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A novel 4-connected binodal Moganite net with three-fold interpenetration

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ABSTRACT

Reported here is a novel Cd(II) coordination polymer (namely $[Cd(L1)_{0.5}(ntd)]_n$ (**1**), L1 = N,N′-di(4-pyridyl) adipoamide, H_2ntd^2 = 1,4-naphthalenedicarboxylic acid). Single-crystal X-ray diffraction reveals that the framework can be represented as metal/organic-binodal 4-connected Moganite net with three-fold interpenetration. Importantly, for the first time, an unusual coordination mode is observed for the acylamide ligand in such manner that every L1 ligand links four Cd(II) ions through two nitrogen atoms from two pyridine groups and two oxygen atoms from two acylamide groups.

In the past years, with the interpenetrating nets attracting more and more attention because of its beautiful esthetics and exceptional entangled phenomena, as well as particular functions, the researchers have obtained some achievements and many 3- and 4-connected networks have been generated, such as $ThSi_2$, NbO, and $CdSO_4$ [1–4]. Notably, the method of mixed N- and O-donor ligands has been extensively adopted for the generation of new interpenetrating networks [5–7]. In literature, to construct the high-dimensional networks, flexible multicarboxylate ligands are of special interest because of their varied coordination modes, abundant structural motifs, and flexible molecular backbones [8–11]. They often act as linkers in the networks and result in fascinating configurations in coordination polymers. While, bis-pyridyl-bis-amide ligands with the unique potential capability of coordinating metal ions have been used in synthesizing coordination polymers [12–17]. In 2012, Huang et al. blend the N,N′,N″-tris(3-pyridyl)trimesic amide, 1,3-benzenedicarboxylic acid and $Zn(NO_3)_2$ in the ratio of 1:1:1, constructed the first 2D → 3D polycatenation array built on (3,4)-connected bilayer nets [17]. Sun et al. mix the N,N′-di(4-pyridyl) adipoamide (L1), terephthalic acid, $Zn(NO_3)_2$ in the ratio of 1:1:1 and synthesized a 2D → 3D interlocking array in a vertical mode [18]. Herein, we utilize L1, 1,4-naphthalenedicarboxylic acid (H_2ntd), and $Cd(NO_3)_2$ and synthesized a novel 3D network, which displays a Moganite matrix with 3-fold interpenetration.

The crystal of $[Cd(L1)_{0.5}(ntd)]_n$ (polymer **1**) was obtained by hydrothermal synthesis (160 °C) for three days [19]. The single crystal X-ray diffraction shows polymer **1** crystallized in the monoclinic, $P2_1/c$ space group [20]. The coordination environment about Cd(II) ions is shown in Fig. 1. Each Cd(II) is five-coordinated in the pyramidal geometry, and connects to three oxygen atoms from two ntd^{2-} ligands ($Cd-O = 2.276(3)\text{-}2.428(2)$Å), one nitrogen atom from the pyridine ring of L1 ($Cd-N = 2.273(2)$Å), and one oxygen atom from amide group of L1 ($Cd-O = 2.340(2)$Å). That is to say, Cd1 links with two L1 ligands and two ntd^{2-} ligands. Moreover, two weak Cd–O coordination bonds ($Cd-O2 = 2.654(x)$Å and $Cd'-O2 = 2.670(x)$Å (not shown in Fig. 1)) are observed. For L1 ligand, which has a center of symmetry at the center of the cyclohexyl ring, the coordination mode is unprecedented, as it links to four Cd(II) ions through two nitrogen atoms from two pyridine groups (this is common in literature) and two oxygen atoms from two acylamide groups (this is never observed in the literature) (see Scheme 1). The adjacent two L1 ligands are parallel across a crystallographic center of symmetry and connected by two Cd(II) ions, forming a 1D line along the a-axis, as shown in Fig. 2. While the coordination mode of ntd^{2-} is $\mu_2:\eta^1\eta^1:\eta^0:\eta^1$ (Scheme 2), it acts as a linear linkers to link two c-glide plane rerated Cd(II) ions and forms a 1D helical chain along c-axis (Fig. 3). The combination of L1 ligands, ntd^{2-} ligands and Cd(II) ions generates a 3D framework, as shown in Fig. 4.

A further insight into the structure of **1** is carried out by topology analysis [21]. If each Cd(II) ion is seen to be a node, then it connects to four other Cd(II) ions through two L1 ligands and two ntd^{2-} ligands, resulting in a four connectivity featuring tetrahedral geometry. Meanwhile, the L1 ligand can also be seen to be a four-connected node, because it links with four Cd(II) ions, giving a plane quadrilateral (see Fig. 2) and ultimately resulting in the overall (4,4)-connected net (see

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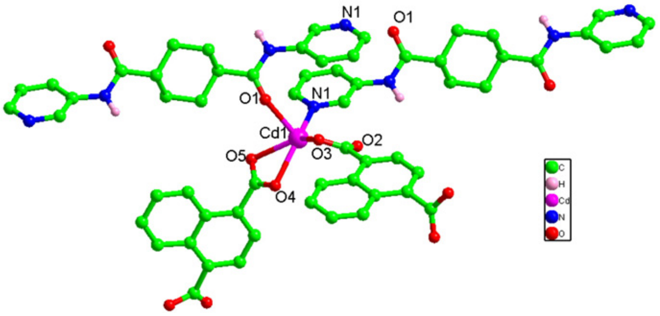
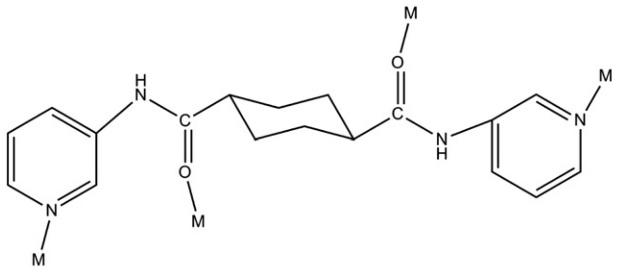


Fig. 1. Schematic description of the coordination environment of Cd.



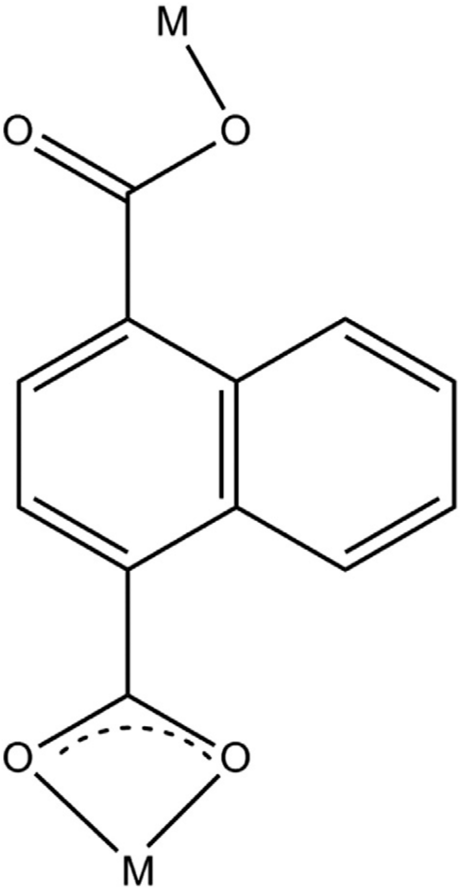
Scheme 1. Schematic description of the coordination mode of L1 ligand.

Fig. 5a). The topology analysis via Topos Program suggests Moganite net with the $(4.6^4.8)_2(4^2.6^2.8^2)$ topology symbol, where the ratio of two kinds of nodes is Cd(tetrahedron)/L1(square) = 2:1. Furthermore, three identical Moganite nets interpenetrate each other (type Ia), as illustrated in Fig. 5b.

Moganite structure is a variant of the quartz structure, which in its simplest conformation with symmetry *Cmmm* also has only three vertices in the repeat unit (two square and one tetrahedron) [22,23]. In recent years, Luo et al. prepared a polymer, $Cu_3(\mu_2\text{-}OH)_2(nic)_4$ (Hnic = isonicotinic acid), which is a Moganite matrix with 2-fold interpenetration built on two distinct copper nodes [24]; Su et al. synthesized a three-dimensional, non-interpenetrating MOFs ($[Cu_3(Pytac)_6](H_2O)_{14}$, Pytac = 2-(4-pyridyl)-thiazole-4-carboxylic acid) with the Moganite topology, also based on two kinds of copper nodes [25]. For the first time, we report an unprecedented Moganite net based on both metal and organic nodes. Interestingly, this work also presents the highest number of interpenetration for Moganite net.

The solid-state photoluminescence properties of **1** were investigated, as shown in Fig. 6. An intense emission occurs at 400 nm with the excitation wavelength at 350 nm. Because in **1**, only L1 ligand has photoluminescence property. Thus, we believe that the photoluminescence emission of **1** is derived from L1.

In conclusion, we have obtained a novel 3D framework, prepared by 1,4-naphthalenedicarboxylate, N,N′-di(4-pyridyl)adipoamide and $Cd(NO_3)_2$. Topological analysis shows that it bears a Moganite net with three fold interpenetration based on both metal and organic nodes. Importantly, an unprecedented coordination mode of L1 ligand is observed, which points out that the acylamide group acts as not only a supramolecular site but also a coordination site.



Scheme 2. Schematic description of the coordination mode of ntd^{2-} ligand.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.10.038.

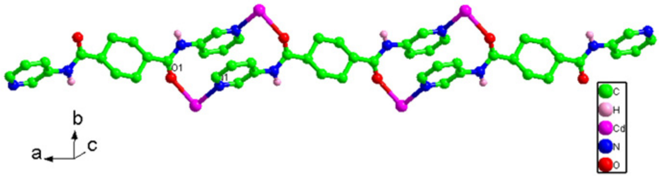

Fig. 2. Schematic description of the connection between L1 ligands.

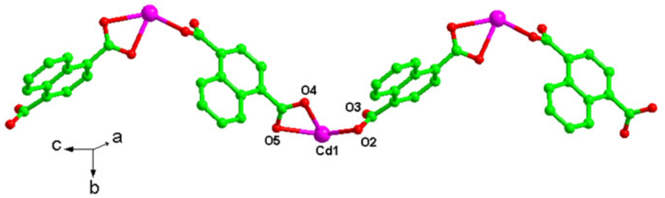

Fig. 3. The schematic description of 1D helical chain formed by ntd^{2-} ligand.