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A linear rod-packing coordination polymer constructed from a non-linear dicarboxylate and the $[\text{Zn}_4\text{O}]^{6+}$ cluster

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A 1-D coordination polymer, $[\text{Zn}_4\text{O}(1,2\text{-BDC})_3]_n$ (1,2-BDC = 1,2-benzendicarboxylate), has been synthesized under solvothermal conditions and structurally characterized by single-crystal X-ray diffraction. The coordination polymer contains $[\text{Zn}_4\text{O}]^{6+}$ clusters with a central μ_4 -oxygen tetrahedrally coordinated by four Zn^{2+} ions, which stack into a linear rod connected by 1,2-BDC units.

Keywords: Coordination polymer; Linear; 1-D; XRD

1. Introduction

The synthesis of novel coordination polymers, metal–organic frameworks (MOFs), and other related materials is of intense interest because of the applications of these materials in areas such as catalysis [1], gas storage [2], non-linear optics [3], molecular separation [2, 4], luminescence [5], and magnetism [3, 6]. These materials offer a wealth of topologies and connectivities from multiple interpenetrated networks to open structures with ultra-high porosities [7]. Coordination polymers and MOFs are constructed from metal ions or clusters that form nodes and organic molecules that are polytopic and link the nodes together. We are interested in crystal engineering of MOF and MOF-like materials to understand how the fundamental building blocks of these materials coordinate to each other forming the most favorable structures. Many MOFs have been synthesized under similar conditions to reproducibly give isorecticular series of MOFs; however, there are gaps in some of the series in terms of structural isomers of the organic molecules employed.

The first MOFs employed aromatic, polytopic pyridines [8] or carboxylate compounds such as 4,4'-bipyridine and 1,4-benzenedicarboxylic acid (1,4- H_2BDC) [9, 10]. There are many examples of small polycarboxylates being components of MOF ligands, notably this is true in the case of MOF-5, where 1,4- H_2BDC links Zn_4O clusters to form a cubic framework [10]. 1,4- H_2BDC is also used in the synthesis of many other MOFs where it is accompanied by a co-ligand, usually a ditopic pyridine or other nitrogen heterocycles,

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commonly forming MOFs with a binuclear paddle-wheel secondary building unit [11–13]. The triacid 1,3,5-benzenetricarboxylic acid (1,3,5- H_3 BTC) has been used in the synthesis of many MOFs including the much researched HKUST-1 ($[Cu_3(1,3,5-BDC)_2]$) [10]. The non-linear 1,3- H_2 BDC diacid has also been employed in the synthesis of novel MOFs, but given its bent shape, it is rarely employed as the sole ligand in a MOF [14–19]. For the equally bent-shaped 1,2- H_2 BDC, there are no examples at this time to the authors' best of knowledge.

The isoreticular synthesis of MOFs was introduced in the early 2000s by Yaghi and O'Keeffe [20, 21]. The main concept is that isostructural MOFs can be synthesized under similar conditions by changing only the organic ligand in the synthesis mixture to give the corresponding new MOF. Isoreticular synthesis relies on the formation of the MOF secondary building unit or cluster in similar reaction conditions. In seeking new MOFs, the precursors – zinc nitrate and dialkylamides were reacted with simple polycarboxylates under solvothermal conditions that have been reported frequently to give MOFs with the Zn_4O secondary building unit [21–26]. In the MOF series, which contains the disubstituted benzenedicarboxylates and the Zn_4O cluster, there is a gap for the MOF generated from 1,2-benzenedicarboxylic acid.

Herein, we report the synthesis and X-ray single-crystal structure of the resulting coordination polymer formed from the solvothermal reaction of 1,2-benzenedicarboxylic acid and zinc nitrate in DEF (DEF = *N,N*-diethylformamide).

2. Experimental

Zinc nitrate hexahydrate, 1,2-benzene dicarboxylic acid, DMF (DMF = *N,N*-dimethylformamide), and DEF were purchased from Sigma–Aldrich and used without purification. 1H NMR (300 MHz) spectra were recorded on a Bruker AV300 spectrometer. FTIR spectra were obtained on a Matterson Satellite (ATR) as solid samples.

2.1. Synthesis of $[Zn_4(O)(1,2-BDC)_3]$

In a 12 mL scintillation vial, $Zn(NO_3)_2 \cdot 6H_2O$ (45 mg, 0.15 mM) and 1,2-benzenedicarboxylic acid (8 mg, 0.05 mM) were dissolved in DEF (10 mL) by sonification for 20 min. The vial was then sealed and heated to 100 °C for 48 h in an isothermal oven. After cooling to room temperature, the crystalline product was quickly filtered and washed with fresh DEF. The solid was then stored in fresh DEF in a sealed vial until further use.

2.2. X-ray crystallography

Data were collected on a Bruker Nonius APEXII diffractometer mounted at the window of an FR591 rotating Mo anode ($\lambda = 0.71073 \text{ \AA}$) with confocal optics. Data collection and processing were performed using the programs COLLECT [27], DENZO [28], and SCALEPACK [28] and a semi-empirical absorption correction was applied using SADABS [29]. The structure was solved by direct methods and refined using full-matrix least-squares using the SHELX97 [30] packages. The structure was refined as a pseudo-merohedral twin, monoclinic with $\beta = 90.011(3)$ emulating orthorhombic. The twin law $(-1\ 0\ 0\ 0\ -1\ 0\ 0\ 0\ 1)$ was applied using the standard TWIN instruction in SHELX and the twin fraction refined to ca. 47%. Various thermal parameter restraints (DELU/SIMU) were applied to chemically

similar groups within the structure and the three diethylformamide molecules were restrained to have similar geometries (SAME). Crystal and structure refinement data are summarized in table 1.

3. Results and discussion

The coordination polymer crystallizes in the $P2_1/c$ space group with three DEF solvent molecules per unit cell giving the formula $[\text{Zn}_4\text{O}(\text{1,2-BDC})_3] \cdot 3\text{DEF}$, see figure 1. The average $\mu_4\text{O-Zn}$ bond distance is 1.928 Å compared to 1.922 Å in $[\text{Zn}_4\text{O}(\text{1,4-BDC})_3]$, MOF-5 [1]. The Zn_4O units stack face to face along the c axis, 7.208 Å apart. Three of the O_2CR groups point down creating one face and the other three O_2CR groups point up forming the other face. These form the corners of a triangle which stacks top to bottom with the Zn_4O units sandwiched between. The sides of the Zn_4O tetrahedron are therefore open to solvent or moisture compared to MOF-5 and its analogs. In the solid state, the carbonyl groups from DEF point toward the central $\mu_4\text{-O}$ in the center. There is an average bond distance of 2.887 Å between the carbonyl oxygen and the three zincs on the face of the Zn_4O tetrahedron closest to DEF. The openness of the secondary building units may account for the extreme sensitivity of $[\text{Zn}_4\text{O}(\text{1,2-BDC})_3]$ to air. When removed from the solvent, the crystals quickly desolvate. Thermogravimetric analysis proved meaningless as the crystals desolvated quickly once removed from the vial. Other characterizations have been conducted rapidly and single X-ray crystallography data collection was performed under a stream of liquid nitrogen.

Bulk amounts of the coordination polymer were synthesized in DMF instead of DEF by direct scaling up of the initial reaction conditions. These samples were characterized by powder X-ray diffraction (PXRD) to confirm their structure (figure S1, Supplementary material). A sample from the larger scale synthesis was dried under vacuum and then digested by sonification in dilute HCl and DMSO- d_6 . The ^1H NMR spectrum (figure S2, Supplementary material) shows the same ratio of three dialkylamide (in this case DMF) molecules per three 1,2-BDC molecules as found in the crystal structure obtained from DEF. A sample of the coordination polymer was solvent exchanged with CHCl_3 over a period of three days. This sample was then dried and the PXRD pattern shown to match that of the as-synthesized material, evidence that the coordination polymer, if handled only

Table 1. Crystal data and structure refinement information for $[\text{Zn}_4\text{O}(\text{1,2-BDC})_3] \cdot 3\text{DEF}$.

Empirical formula	$\text{C}_{39}\text{H}_{45}\text{N}_3\text{O}_{16}\text{Zn}_4$
Formula weight	1073.26
Crystal system	Monoclinic
Space group	$P2_1/c$
a	18.3857(9) Å
b	16.2180(6) Å
c	14.4062(7) Å
β	90.011(3)°
Volume	4295.6(3) Å ³
Z	4
Reflections	32,050
Independent reflections	7462 [$R_{\text{int}} = 0.1104$]
Final R indices [$F^2 > 2\sigma(F^2)$]	
R_1	0.0713
wR_2	0.1260

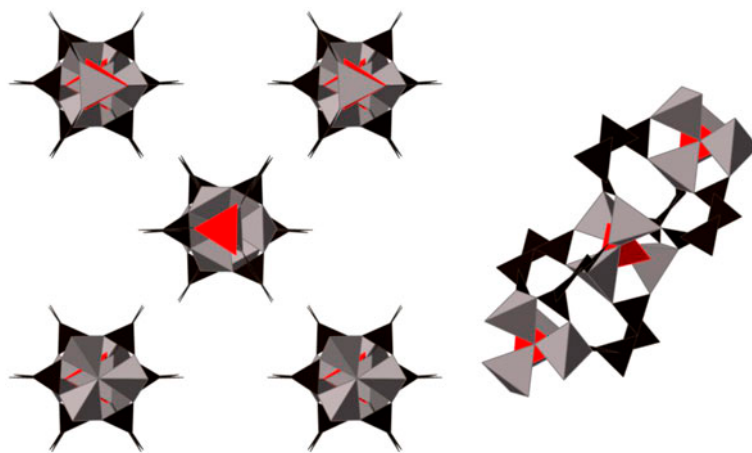


Figure 1. Crystal structure of $[\text{Zn}_4\text{O}(\text{1,2-BDC})_3]$ omitting DEF molecules (left: view of rod packing along the c axis; right: side-on view of three Zn_4O units).

briefly in air, is stable to solvent (figure S1, Supplementary material). The infrared spectrum of the dried coordination polymer shows characteristic absorptions for an O–H stretch (w , 3384 cm^{-1}), aromatic C–H stretch (m , 3064 cm^{-1}), alkyl C–H stretches (w , 2954 and 2839 cm^{-1}), carboxylate C=O stretch (s , 1715 cm^{-1}) and aromatic C–C stretch (s , 1591 cm^{-1}) (figure S3, Supplementary material). The weak O–H stretch suggests the presence of moisture in the sample or free hydroxyls on the surface of the crystals. The presence of a small amount of DMF is shown by the alkyl C–H doublet.

4. Conclusions

We have synthesized a coordination polymer that completes the set of coordination polymers synthesized upon solvent–thermal reaction of zinc nitrate and simple benzenedicarboxylates. Interestingly, the only way that the Zn_4O secondary building units can connect when benzene-1,2-dicarboxylate is employed is to form a rod-like coordination polymer rather than a 2-D or 3-D structure. By using a ligand where the coordinating functional groups are constrained within close proximity to one another, a new material has been obtained. This system is yet another example of the rigidity of the solvothermal synthesis employed to produce many other MOF-like structures.

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References

- [1] M. Ranocchiari, J.A. van Bokhoven. *Phys. Chem. Chem. Phys.*, **13**, 6388 (2011).
- [2] J.R. Li, R.J. Kuppler, H.C. Zhou. *Chem. Soc. Rev.*, **38**, 1477 (2009).
- [3] C. Janiak. *Dalton Trans.*, 2781 (2003).

- [4] B.L. Chen, S.C. Xiang, G.D. Qian. *Acc. Chem. Res.*, **43**, 1115 (2010).
- [5] M.D. Allendorf, C.A. Bauer, R.K. Bhakta, R.J.T. Houk. *Chem. Soc. Rev.*, **38**, 1330 (2009).
- [6] L. Qiu, G.S. Zhu. *Coord. Chem. Rev.*, **253**, 2891 (2009).
- [7] P. Hubbertstey, X. Lin, N. RY. Champness, M. Schröder. In *Metal-Organic Frameworks: Design and Application*, L.R. MacGillivray (Ed.), p. 131. John Wiley & Sons, Inc., Hoboken, NJ (2010).
- [8] O.M. Yaghi, H.L. Li. *J. Am. Chem. Soc.*, **117**, 10401 (1995).
- [9] H. Li, M. Eddaoudi, T.L. Groy, O.M. Yaghi. *J. Am. Chem. Soc.*, **120**, 8571 (1998).
- [10] H. Li, M. Eddaoudi, M. O’Keeffe, O.M. Yaghi. *Nature*, **402**, 276 (1999).
- [11] D.N. Dybtsev, H. Chun, K. Kim. *Angew. Chem. Int. Ed.*, **43**, 5033 (2004).
- [12] H. Chun. *Chem. Eur. J.*, **11**, 3521 (2005).
- [13] B.Q. Ma, K.L. Mulfort, J.T. Hupp. *Inorg. Chem.*, **44**, 4912 (2005).
- [14] G.-B. Che, C.-B. Liu, L. Wang, Y.-C. Cui. *J. Coord. Chem.*, **60**, 1997 (2007).
- [15] F. Luo, Y.-X. Che, J.-M. Zheng. *Inorg. Chem. Commun.*, **11**, 358 (2008).
- [16] F. Zhang, F.-L. Bei, J.-M. Cao. *J. Chem. Crystallogr.*, **38**, 561 (2008).
- [17] E.Y. Kim, Y.J. Song, H.G. Koo, J.H. Lee, H.M. Park, C. Kim, T.-H. Kwon, S. Huh, S.-J. Kim, Y. Kim. *Polyhedron*, **29**, 3335 (2010).
- [18] N.L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O’Keeffe, O.M. Yaghi. *J. Am. Chem. Soc.*, **127**, 1504 (2005).
- [19] Z. Wang, Y.-H. Xing, C.-G. Wang, L.-X. Sun, J. Zhang, M.-F. Ge, S.-Y. Niu. *CrystEngComm.*, **12**, 762 (2010).
- [20] O.M. Yaghi, M. O’Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim. *Nature*, **423**, 705 (2003).
- [21] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe, O.M. Yaghi. *Science*, **295**, 469 (2002).
- [22] M.C. Das, H. Xu, Z. Wang, G. Srinivas, W. Zhou, Y.-F. Yue, V.N. Nesterov, G. Qian, B. Chen. *Chem. Commun.*, **47**, 11715 (2011).
- [23] J. Lincke, D. Lässig, K. Stein, J. Moellmer, A.V. Kuttathayil, C. Reichenbach, A. Moeller, R. Staudt, G. Kalies, M. Bertmer, H. Krautscheid. *Dalton Trans.*, 817 (2012).
- [24] M. Sabo, A. Henschel, H. Fröde, E. Klemm, S. Kaskel. *J. Mater. Chem.*, **17**, 3827 (2007).
- [25] K. Koh, A.G. Wong-Foy, A.J. Matzger. *J. Am. Chem. Soc.*, **132**, 15005 (2010).
- [26] K. Gedrich, I. Senkowska, I.A. Baburin, U. Mueller, O. Trapp, S. Kaskel. *Inorg. Chem.*, **49**, 4440 (2010).
- [27] Nonius B.V. *COLLECT Data Collection Software*. Delft, Nonius B.V. (1998).
- [28] Z. Otwinowski, W. Minor. In *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology*, C.W. Carter, Jr., R.M. Sweet (Eds), Vol. 276, Macromol. Crystallogr., Part A, pp. 307–326, Academic Press, New York (1997).
- [29] G.M. Sheldrick. SADABS – Bruker Nonius area detector scaling and absorption correction – V2.10.
- [30] G.M. Sheldrick. *Acta Crystallogr.*, **A64**, 112 (2008).