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[Cd(mpdc)]: A novel five-connected 3-D zeolite-like framework with intersecting helical chains in diamondoid net of Cd^{II} (mpdc = 2,6-dimethylpyridine-3,5-dicarboxylate)

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Abstract

Under hydrothermal conditions, a novel five-connected three-dimensional metal-organic coordination polymer [Cd(mpdc)] is self-assembled from 2,6-dimethylpyridine-3,5-dicarboxylate (mpdc), by taking advantage of simple modifications of pyridyldicarboxylates, and cadmium ions. The X-ray single diffraction reveals that the [Cd(mpdc)] with M_5L_5 mode exhibits zeolite-like framework with interesting helical chains in diamondoid net of Cd^{II}. In addition, the compound with high thermal stability up to the temperature of 430 °C exhibits strong photoluminescent at room temperature in the solid state.

Keywords: Cadmium; Coordination polymer; Helical chain; Diamondoid network; Photoluminescence

1. Introduction

Metal-organic framewoks (MOFs) have been investigated as a new kind of solid materials that are expected to be more designable in pore sizes and shape, as well as exhibiting wide structural diversity [1]. Recently, an increasing interest is in the synthesis of MOFs with zeolite or zeolite-like topology [2] based on O-ligands (such as carboxylate and phosphonate) or N-ligands (e.g. imidnazote and urotropine), for example, *rho*-ZMOF [3], *sod*-ZMOF [3], $[Zn(mim)_2{\cdot}H_2O]_\infty$ (SOD) [4], $[Cu(x\text{-pymo-N1,N3})_2]_n$ ($x = 2,4$) (SOD) [5], $[Zn(eim)_2{\cdot}2H_2O]_\infty$ (ANA) [4], $[Zn(mim/eim{\cdot}1.25H_2O)_\infty$ (RHO) [3], $\{Na[Zn(O_3PC_2H_4CO_2H){\cdot}H_2O]\}$ (ABW) [6], $\{Co_5(im)_{10}{\cdot}2MB\}_\infty$ [7], $[Zn(O_3PC_2H_4CO_2H){\cdot}1.5H_2O]$ [8], and $[Zn(O_3PC_2H_4NH_2)]$ [9]. Although some progress has been made as mentioned above, crystal engineering of MOFs with zeolite-type or zeolite-like motifs is still facing great challenges in controlling of structure and stability [4]. Here, we report a five-connected three-dimensional (3-D) zeolite-like coordination polymer of metal pyridylcarboxylate [Cd(mpdc)] (**1**) (mpdc = 2,6-dimethylpyridine-3,5-dicarboxylate, O–N ligand) with intersecting double-stranded helical motif in diamondoid net of Cd^{II}.

2. Experimental section

2.1. General methods

All chemicals used in these syntheses are of reagent grade and used as purchased without further purification. Infrared (IR) spectra are recorded from KBr pellets in the range of 400–4000 cm^{-1} on a Nicolet Impact 410 FTIR spectrometer. Elemental analyses are performed on a Perkin-Elmer 2400 element analyzer. The thermogravimetric analyses are performed with a Mettler Toledo TGA/SDTA 851e analyzer in N_2 with a heating rate of 5 °C min^{-1} from 30 to 800 °C.

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2.2. Syntheses

2,6-Dimethylpyridine-3,5-dicarboxylic acid (**H_2mpdc**) was prepared by hydrolyzation of diethyl 2,6-dimethylpyridine-3,5-dicarboxylate[10].

2.2.1. *Synthesis of 1*

A solution H_2O (10 mL) containing the acid form of mpdc (H_2mpdc) (0.2 mmol), $Cd(NO_3)_2{\cdot}6H_2O$ (0.2 mmol) and Et_3N (0.055 mL) is sealed in a reactor of 23 mL and heated at 180 °C for 72 h, then cooled to room temperature. The colorless crystals are washed with ethanol (3 × 4 mL) to give compound **1** (0.03 g, 48% yield). Elemental analysis calcd (%) for $C_9H_7NO_4Cd$ = [Cd (mpdc)]: C 35.38, H 2.31, N 4.58; found C 35.42, H 2.29, N 4.45. FT-IR (KBr): $\tilde{v}$ = 3233 cm^{-1} (m), 3053(m), 2914(m), 2854(w), 1591(vs), 1536(s), 1428(s), 1379(vs), 1151(m), 1096(w), 860(s), 789(m), 729(s), 675(m).

2.3. Crystallographic studies

A suitable single crystal is glued to a thin glass fiber and mounted on a Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (graphite-monochromatic Mo-K_α radiation (λ = 0.71073 Å)) operating at 50 kV and 40 mA. Intensity data are collected at room temperature. Data processing is performed using the SAINT processing program. The structure is solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL97 [11]. All non-hydrogen atoms are easily found from the different Fourier maps and refined anisotropically. The crystallographic data and details on refinements for **1** is summarized in Table 1. Selected bond distances and angles are listed in Table 2.

Table 1
Crystallographic data and structure refinement summary for compound **1**

Formula	$C_{36}H_{28}N_4O_{14}Cd_4$
fw	1222.22
Size (mm)	0.20 × 0.16 × 0.11
Crystal system	Monoclinic
Space group	*C2/c*
a (Å)	9.011(4)
b (Å)	14.198(3)
c (Å)	7.606(8)
α (deg)	90
β (deg)	116.186(2)
γ (deg)	90
V (Å^3)	873.4(3)
Z	1
T (K)	298(2)
Wavelength (Å)	0.71073
ρ_{calcd} (mg m^{-3})	2.324
F(000)	592
θ (deg)	2.87–24.97
Reflections collected	2203
Independent reflections	767 [*R*(int) = 0.0178]
Data/parameters	767/70
GooF	1.154
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0219, wR_2 = 0.0583
R indices (all data)	R_1 = 0.0231, wR_2 = 0.0594

Table 2
Selected interatomic distances (Å) and angles (deg) for **1**

Cd(1)–O(2)#1	2.220(3)
Cd(1)–O(2)#2	2.220(3)
Cd(1)–N(1)	2.305(4)
Cd(1)–O(1)#3	2.419(3)
Cd(1)–O(1)#4	2.419(3)
O(2)#1–Cd(1)–O(2)#2	127.74(14)
O(2)#1–Cd(1)–N(1)	116.13(7)
O(2)#1–Cd(1)–O(1)#3	101.43(9)
O(2)#2–Cd(1)–O(1)#3	87.04(9)
N(1)–Cd(1)–O(1)#3	80.43(7)
O(1)#3–Cd(1)–O(1)#4	160.85(13)

#1, $x - 1/2$, $y - 1/2$, z; #2, $-x + 3/2$, $y - 1/2$, $-z + 3/2$; #3, $-x + 3/2$, $-y + 3/2$, $-z + 2$; #4, $x-1/2$, $-y + 3/2$, $z - 1/2$.

3. Results and discussion

The colorless crystalline compound (**1**) is synthesized by treating $Cd(NO_3)_2$ with H_2mpdc in the molar ratio of 1:1 in a solution of H_2O and triethylamine at pH 6 and 180 °C. X-ray diffraction analysis reveals that **1** crystallizes in the space group *C2/c*. The compound **1** consists of a neutral Cd(mpdc) network. The material is stable in air and is insoluble in common organic solvents such as methanol, ethanol, acetonitrile, acetone, and DMF. The formulation of **1** is supported by FT-IR, microanalysis, and thermogravimetric analysis (TGA). The X-ray power diffraction pattern proves the sample is pure-phase (see the supporting information).

In the structure of **1**, the Cd center adopts five-coordinated mode with a distorted trigonal bipyramid (CdO_4N) *via* binding to one pyridyl nitrogen atom and four oxygen atoms originating from four different CO_2^- groups of $mpdc^{2-}$ ligands. Each $mpdc^{2-}$ ligand bridges five different Cd atoms to form a 3-D zeolite-like framework (Fig. 1a). The Cd–O bond lengths are in the ranges of 2.220–2.419 Å and Cd1-N1 bond length is 2.305 Å (Figure S1), which are similar to those observed in previous Cd coordination polymers, such as [Cd(bpea)(phen)$_2$] [12], [Cd(2-PEB)$_2{\cdot}H_2O$] [13], Cd(2-CEQA)(Py) [13], {[Cd(*o*-O_2C-C_6H_4COFc)$_2$(bpe)(MeOH)$_2$]·2H_2O} [14] and cadmium (4-pyridyl)acrylate [15].

The most fascinating in the structure of **1** is the arrangement of $mpdc^{2-}$ spacers and Cd(II) ions resulting in a zeolite-like framework. First the linkage of $mpdc^{2-}$ ligands with Cd^{2+} ions *via* Cd1–O2 and Cd1–N1 bonds gives rise to three-connected 2-D layers. The layers are pillared by Cd1–O1–C5 contacts with the interlayer Cd1···C5 distance of 3.274 Å (Fig. 1b) resulting in a 3-D zeolite-like framework including 20-membered rhombic channels occupied by methyl groups of $mpdc^{2-}$ ligands (Fig. 1c and Figure S1). But the same framework cannot be obtained by using pyridine-3,5-dicarboxylic acid as spacer and $Cd(NO_3)_2$ under the same conditions. This may be due to the existence