁻,⁵ in which the Himdc²⁻ ligands assume an *mmgg* arrangement around the dodecahedral In^{III} ion. An SOD-type ZMOF with the same framework formula, in which the In^{III} ion assumes a MN₄O₂ pseudo-octahedral geometry, has also been described by the same authors. In these two materials, the coordination polyhedrons are linked by the imidazole rings in an vertex-to-vertex fashion (Fig. 3c), and the formation of the zeolitic topology is mainly directed by the specific coordination directions of the imidazole ring, as found in the ZMOFs based on imidazoles and tetrahedral metal ions.⁴ The carboxylate groups in the structures serve as an auxiliary coordinative sites that fulfil the coordination number and help to lock the metal ion in position and to adjust the M···M···M angles to appropriate values. Differently, the dodecahedrons in **1** are linked in the *m*-edge-to-*m*-edge fashion by the N₂C–CO₂ bis(bidentate) fragments of the ligands, and the formation of the RHO framework is facilitated by the perfect match of the asymmetry of the *pymc* ligand with the dodecahedral geometry. In particular, the replacement of one carboxylate group of ox by the *pym* ring in the *mmmm* dodecahedral geometry prevents the formation of the zigzag chains featuring the diamond topology but forces the polyhedrons into the octagonal SBUs of the RHO framework.

Thermogravimetric (TG) analysis (Fig. S1†) showed that compound **1** releases all the included water molecules before 100 °C (weight loss 26.2 wt%, calcd. 26.0 wt%). No further weight loss occurs up to 270 °C. Powder XRD measurements (Fig. S2†) suggested that the release of water guests is accompanied by the loss of crystallinity. Interestingly, the crystallinity can be recovered by immersing the amorphous sample in water (typically, 60 °C for 24 h). The sample evacuated under vacuum at 60 °C for 2 h exhibits a typical type I isotherm with no hysteresis (Fig. S3†). The apparent Langmuir surface area was estimated to be 804 m² g⁻¹. TG analyses on the samples after the N₂ sorption measurement indicated that the water guests were not completely evacuated out. Evacuating the sample at 100 °C led to decreased N₂ sorption, perhaps due to the collapse of the framework.

To summarize, we have explored the strategy of constructing ZMOFs from eight-coordinated metal ions as “tetrahedral” nodes and bis(bidentate) ligands as ditopic linkers. The asymmetry of the ligands and the size of the donor groups play critical roles in determining the coordination geometry and the MOF topology. In particular, the asymmetry of the *pymc* ligand matches perfectly with the dodecahedral *mmmm* coordination and the RHO topology and prevents the formation of the default diamond topology that is adopted by

oxalates. On the other hand, the *pymtz* ligands prefer the square prismatic or antiprismatic *llll* coordination, which leads to 2D square grid networks. The assembly of the present RHO framework is different from the previous imidazole-based ZMOFs^{4,5} that are directed by the specific coordination directions of the imidazole ring. Therefore, the present RHO framework may illustrate a new challenging approach to ZMOFs.

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