

## A Two-fold Interpenetrated Diamond-like 3D Metal-Organic Cd(II) Complex Based on 5-Iodo-isophthalic Acid and 1,3-Bi(4-pyridyl)propane

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A metal-organic framework based on 5-iodo-isophthalic acid (5-iipaH<sub>2</sub>) and the ancillary nitrogen ligand 1,3-bi(4-pyridyl)propane (bpp), namely [Cd(5-iipa)(bpp)(H<sub>2</sub>O)]<sub>n</sub> (**1**), has been synthesized, and characterized by IR spectroscopy, elemental analysis, thermogravimetry, and X-ray crystallography. Complex **1** shows a two-fold interpenetrating 3D diamond-like architecture that is stabilized by hydrogen bonding,  $\pi \cdots \pi$ , I $\cdots \pi$ , and C–H $\cdots \pi$  interactions.

**Key words:** 5-Iodo-isophthalic Acid, Lattice Interpenetration, Diamond-like Architecture, Supramolecular Structure, Cadmium

### Introduction

The rational design and construction of coordination polymers with interpenetrating structures have been an increasingly active research area over recent years because many of such systems show an intriguing variety of structures, useful properties and potential applications [1–5]. A great number of architectures with new topological types have been reported [6–9]. One of the rational strategies to generate interpenetrating structures is the judicious selection of suitable multifunctional organic ligands and metal centers. It is well known that multicarboxylate ligands [10] can influence the structure of the coordination polymers by providing different coordination modes. Long organic spacers such as 1,2-bis(4-pyridyl)ethane (bpe) [11, 12] and 1,3-bis(4-pyridyl)propane (bpp) [13–15] often show diverse conformations in the self-assembly process and have therefore proven to be good candidates to construct uncommon interpenetrated architectures. The

mixture of multicarboxylate ligands and flexible *N*-donor ligands has been used to generate a variety of coordinating polymers under various reaction condition [16–21]. Recently, we chose 5-iodo-isophthalic acid (5-iipaH<sub>2</sub>) and 1,3-bi(4-pyridyl)propane (bpp) as ligands to construct novel architectures. Here we report the new two-fold interpenetrating diamond-like 3D metal-organic complex [Cd(5-iipa)(bpp)(H<sub>2</sub>O)]<sub>n</sub> (**1**).

### Experimental Section

#### Materials and general procedures

5-Iodo-isophthalic acid was prepared according to the literature [22]. All other starting materials were of analytical grade and obtained from commercial sources and used without further purification.

#### Synthesis of [Cd(5-iipa)(bpp)(H<sub>2</sub>O)]<sub>n</sub> (**1**)

Complex **1** was synthesized hydrothermally in a Teflon-lined stainless-steel container by heating a mixture of 5-iodo-isophthalic acid (0.0146 g, 0.05 mmol), 1,3-bi(4-pyridyl)propane (bpp) (0.01 g, 0.05 mmol), Cd(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O (0.02 g, 0.05 mmol), KOH (0.006 g, 0.1 mmol), and acetonitrile (0.5 mL) in 7 mL of distilled water at 160 °C for 3 d. Subsequent cooling to room temperature yielded colorless crystals of **1** (75% yield based on cadmium). – C<sub>21</sub>H<sub>19</sub>CdIN<sub>2</sub>O<sub>5</sub> (618.68): calcd. C 40.77, H 3.10, N, 4.53; found C 40.70, H 3.07, N 4.61. – IR (KBr, cm<sup>–1</sup>):  $\nu$  = 3441(s), 2942(w), 1607(vs), 1560(m), 1424(s), 1398(m), 1347(s), 1224(m), 819(m), 770(m), 715(s).

#### Physical measurements

Elemental analysis for C, H, and N was performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range from 4000 to 400 cm<sup>–1</sup> on a Bruker VECTOR 22 spectrometer. Thermal analysis was performed on a SDT 2960 thermal analyzer from room temperature to 800 °C at a heating rate of 20 °C min<sup>–1</sup> under nitrogen flow.

#### X-Ray crystallography

A single crystal suitable for X-ray diffraction was mounted on a Bruker SMART APEX CCD diffractometer [23]. The intensity data collection was carried out using graphite-monochromatized MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at room temperature using the  $\omega$ -scan technique. Lorentz, polarization and absorption corrections were applied. The structure was solved by Direct Methods with SHELXS-97 [24] and refined with full-matrix least-squares techniques using SHELXL-97 [25]. Anisotropic displacement

Table 1. Crystal data and numbers pertinent to data collection and structure refinement of **1**.

Compound	<b>1</b>
Formula	C <sub>21</sub> H <sub>19</sub> CdIN <sub>2</sub> O <sub>5</sub>
<i>M<sub>r</sub></i>	618.68
Crystal system	monoclinic
Space group	<i>C2/c</i>
<i>a</i> , Å	14.401(3)
<i>b</i> , Å	19.253(4)
<i>c</i> , Å	16.574(3)
$\beta$ , deg	102.91(3)
<i>V</i> , Å <sup>3</sup>	4479.2(2)
<i>Z</i>	8
<i>D</i> <sub>calcd.</sub> , g cm <sup>-3</sup>	1.84
<i>F</i> (000), e	2400
<i>hkl</i> range	±17, ±22, ±19
Reflections collected/independent/ <i>R</i> <sub>int</sub>	22 330/3943/0.0353
Refined parameters	281
<i>R</i> 1/ <i>wR</i> 2 [ <i>I</i> > 2σ( <i>I</i> )] <sup>a, b</sup>	0.0426/0.1317
<i>R</i> 1/ <i>wR</i> 2 (all data) <sup>a, b</sup>	0.0457/0.1351
Weighting scheme A/B <sup>b</sup>	0.0836/4.0421
GoF <sup>c</sup>	1.088
Δρ <sub>fin</sub> (max/min), e Å <sup>-3</sup>	0.41/−0.52

<sup>a</sup>  $R1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$ ;

<sup>b</sup>  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ,  $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$ ;

<sup>c</sup>  $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$ .

parameters were assigned to all non-hydrogen atoms. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated. I1 in **1** has two disordered positions with occupancy ratios of 0.43 : 0.56. The crystallographic data and selected bond lengths and angles for **1** are listed in Tables 1 and 2.

CCDC 778217 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Results and Discussions

### Structure description of [Cd(5-iipa)(bpp)(H<sub>2</sub>O)]<sub>n</sub> (**1**)

As is shown in Fig. 1, the asymmetric unit of **1** contains one Cd dication, one 5-iipa<sup>2-</sup> dianion and one

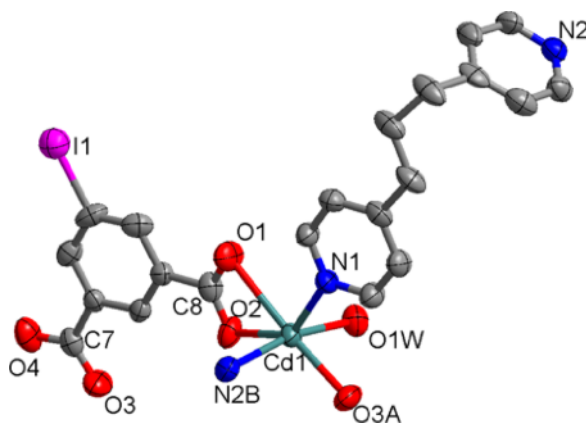


Fig. 1 (color online). Metal coordination and atom labeling in complex **1** (displacement ellipsoids at the 50% probability level; all hydrogen atoms are omitted for clarity).

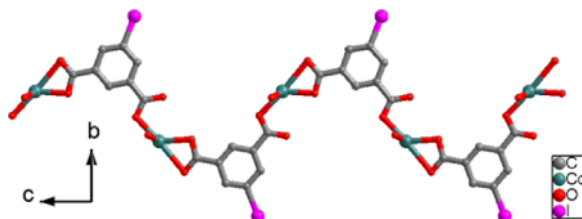


Fig. 2 (color online). A view of the [Cd(iipa)]<sub>n</sub> chain running along the crystallographic *c* axis.

bpp ligand. The Cd(II) center is coordinated by two O atoms from two different 5-iipa<sup>2-</sup> ligands [O(2), O(3A)], two pyridyl nitrogen atoms from different bpp ligands and one water oxygen atom to form a distorted trigonal-bipyramidal environment. Furthermore, an additional oxygen atom of the 5-iipa<sup>2-</sup> ligand is coordinated in an albeit longer and weaker bond (Cd(1)–O(1) 2.634(4) Å).

The bpp ligand adopts the *TG* conformation, with an N...N distance of 8.336 Å and a dihedral angle of 86.6 °C between the two pyridyl rings. The 5-iipa<sup>2-</sup> ligand acts as a bridge with one carboxylate group

Cd(1)–O(3A)	2.230(4)	Cd(1)–O(2)	2.241(4)	Cd(1)–N(1)	2.287(4)
Cd(1)–O(1W)	2.361(4)	Cd(1)–N(2B)	2.376(4)	Cd(1)–O(1)	2.634(4)
O(3A)–Cd(1)–O(2)	131.1(2)	O(3A)–Cd(1)–N(1)	89.6(2)	O(2)–Cd(1)–N(1)	139.3(1)
O(3A)–Cd(1)–O(1W)	80.7(2)	O(2)–Cd(1)–O(1W)	88.7(1)	N(1)–Cd(1)–O(1W)	96.5(1)
O(3A)–Cd(1)–N(2B)	91.5(2)	O(2)–Cd(1)–N(2B)	88.9(2)	N(1)–Cd(1)–N(2B)	93.5(2)
O(2)–Cd(1)–O(1)	52.7(1)	N(1)–Cd(1)–O(1)	86.6(1)	O(1W)–Cd(1)–O(1)	98.3(1)
N(2B)–Cd(1)–O(1)	90.2(1)				

Table 2. Selected bond lengths (Å) and angles (deg) for **1**<sup>a</sup>.

<sup>a</sup> Symmetry codes: A: *x*, −*y*, *z* + 1/2; B: *x* − 1/2, −*y* + 1/2, *z* − 1/2.

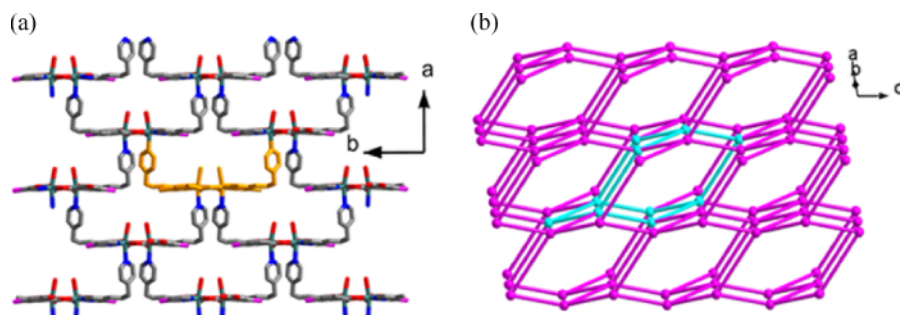


Fig. 3 (color online). a) One set of the 3D framework (one segment is highlighted in orange); b) schematic view of the diamond-like net (one fragment is highlighted in turquoise).

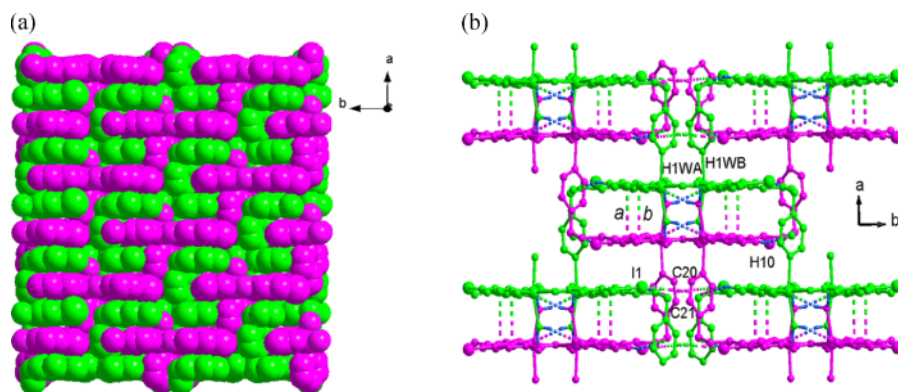


Fig. 4 (color online). a) Space-filling diagram of the interpenetrating 3D framework; b) the different non-covalent interactions in the architecture. (*a* and *b* represent the  $\pi\cdots\pi$  stacking between pyridine rings and phenyl rings, respectively).

[C(7)] in a monodentate and the other [C(8)] in an unsymmetrical chelating bidentate fashion linking the Cd atoms to form a zig-zag chain (Fig. 2). Each chain is connected to four other such chains through bpp ligands to yield a 3D framework, as shown in Fig. 3a. If the Cd center is considered as a four-connected node (connecting to four other Cd centers *via* two 5-iipa<sup>2-</sup> and two bpp ligands), the 3D structure of **1** can be classified as a diamond-type (6, 4) net with a (6<sup>6</sup>) Schläfli symbol (Fig. 3b) [26].

The presence of the large voids (*ca.*  $18.00 \times 6.69 \text{ \AA}^2$ ) opens up the way for the existence of interpenetration, and two sets of such 3D frameworks are interlaced in a parallel fashion to give rise to a two-fold interpenetrated architecture (Fig. 4a). Further investigation of this structure has indicated that different non-covalent interactions can be detected between the two sets of 3D frameworks, as shown in Fig. 4b. The short distances between neighboring aromatic rings which belong to different motifs [centroid-centroid distance  $3.714 \text{ \AA}$  between the pyridine rings which contain the N1 atom, and  $3.609 \text{ \AA}$  between the phenyl ring which contains C1–C6; H10–center of the pyridine ring

which contains the N2 atom:  $2.952 \text{ \AA}$ ] suggest that there are face-to-face  $\pi\cdots\pi$  stacking and C–H $\cdots\pi$  interactions. H1WA and H1WB are hydrogen bonded to O2 and O4 atoms, respectively, which come from

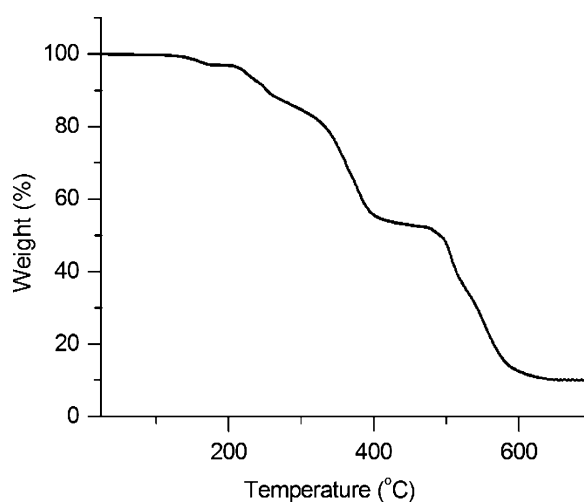


Fig. 5. Thermogravimetric analysis (TGA) curve for compound **1**.

another set of the framework, (O1W–O4C, 2.69 Å; O1W–O2D, 2.89 Å; symmetry codes: C  $-x+1, y, -z-1/2$ ; D  $-x+1, -y, -z$ ). The two-fold interpenetrated architecture is stabilized by these different non-covalent interactions. The distance of 3.847 Å between I1 and the nearest edge (C20–C21) of an aromatic ring which comes from another motif suggests that there are weak  $I\cdots\pi$  interactions [27] which also contribute to the formation of the structure.

#### Thermogravimetric analysis

Thermogravimetric analysis (TGA) of complex **1** was performed to study its thermal stability. The TGA curve is shown in Fig. 5. The weight loss of the coordinated water molecules occurs in the range of 128–176 °C (observed, 2.90%; calculated, 2.91%). The decomposition of the anhydrous compound begins at 210 °C.

#### Luminescence properties

Considering that some Cd(II) complexes have excellent luminescence properties, the photoluminescence

of complex **1** in the solid state was investigated at room temperature. However, the compound presents only very weak photoluminescence. The reason for this phenomenon may be the heavy-atom effect [28].

#### Conclusion

In this study, we have synthesized and characterized a novel Cd(II) coordination polymer based on the 5-iipa<sup>2-</sup> ligand and the *N,N'*-type ligand bpp. The complex features a two-fold interpenetrating diamond-like 3D metal-organic framework. The result shows that the mixture of the rigid multicarboxylate ligand and the flexible *N*-containing ligand should further be considered in the design of intriguing architectures, and our future research will therefore focus on interpenetrated coordination polymers with potential functionalities by using different ligands and metal ions.

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