

A cadmium oxybisbenzoate/pyridylnicotinamide coordination polymer with a new 8-connected self-penetrated topology



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ABSTRACT

Crystals of $\{[\text{Cd}(\text{oba})(4\text{-pna})] \cdot 0.25\text{H}_2\text{O}\}_n$ (**1**, oba = oxybisbenzoate, 4-pna = 4-pyridylnicotinamide) were prepared by hydrothermal methods. A single-crystal structure determination showed the presence of two-fold interpenetrated $[\text{Cd}_2(\text{oba})_2]_n$ dimer-based (4,4) layers, featuring embedded $\{\text{Cd}_2\text{O}_2\}$ dimers that serve as 4-connected nodes. In turn these layers are connected by the dipodal 4-pna ligands into a $[\text{Cd}(\text{oba})(4\text{-pna})]_n$ 3-D coordination polymer network. Including these connections, the $\{\text{Cd}_2\text{O}_2\}$ dimers can be considered as 8-connected nodes; these build a new but simple self-penetrated network with a $4^{24}6^4$ topology substantially different from a standard body centered cubic **bcu** net. Luminescent and thermal properties of **1** are also reported.

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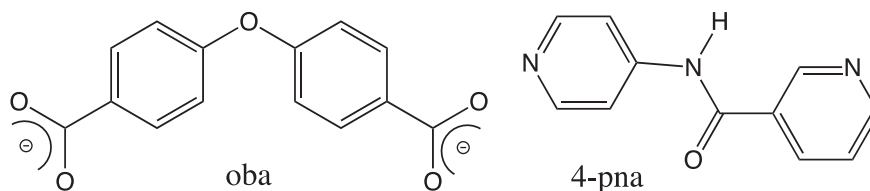
Crystalline coordination polymer solids are presently under intense investigation because of their wide potential applications [1] in gas storage [2], molecular separations [3], ion exchange [4], heterogeneous catalysis of industrially relevant organic transformation [5], explosive residue detection [6], and second harmonic generation [7]. A popular and successful approach in the construction of these extended phases is the hydrothermal reaction of a divalent metal salt with an organic dicarboxylic acid and a neutral dipodal dipyriddy-type coligand [8]. In addition to their potential utility, the striking aesthetics of their molecular structures and underlying network topologies surely provides further impetus for research [9]. Coordination polymer networks frequently exhibit topologies that mimic those of well-known crystalline solids (e.g. α -Po primitive cubic, diamond, PtS, and SrAl_2), with longer tethering dicarboxylate or dipyriddy ligands promoting higher degrees of mutual interpenetration [10]. Some coordination polymers manifest more rarely encountered self-penetration, in which linking ligands within the network penetrate through the shortest circuits of the same network [11–20].

Among the variety of self-penetrated topologies reported to date [21], some are extremely simple, such as the regular (12,3)-**twt** net in the cationic $[\text{Ni}(\text{tpt})]_n^{2n+}$ framework (tpt = tri-4-pyridyl-1,3,5-triazine) [11]. They can also be quite complicated and multiply self-interwoven, built from higher connected nodes and employing long-spanning “V-shaped” dicarboxylate ligands such as oxybisbenzoate (oba, Scheme 1). $\{[\text{Ni}(\text{oba})(4,4'\text{-bipyridine})] \cdot \text{H}_2\text{O}\}_n$ has a $(4.8^2)(4.6^4.8^4.10)$ (3,5)-connected

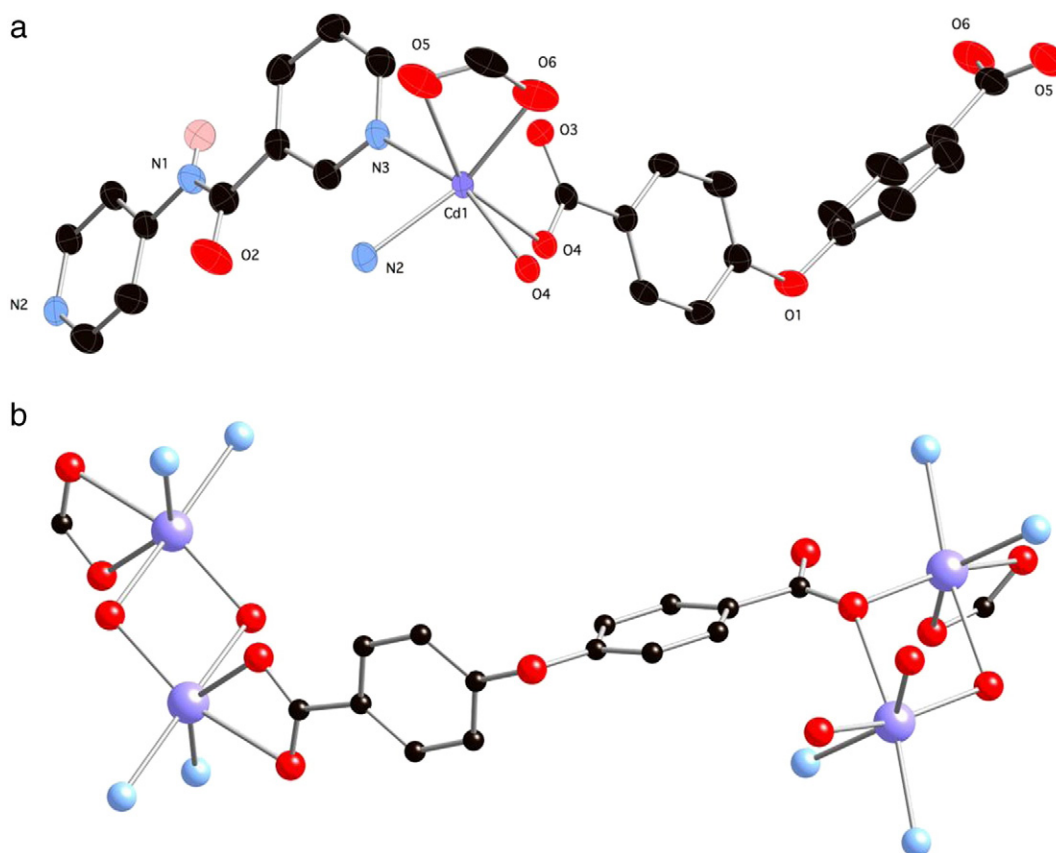
binodal self-penetrated topology [12], while $\{\text{Co}_3(\text{oba})_3(\text{bpmp})_2\}$ (bpmp = bis(4-pyridylmethyl)piperazine) possesses a uninodal 8-connected self-penetrated net with a unique $4^45^{17}6^7$ topology [13]. The kinked hydrogen-bonding capable 4,4'-dipyridylamine (dpa, Scheme 1) has also proved extremely useful in the design of intriguing self-penetrated coordination polymers. $\{[\text{Ni}(\text{dpa})_2(\text{succinate})_{0.5}]\text{Cl}\}_n$ is the only known example of a uniform 6^{10} topology self-penetrated network [14], constructed from the interlocking of a four-fold interpenetrated diamondoid $[\text{Ni}(\text{dpa})_2]_n$ cationic framework by succinate ligands. $\{[\text{Cd}(\text{pht})(\text{dpa})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}\}_n$ (pht = phthalate) possesses a simple yet unique 4-connected uninodal 3-D self-penetrated net with 7^48^2 **yyz** topology, constructed from the interlocking of $[\text{Cd}(\text{dpa})]_n$ double helices with $[\text{Cd}(\text{pht})]_n$ single helices [15]. Using the two “V-shaped” ligands simultaneously resulted in $\{[\text{Co}(\text{oba})(\text{dpa})] \cdot \text{H}_2\text{O}\}_n$, which displays an exceptionally rare 2-D self-penetrated layer motif with 6^6 topology [16]. We thus sought to explore whether novel self-penetrated networks could be obtained by using the “V-shaped” oba ligand with the seldom used yet easily accessible 4-pyridylnicotinamide ligand (4-pna, Scheme 1) [22–25]. The 4-pna ligand is structurally similar in many respects to dpa, but also has a hydrogen-bonding accepting carbonyl group embedded within its central amide moiety which would exert substantial different supramolecular structure directing effects. In this contribution, we report the synthesis, crystal structure, and luminescent and thermal degradation properties of $\{[\text{Cd}(\text{oba})(4\text{-pna})] \cdot 0.25\text{H}_2\text{O}\}_n$ (**1**), which exhibits a new yet simple dimer-based 8-connected self-penetrated topology.

Colorless crystals of **1** were prepared in moderate yield [26] by the hydrothermal reaction of cadmium nitrate, oxybisbenzoic acid, 4-pyridylnicotinamide, and sodium hydroxide. Slightly broadened spectral bands at 1592 cm^{-1} and 1423 cm^{-1} in the infrared spectrum of **1** (Fig. S1) denote the presence of the carboxylate groups of the oba

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Scheme 1. Ligands used in this study.

Fig. 1. a) Coordination environment of **1**. b) Binding mode of the oba ligand in **1**, showing two $\{Cd_2O_2\}$ dimeric units.

ligand. The carbonyl groups of the 4-pna ligand are marked by a C=O stretching band at 1676 cm^{-1} . The C–O stretching band of the ether functional group within the oba ligand appears at 1243 cm^{-1} .

Single crystal X-ray diffraction [27] revealed that the asymmetric unit of **1** contains a divalent cadmium atom, a fully deprotonated oba ligand, a 4-pna ligand, and a water molecule of crystallization best refined at a quarter occupancy. The coordination environment at cadmium is a distorted $\{CdO_4N_2\}$ octahedron, with a chelating oba carboxylate group, an oxygen atom donor from a second oba ligand, and a 4-pyridylamine nitrogen donor from a 4-pna ligand in the equatorial plane (Fig. 1a). The axial sites are taken up by an oxygen atom donor from a third oba ligand, and the nicotinamide nitrogen donor from a second 4-pna ligand. Bond lengths and angles within the coordination sphere are listed in Table 1.

The oba ligands in **1** adopt a $\mu_3\text{-}\kappa^3O,O':O'',O'''$ binding mode, in which one carboxylate group chelates to a cadmium atom, while a single atom belonging to the other carboxylate group bridges two cadmium atoms. A 79.85° dihedral angle exists between the two phenyl rings of the oba ligands. Dimeric $\{Cd_2O_2\}$ pinched rhomboids are formed by bridging oxygen atoms belonging to two different oba ligands (Fig. 1b).

These have a Cd–Cd distance of 3.730 \AA and an O··O distance of 2.989 \AA , with Cd–O–Cd and O–Cd–O angles of 102.66° and 77.33° , respectively. Each $\{Cd_2O_2\}$ unit is connected to four others by oba ligands, forming $[Cd_2(oba)_2]_n$ (4,4) grid-like coordination polymer motifs with dimer centroid–dimer centroid through-space distances of 17.883 \AA

Table 1
Selected bond distance (Å) and angle ($^\circ$) data for **1**.

Cd1–O4 ^{#1}	2.2466(18)	N2 ^{#3} –Cd1–N3	83.62(8)
Cd1–O6 ^{#2}	2.253(2)	O4 ^{#1} –Cd1–O5 ^{#2}	154.66(8)
Cd1–N2 ^{#3}	2.288(2)	O6 ^{#2} –Cd1–O5 ^{#2}	54.59(9)
Cd1–N3	2.353(2)	N2 ^{#3} –Cd1–O5 ^{#2}	91.71(8)
Cd1–O5 ^{#2}	2.522(3)	N3–Cd1–O5 ^{#2}	84.28(8)
Cd1–O4	2.5253(19)	O4 ^{#1} –Cd1–O4	77.33(7)
O4 ^{#1} –Cd1–O6	100.38(8)	O6 ^{#2} –Cd1–O4	85.01(8)
O4 ^{#1} –Cd1–N2 ^{#3}	112.87(8)	N2 ^{#3} –Cd1–O4	80.78(7)
O6 ^{#2} –Cd1–N2 ^{#3}	139.61(9)	N3–Cd1–O4	163.39(7)
O4 ^{#1} –Cd1–N3	103.81(7)	O5 ^{#2} –Cd1–O4	101.78(7)
O6 ^{#2} –Cd1–N3	110.78(9)		

Transformation for symmetry equivalent positions: #1 $-x + 1, -y - 2, -z$; #2 $x, -y + 1, z + 1/2$; #3 $-x + 1/2, y - 1/2, -z - 1/2$.

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