Journal of Molecular Structure 1156 (2018) 224–229

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Three new 5-fold interpenetrating diamondoid frameworks constructed by rigid diimidazole and dicarboxylate ligands

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ARTICLE INFO

Article history:
Received 2 October 2017
Received in revised form
25 November 2017
Accepted 26 November 2017
Available online 27 November 2017

Keywords:
Crystal structure
Metal–organic frameworks
MOFs
5-Fold interpenetrating diamondoid framework
1,4-Di(1*H*-imidazol-1-yl)benzene
Trans-cyclohexane-1,4-dicarboxylic acid
Succinic acid

ABSTRACT

A series of three-dimensional coordination polymers, namely, $[Cd(BIMB)(SCA)]_n$ (**1**), $[M(BIMB)(\textit{trans}\text{-}CHDC)]_n$ (**2**, M = Cd^{2+}; **3**, M = Co^{2+}), where BIMB = 1,4-di(1*H*-imidazol-1-yl)benzene, SCA^{2-} = succinate dianion, $CHDC^{2-}$ = cyclohexane-1,4-dicarboxylate dianion) are synthesized hydro/solvatothermal methods. The products are characterized by elemental analysis and single–crystal X-ray diffraction data. Both the dianion and BIMB bridge different pairs of the metal ions, the three complexes are polymeric and their three-dimensional topology feature a diamond-like metal–organic framework (MOF). Owing to the length of the two bridging ligands, moderate size voids are formed in the diamondoid networks. However, the voids are filled by mutual interpenetration of four independent equivalent frameworks in a 5-fold interpenetrating architecture, and there is no sufficient void volume available for any guest molecules. The phase purity and thermal stability of the compounds are verified by powder X–ray diffraction (PXRD) and thermogravimetric (TG) data. The solid–state fluorescence spectra for the $3d^{10}$ Cd^{2+} MOF's **1** and **2** reveal significant enhancement in their emission intensities in comparison to the non-metallated BIMB. The enhanced emission is attributed to perturbation of intra-ligand emission states due to Cd^{2+} coordination.

1. Introduction

The rapid expansion of research endeavors related to metal organic frameworks (MOFs) and coordination polymers (CPs) in recent years is ascribed in part to the designability of pores in such materials to the scale of molecular length [1]. Considerable effort has been focused on the rational design and synthesis of MOFs, and this field continues to be intensely active also due to the fascinating structural diversity of the new materials synthesized and their potential applications in gas storage, chemical separations, drug delivery, ion displacement, sensor technology, and heterogeneous catalysis [2–6].

In general, the structures and properties of MOFs are affected by their constituent metal centers and organic linkers [7]. Reaction conditions such as solvents used, pH, temperature, and reaction time also influence the type of MOF's formed and their overall physical and chemical behavior. However, the metal ions and organic ligands present in the MOFs are critical in determining their final structure. In this paper, we have employed two structurally flexible aliphatic dicarboxylic acid ligands, namely, cyclohexane-1,4-dicarboxylic (*trans*-H_2CHDC) and succinic acid (H_2SCA) together with an aromatic linker ligand: 1,4-di(1*H*-imidazol-1-yl)benzene (BIMB) to construct novel 5-fold interpenetrating frameworks with low porosity. Our interest in BIMB as a linker stems from its well demonstrated ability to act as a rigid bridging ligand in the μ_2 coordination mode [8–10]. We hoped that the complexation of the binucleating BIMB and the two dicarboxylic acid ligands with appropriate metal ions would lead to products with extended 3D network structures with molecular-size voids. As discussed below, the syntheses lead to MOF complexes that feature rare interpenetrating diamondoid networks.

2. Experimental

2.1. Synthesis and crystallization

[Cd(BIMB)(SCA)] (1). $Cd(NO_3)_2\cdot 4H_2O$ (31 mg, 0.10 mmol), H_2SCA (11 mg, 0.10 mmol) and BIMB (21 mg, 0.10 mmol) were dissolved in $DMF:H_2O$ (1:3 v/v, 5 mL) solvent mixture in a

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https://doi.org/10.1016/j.molstruc.2017.11.111

screw-capped sample vial. The mixture was heated in an oven at 95 °C for 3 d. The clear solution was slowly cooled to room temperature. The colorless cubic crystals of **1** formed were collected by filtration, washed with DMF:H_2O (1:3 v/v, 5 mL), and dried in air. Yield: 58% (based on Cd). Anal. Calcd. for $C_{16}H_{14}CdN_4O_4$: C 43.64, H 3.21, N 12.73%; found: C 43.80, H 3.22, N 12.77%.

[Cd(BIMB)(*trans*-CHDC)]·H_2O (2). A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (31 mg, 0.10 mmol), *trans*-H_2CHDC (17 mg, 0.10 mmol), 1,4-BIMB(21 mg, 0.10 mmol) and DMF:H_2O (1:3 v:v, 5 mL) taken in a 25 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated in an oven at 95 °C for 3 d and then cooled to ambient temperature. The colorless cubic crystals of **2** formed were collected by filtration, washed with DMF:H_2O (1:3 v:v, 5 mL) and dried in air. Yield: 62% (based on Cd). Anal. Calcd. for $C_{20}H_{22}CdN_4O_5$: C 46.87, H 4.33, N 10.94%; found: C 47.02, H 4.34, N 10.97%.

[Co(BIMB)(*trans*-CHDC)]·H_2O (3). $Co(NO_3)_2\cdot 6H_2O$ (29 mg, 0.10 mmol), *trans*-H_2CHDC (17 mg, 0.10 mmol) and 1,4-BIMB (21 mg, 0.10 mmol) were dissolved in DMF:H_2O (1:3 v:v, 5 mL) in a screw-capped sample vial. The mixture was heated in an oven at 95 °C for 3 d and then cooled to room temperature. The pink cubic crystals of **3** formed were collected by filtration and washed with DMF:H_2O (1:3 v/v, 5 × 3 mL). Yield: 60% (based on Co). Anal. Calcd. for $C_{20}H_{22}CoN_4O_5$: C 52.50, H 4.85, N 12.25%; found: C 52.52, H 4.85, N 12.24%.

2.2. Crystallographic data

X-ray diffraction data were measured at room temperature (296 K) on a Bruker SMART APEX II CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube operated at 1.5 kW power (50 kV, 30 mA). A series of narrow frames of data were collected and integrated with the Bruker SAINT Software package using a narrow-frame integration algorithm. The data were corrected for absorption effects by the multi-scan method (SADABS). Crystallographic data collection parameters and refinement data are collected below in Table 1. The structure was solved by the direct methods using the Bruker SHELXTL (V2014.11–0) Software Package [11]. All non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. All of the H atoms in the structures of **1** and **2** were located in successive Fourier maps and refined isotropically. All H atoms except the solvated water molecules were placed in calculated positions and refined isotropically adopting a riding model with fixed positional parameters. The latter H atoms were located in the Fourier maps and refined isotropically.

3. Results and discussion

3.1. Synthesis and structure

The reactions of cadmium(II) and cobalt(II) nitrates with the BIMB and aliphatic dicarboxylic acid ligands dissolved in a DMF:water mixed solvent system at 95 °C over a period of 3 d followed by slow cooling to ambient temperature yielded crystals of the corresponding MOFs except in the case of the reaction with cobalt(II) nitrate, BIMB and succinic acid. Despite our best efforts, no crystalline product could be obtained from the latter reaction. The three products successfully prepared are isolated in moderate yields. Whereas [Cd(BIMB)(SCA)] (**1**) and [Cd(BIMB)- (CHDC)]·H_2O (**2**) are colorless, [Co(BIMB)(CHDC)]·H_2O (**3**) is pink. In the solid state all of them are stable in the presence of atmospheric air. The products are characterized by single crystal X-ray diffraction data and elemental analysis. The crystallographic data reveal that the compounds are structurally isoreticular (Table 1) containing similarly interpenetrating 5-fold coordination networks, although the structures also exhibit unique structural features as discussed below.

Crystal structure of [Cd(BIMB)(SCA)] (1). As depicted in Fig. 1, the asymmetric unit consists of a Cd^{2+} ion situated on a mirror plane, and two halves of the fully deprotonated SCA^{2-} and neutral BIMB ligands. The ligands are located on two-fold rotation axes. The metal center is hexa-coordinated by virtue of the various symmetries with two sets of equivalent BIMB and SCA^{2-} ligands. As could be expected, BIMB binds two metal centers through one each of the imidazole N atoms. The SCA^{2-} ligands also coordinate to two different Cd^{2+} centers but each of the carboxylate groups acts as a chelate with unequal Cd–O bond distances of 2.202(1) and 2.620(2)

Table 1
Crystal data and refinement parameters for **1**–**3**.

	1	2	3
CCDC Number	1502071	1502031	1502072
formula	$C_{16}H_{14}CdN_4O_4$	$C_{20}H_{22}CdN_4O_5$	$C_{20}H_{22}CoN_4O_5$
M_r	438.71	510.82	457.34
radiation type	Mo Kα	Mo Kα	Mo Kα
crystal system	monoclinic	monoclinic	monoclinic
space group	$C2/c$ (15)	$P2_1/c$ (14)	$P2_1/c$ (14)
temperature (K)	296	296	296
a (Å)	13.1035(13)	11.211(3)	11.173(7)
b (Å)	19.724(2)	23.066(6)	22.738(15)
c (Å)	7.4890(7)	7.684(2)	7.875(5)
β (°)	123.341(10)	91.846(8)	95.598(6)
V (Å^3)	1617.0(3)	1986.0(9)	1991(2)
Z	4	4	4
μ (mm^{-1})	1.38	1.14	0.90
crystal size (mm)	0.25 × 0.22 × 0.20	0.26 × 0.21 × 0.19	0.24 × 0.22 × 0.18
T_{min}, T_{max}	0.724, 0.770	0.756, 0.804	0.812, 0.894
reflns collected	5532	15052	11289
ind reflns (R_{int})	1992 (0.0211)	4857 (0.0300)	4630 (0.0468)
obsd reflns [$I > 2\sigma(I)$]	1932	4177	3098
R_1 [$F^2 > 2\sigma(F^2)$]	0.0191	0.0239	0.0492
wR_2 (F^2)	0.0480	0.0601	0.1008
goodness of fit, S	1.093	1.035	1.064
data/parameters	1992/143	4857/359	4630/278
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.543, −0.523	0.424, −0.911	0.440, −0.748