Synthesis and Structural Characterization of Two-dimensional Metal-organic Framework by Using Bent Ditopic Carboxylate Ligands

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Abstract

To design and make new metal-organic frameworks with desired structure and consequently spatial properties, there need to choose both metal ion as a node and ligands as their linkers. In pillared metal-organic frameworks, the presence of two linkers make bifunctional MOFs. Here, a pillar two-dimensional metal-organic framework (MOF) with molecular formula \([\text{Zn}(\text{cba})(\text{bpdb})].\text{DMF (2DTMU-1})\) was obtained by the reaction of zinc(II) nitrate with 4,4'-methylenedibenzoic acid \((H2cba)\) as the carboxylate linker and 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (bpdb) as the N-donor pillar. The structure was determined by single-crystal X-ray diffraction and Fourier-transform infrared spectroscopy (FT-IR). \textbf{2DTMU-1} is based on a binuclear paddlewheel Zn(II) unit complexed by four bridging bidentate (dicarboxylate) V-shaped ligand, 4,4'-methylenedibenzoic acid \((H2cba)\), this tetragonal array being connected by \textit{bpdb} with a bridging azine group in the middle as a potential Lewis basic site, making two-dimensional metal-organic framework structure and shows a pore size of \(18 \times 12 \text{ Å}^2\).

1. Introduction

Metal-organic Frameworks (MOFs) are subclasses of coordination polymers, which are often porous and created by careful selection of metal ions or metal clusters alongside connecting linkers. Different properties and applications in chemistry and materials branches of metal-organic frameworks have been developed that show MOFs can be very excellent candidate in various applications, such as gas storage and separation, liquid separation and purification, electrochemical energy storage, catalysis, and sensing\([1–3]\).

While coordination polymers involve different dimensionalities from zero- to three-dimensional structures, metal-organic frameworks are often three-dimensional. Recently, some two-dimensional metal-organic frameworks have also been developed \([3–6]\). In recent years, a great attention has been focused on construction of 2D-MOFs owing to their fascinating structural features such as high surface area and a high density of exposed functional sites advantageous for various applications \([7–9]\).

On the other hand, pillared MOFs based on paddle-wheel nodes can be structurally classified in two different groups depending on the geometry and multtopic nature of carboxylate linkers. In first group, 2D metal-carboxylate layers are developed due to coordination of deprotonated carboxylate functions to the metal ions and formation of paddle-wheel inorganic nodes. In this regard, tetratopic planar \([10]\) and linear ditopic \([11]\) carboxylate linkers can form these 2D layers. Then, these 2D metal-carboxylate linkers can be connected together through coordination of N-donor pillars to construct 3D frameworks. In a second group, 1D metal-carboxylate chains can be constructed by the coordination of bent ditopic carboxylate linkers. In some cases, like 4,4'-methylenedibenzoic acid \((H2cba)\), mentioned 1D chains can be connected together through N-donor pillars and forms 2D frameworks \([12]\), while in cases like 4,4’-oxybis(benzoic acid) with helix like 1D metal-carboxylate linkers \([13]\) the 1D chains can be connected together by N-donor pillar to form 3D frameworks \([14]\). So based on this criteria, in this work, we have synthesized a Zn(II) metal–organic framework, \([\text{Zn}(\text{cba})(\text{bpdb})].\text{DMF (2DTMU-1})\), based on a V-shaped
flexible dicarboxylate ligand, 4,4'-methylenebienzoic acid (H2cba), and the N-donor ligand, 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (bpdb), and the effect of the -CH2- group of the H2cba was compared with similar reported pillared MOFs, TMU-4 and TMU-5. The 4,4’-oxybis(benzoic acid) (H2oba) as a linker has been used in TMU-4 and TMU-5 structures (Scheme 1).

2. Experimental Section

2.1. Materials and physical measurements

All the starting materials and solvents for the preparation and spectroscopic analysis were commercially purchased from Aldrich and Merck Company and used as received. The ligand bpdb (1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene) was synthesized by method reported in reference 15 [15]. Melting points were measured on an Electrothermal 9100 apparatus. infrared spectra were recorded using Thermo Nicolet IR 100 FT-IR. Suitable crystal for single crystal X-ray diffraction (SCXRD) analysis of 2DTMU-1 was prepared by reaction of Zn(NO3)2·6H2O (0.297 g, 1 mmol), 4,4'-methylenebienzoic acid (H2cba) (0.254 g, 1 mmol) and 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (bpdb) (0.105 g, 0.5 mmol) in 30 mL of DMF. This reaction mixture was sonicated for uniformly dispersion (~3 min), and it was then heated at 80°C. After 72 hours, yellow crystals of 2DTMU-1 were collected (0.420 g, yield 71% based on H2cba), d.p. >300°C. IR data (KBr pellet, ν/cm−1): selected bands: 775(s), 874(m), 1088(s), 1159(s), 1242(vs), 1413(vs-br), 1503(s), 1602(vs), 1679(vs) and 3418(w-br). For X-ray crystal structure determination, one of the approximately spherical habit was measured at 100K under liquid nitrogen stream using a RIGAKU XtaLabPro diffractometer equipped with a Mo microfocus sealed tube MM003 generator coupled to a double-bounce confocal Max-Flux® multilayer optic and a HPAD PILATUS3R 200K detector. CrysAlisPro 1.171.41.123a [16], implementing a combination of spherical and empirical absorption corrections using equivalent radius and absorption coefficient on one hand and spherical harmonics on the other one into SCALE3 ABSPACK scaling algorithm, was used for the data processing, and to deal with icing problems during data collection. The structure was solved by intrinsic phasing methods (SHELXT program) [17], then full-matrix least-squares methods on F2 using SHELX-L was applied for refinement [18]. All non-hydrogen atoms were improved by anisotropic refinement. Aromatic H atoms were placed in idealized positions and constrained to ride on their parent atoms with relative isotropic displacement coefficients, Uiso(H) set to 1.2Ueq(C). The structure of 2DTMU-1 also contains 1100 Å³ (ca 41% of the unit-cell volume) of solvent-accessible voids revealed by the SQUEEZE routine [19] as implemented in the program PLATON (Spek, 2020), and occupied by an estimation of 267 electrons corresponding to ca 6.7 solvent molecules of DMF. Nevertheless, four DMF molecules could be modelled inside these cavities and among them, two DMF with static disorder constrained with SHELXL instructions (SADI, DELU, SIMU, and EADP). Methyl hydrogens were treated as rigid groups allowed to rotate but not tip with Uiso(H) set to 1.5Ueq(C). Crystal data, data collection and details of structure refinement are summarized in Table 1. CCDC 2153128 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
3. Results And Discussion

A new two-dimensional Zn(II) metal–organic framework, [Zn(cba)(bpdb)].DMF (2DTMU-1) has been synthesized by mixing of zinc(II) nitrate with a V-shaped flexible dicarboxylate ligand, 4,4′-methylenedibenzoic acid (H2cba), and the N-donor ligand, 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (bpdb). The structure of this new compound has been confirmed by infrared spectroscopy and single crystal X-ray crystallography. The infrared spectrum of 2DTMU-1 (Fig. 1) shows the main peaks of both cba2− carboxylate linker and bpdb N-donor pillar and the characteristic peaks of the dicarboxylate groups of the cba2− ligands is at ca. 1633 and 1406 cm−1 for the symmetric and asymmetric vibrations, respectively, which show the coordination of carboxylate ligands to metal ions. Also, the characteristic absorption band (νC=O at 1674 cm−1) of DMF are presented in the infrared spectrum of 2DTMU-1. The peak at 1674 cm−1 has been disappeared after solvent exchange and heating under evacuation (Fig. 1).

The single crystal structure determination shows the framework 2DTMU-1 is a pillar-layered framework based on ditopic bent cba2− carboxylate linker and bpdb N-donor pillar. 1D metal-carboxylate chains are constructed based on paddle-wheel inorganic nodes via the coordination of deprotonated H2cba linkers to the Zn(II) metal ions (Fig. 2). Then these 1D chains are connected together by bpdb pillar spacer to form 2D framework of 2DTMU-1 (Fig. 3a). Inter-digited layers of 2DTMU-1 are presented in Fig. 3b. Since, bpdb linkers bear azine function, and in fact the 2D framework of 2DTMU-1 is functionalized with azine functional groups (Fig. 3b). 2DTMU-1 has 2D (4,4) layered structure and crystallizes in the triclinic with space group of Pī. The Zn(II) center is five-coordinated by four oxygen atoms from four cba2− ligands and one nitrogen atom from one bpdb ligand, giving a geometry with distorted trigonal bipyramidal structure. The Zn−O and Zn−N bond lengths and O−Zn−O and O−Zn−N bond angles are from 2.032(3) to 2.051(3) Å and 87.74 (12) to 163.68(11) °, respectively, within the region of values observed for similar Zn(II) complexes with five coordination number and oxygen and nitrogen donor ligands [20–22]. In the crystal structure of 2DTMU-1, the cba2− ligands bridge the same mode to link four Zn(II) centers, whereas the bpdb acts as a trans-bidentate bridging ligand to link pairs of Zn atoms. In this manner, the binuclear Zn units are bridged into a linear chain via cba2− anions with a Zn···Zn separation of 19.63 Å. The bpdb ligands also link the binuclear zinc(II) atoms to construct a linear structure with a Zn···Zn distance of 12.63 Å. The two kinds of parallel structures are perpendicularly intersected by the dinuclear zinc atoms, causing in a two-dimensional (4,4) network (Fig. 3b) when the dimer zinc atoms and the organic parts are considered as nodes and linkers, respectively. Each ring forms from four cba2− ligands, two bpdb ligands and two Zn(II) atoms. The big voids with size ca. 18 × 12 Å2 for each two-dimensional coordination polymer allow the formation of interpenetration between adjacent structures in a parallel way (Fig. 4).

There have been reported two similar pillar-layered metal-organic frameworks [14] with the similar linker (H2oba) and the same pillar ligands (bpdb and bpdh), azine decorated TMU-4 with the formula [Zn(oba)(bpdb)0.5]n·2DMF, azine-methyl functionalized TMU-5 with the formula [Zn(oba)(bpdh)0.5]n·1.5DMF, where H2oba = 4,4′-oxybis(benzoic acid), bpdb = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene, bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene. Figure 5 shows two different linkers, H2oba and H2cba but the same
bpdb pillared ligands applied for preparing of two structurally different MOFs, TMU-4 and 2DTMU-1, along with their 3D and 2D structures. As it can be seen from their building blocks, the pillar ligands in both compounds is bpdb and ditopic carboxylate linker is different, in TMU-4 is H2oba and in 2DTMU-1 is H2cba. The main part of two linkers is the same and the only difference is in middle spacer part of these linkers, in H2oba the -O- group has been replaced with -CH2- group in the H2cba. This replacement has influenced on type of structures grown in the three dimensional manner, As it can be seen in the structure of 2DTMU-1, bridging of the cba2− linkers to the paddle-wheel zinc acetate type nodes makes one-dimensional chains (Fig. 5) and then these 1D chains connect together through N-donor bpdb pillars and forms 2D frameworks while in case of TMU-4 theoba2− linkers bridged to the paddle-wheel zinc acetate type nodes and makes helix like one-dimensional metal-carboxylate linkers and then these 1D helix like chains can be connected together by N-donor bpdb pillar to form 3D frameworks.

However, 2DTMU-1 is formed on a binuclear paddlewheel Zn(II) unit (Zn# 1 and Zn# 2) complexed by four bridging bidentate (dicarboxylate) V-shaped ligand, 4,4′-methylenedibenzoic acid (H2cba), this tetragonal array being connected by bpdb with a azine group bridging in the middle as potential Lewis basic site. This assembly is similar to that obtained for the TMU-5 [14] complex in which both ligands had been replaced (H2cba by H2oba and bpdb by bpdbh, respectively) and not to TMU-4 which simply differs by one atom in the V-shaped ligand (O replaced by C, Fig. 6). Nonetheless, 2DTMU-1 crystallizes in the centrosymmetric triclinic space group conversely to TMU-5 in a higher symmetry space group (C2/c) as a mark of a bigger distortion of the paddlewheel unit: indeed the square pyramidal geometry around the Zn centers coordinated by four carboxylate O atoms (for Zn# 1: O1, O3, O5, O7 and for Zn# 2: O2, O4, O6, O8) from four fully deprotonated cba2− ligands with bite averaged angle of 125.4°, and one N atom (Zn# 1: N1 and Zn# 2: N4 from the bpdb ligand in the axial direction appears particularly deformed with Zn#1–O distance ranging from 2.040(3) to 2.056(2)Å (respectively for Zn#2: from 2.033(3) to 2.098(2)Å) but with similar Zn–N distances 2.0412(3)Å (Fig. 4). The averaged r.m.s.d of the atoms in the equatorial planes delineated by facing carboxylates at 89.5° from each other has value of 0.125Å. The separation between Zn# 1 and Zn# 2 is 2.934(1) Å, the same order of magnitude than in TMU-5. The bond lengths and bond angles of 2DTMU-1 are listed in Table 2.
Table 2
Selected bond lengths [Å] and angles [°] for 2DTMU-1.

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<th>Bond</th>
<th>Length</th>
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Declarations

Acknowledgments

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References


**Scheme**

Scheme 1 is available in supplementary section.

**Figures**
Figure 1

IR spectra of the 2DTMU-1 before and after the activation process.
Figure 2

1D chains of Zn-cba in 2DTMU-1 framework.

Figure 3

2D framework of 2DTMU-1. (a) Along with A axis. (b) Along with B axis. (c) Along with C axis.
Figure 4

a) Showing of interdigitated layers and b) showing azine decorated framework of 2DTMU-1.
Figure 5

A schematic illustration of linkers and pillars used in the TMU-4 (up) and 2DTMU-1 (low) structures with their 3D and 2D structures
Figure 6

(a) Representation of the Zn2 paddlewheel unit within 2DTMU-1. (b) Layers of Zn(II)-cба (in red) pillared by bpdb (in blue) along the c direction in the presence (left) or absence of solvent representation (right). (c) Connolly surface representation along b-axis (left) and bc direction (right), showing that 2DTMU-1 is porous and comprises interconnected pores. (d) Representation of the pores, highlighting the azine groups (in sea blue). Color code: O: red; N: blue; C: gray; and Zn: magenta. Connolly surface: gold represents outside the surface and dark gold, inside the surface.

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