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Rapid Communication

A new zinc-1,3,5-benzenetricarboxylate framework integrated three distinct subunits (SBUs)

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ABSTRACT

A new metal-organic framework (MOF) $[Zn_5(btc)_3(H_2O)_{0.5}(O)_{0.5}(DMA)_3]\cdot 1.75(DMA)$ (**1**; btc=1,3,5-benzenetricarboxylate; DMA=*N*,*N*′-dimethyl acetamide) has been solvothermally synthesized. Unusually, three distinct subunits (SBUs), $[Zn_2(CO_2)_4(DMA)_2]$, $[(\mu_3\text{-}H_2O)Zn_3(CO_2)_6(DMA)]$ and $[(\mu_4\text{-}O)Zn_4(CO_2)_6(DMA)_2]$ are observed in **1** simultaneously. The integration of three distinct SBUs leads to an interesting Zn-btc framework materials with unusual structural topology.

1. Introduction

The construction of metal-organic frameworks (MOFs) has been attracted much attention not only for their potential applications but also for their intriguing topologies [1,2]. The design of MOFs is mainly dependent on the selection of suitable organic ligands and inorganic secondary building units (SBUs). Many famous MOFs materials such as HKUST-1 [3a], MOF-5 [3b] and MIL-101 [3c] etc., are all based on well-known SBUs, dimeric $[Cu_2(CO_2)_4]$, tetrameric $[Zn_4O(CO_2)_6]$ and trimeric $[Cr^{III}_3O(CO_2)_6]$ SBUs, correspondingly. In most cases, the SBUs are generated in situ, so reactants, reaction ratio, pH, temperature and solvent, et al. always play crucial roles on controlling the shape and geometry of the SBUs [4,5]. As one of the most common carboxylate ligands, 1,3,5-benzenetricarboxylic acid (=H_3btc) was selected into the self-assembly with zinc salts under different synthetic conditions. Up to now, many Zn-btc compounds have been known and several Zn-carboxylate SBUs have been explored [6–8]. Generally, one SBU is observed in one compound. Recently some prominent work has shown that the unity of two different SBUs in one self-assembly system could result in distinct frameworks and topologies [8d,e]. However, the relating reports are very rare at current stage because it is more difficulty to form more than one SBU in one self-assembly system.

In this work, by employing DMA as solvent, one new porous Zn-btc framework is successfully synthesized and structurally characterized by single-crystal X-ray diffraction. Three distinct subunits (SBUs), $[Zn_2(CO_2)_4(DMA)_2]$, $[(\mu_3\text{-}H_2O)Zn_3(CO_2)_6(DMA)]$ and $[(\mu_4\text{-}O)Zn_4(CO_2)_6(DMA)_2]$ are observed in **1** simultaneously. The integration of three distinct SBUs leads to an interesting Zn-btc framework materials with unusual structural topology.

2. Experimental

2.1. Materials and methods

All reagents and solvents for the syntheses were purchased from commercial sources and used as received. The IR spectra (KBr pellets) were recorded on a Magna 750 FT-IR spectrophotometer. Powder X-ray diffraction data were recorded on a Rigaku MultiFlex diffractometer with a scan speed of 10 °C min^{-1}. Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer under N_2 (30–800 °C range) at a heating rate of 10 °C min^{-1}.

2.2. Synthesis of $[Zn_5(btc)_3(H_2O)_{0.5}(O)_{0.5}(DMA)_3]\cdot 1.75(DMA)$ (1)

$Zn(NO)_2\cdot 6\,H_2O$ (0.166 g, 0.5 mmol), pyrazine (0.015 g, 0.2 mmol), 1,3,5-benzenetricarboxylic acid (H_3btc, 0.052 g, 0.2 mmol), 1*H*-tetrazole-1-acetic acid (0.055 g), tetrabutyl ammonium bromide (TBAB, 0.028 g) and DMA 5 mL in a 23 mL Teflon-lined airtight reactor was heated at 120 °C for 2 days, and then cooled to room-temperature. After washing with ethanol, colorless crystals of **1** were obtained

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(70% yield based on H_3btc ligand). Elemental analysis (EA) for **1**, $C_{50}H_{60.75}N_{4.75}O_{23.75}Zn5$ (1435.20): Calcd. C 41.84, H 4.27, N 4.64. Found. C 41.74, H 4.33, N 4.61.

2.3. Crystal structure determination

X-ray diffraction data were collected on Rigaku Saturn724 CCD X-ray diffractometer with graphite monochromated Mo*K*α radiation (λ=0.71073 Å) at 293 K. CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by direct method of SHELXS-97 and refined by full-matrix least-square techniques using the SHELXL-97 program [9]. The coordinated H_2O and O^{2-} in compound **1** are determined according to charge balance and a rational experimental bond and angle parameters which is well consistent with the experiment data ever reported [3b,8]. The contribution of the disordered solvent molecules was subtracted from the reflection data by the SQUEEZE method as implanted in PLATON program [10]. An accurate determination of solvent molecules in the structure is obtained from the thermalgravimetric analysis (TGA) curves and elemental analysis (EA) results, and the results are attached to the CIF file. The details of the structural analysis are summarized in Table 1. Selected bond lengths and angles for **1** are listed in Table 2.

3. Results and discussion

3.1. Description of crystal structure

Seven different zinc atoms are observed in **1** having different occupancy factors (Zn1, 0.5; Zn2, 1; Zn3, 0.5; Zn4, 1; Zn5, 0.5; Zn6, 0.5; Zn7, 1) and different coordination geometry (Fig. 1).

The prominent structural feature of **1** is the coexistence of three distinct SBUs (Fig. 2a). The first one is the classic paddle-wheel SBU, $[Zn_2(CO_2)_4(DMA)_2]$ (Zn_2), formed by four carboxyl groups linking two zinc atoms (Zn_6 or Zn_7), in which the axial positions are occupied by two DMA molecules. Second, two Zn_4 and one Zn_5 atoms are bridged by the μ_3-OH_2 to form an irregular trimeric $[(\mu_3\text{-}H_2O)Zn_3(CO_2)_6(DMA)]$ (Zn_3) SBU, in which four carboxylate groups bridge two 4-coordinate and one 6-coordinate Zn center, another two carboxylate groups as the mono-dentate ligands and one DMA occupied remaining coordination sites. The μ_3-O–Zn distance is from 1.961(6) Å to 2.133(10) Å. Third, two Zn_2, one Zn_1 and one Zn_3 atoms are bridged by the μ_4-O^{2-} to form an irregular $[(\mu_4\text{-}O)Zn_4(CO_2)_6(DMA)_2]$ (Zn_4) SBU, in which six carboxylate groups and one DMA bridge two 4-coordinate, one 5-coordinate and one 6-coordinate Zn center, one DMA occupied remaining coordination sites. The μ_4-O–Zn distance is from 1.846 (6) Å to 1.974(10) Å.

Though three btc ligands have two different coordination modes (Fig. 2a), all of them act as 3-connected nodes to link three

Table 1
The crystal data of compound **1**.

Compound reference	*a*
Chemical formula	$C_{31}H_{18}O_{19}Zn_5 \cdot 4.75(C_4H_9NO)$
Formula Mass	1435.20
Crystal system	Orthorhombic
a (Å)	44.665(7)
b (Å)	19.739(3)
c (Å)	29.107(5)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
Unit cell volume (Å^3)	25661(7)
Temperature (K)	293(2)
Space group	*Ibam*
No. of formula units per unit cell (*Z*)	16
No. of reflections measured	109,094
No. of independent reflections	14,898
R_{int}	0.0973
Final R_1 values ($I > 2\sigma(I)$)	0.0683
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1833
Final R_1 values (all data)	0.0913
Final $\omega R(F^2)$ values (all data)	0.1945
Goodness of fit on F^2	0.953

$R_1 = (|F_o| - |F_c|)/|F_o|$ $\omega R_2 = [\, w(F_o^2 - F_c^2)/w(F_o^2)^2]^{1/2}$.

Table 2
Selected bond lengths and angles for **1**.

Zn(1)–O(20)	1.966(4)	Zn(4)–O(19)	1.9721(19)
Zn(1)–O(10)#1	2.048(3)	Zn(4)–O(12)	1.983(4)
Zn(1)–O(10)	2.048(3)	Zn(5)–O(11)#1	2.069(3)
Zn(1)–O(1)#1	2.056(3)	Zn(5)–O(11)	2.069(3)
Zn(1)–O(1)	2.056(3)	Zn(5)–O(25)	2.104(5)
Zn(2)–O(20)	1.858(3)	Zn(5)–O(6)#1	2.089(3)
Zn(2)–O(2A)	1.923(13)	Zn(5)–O(6)	2.089(3)
Zn(2)–O(23)	2.006(8)	Zn(5)–O(19)	2.139(6)
Zn(2)–O(16A)	1.986(7)	Zn(6)–O(22)	1.975(6)
Zn(2)–O(2)	2.235(5)	Zn(6)–O(8)#2	2.016(3)
Zn(2)–O(16)	2.332(6)	Zn(6)–O(8)	2.016(3)
Zn(3)–O(24)	1.857(11)	Zn(6)–O(7)#2	2.071(3)
Zn(3)–O(20)	1.894(4)	Zn(6)–O(7)	2.071(3)
Zn(3)–O(15)	2.115(4)	Zn(7)–O(21)	1.960(3)
Zn(3)–O(15)#1	2.115(4)	Zn(7)–O(18)	2.021(3)
Zn(3)–O(9)#1	2.391(7)	Zn(7)–O(4)	2.020(3)
Zn(3)–O(9)	2.391(7)	Zn(7)–O(3)	2.072(3)
Zn(4)–O(14)	1.929(3)	Zn(7)–O(17)	2.079(3)
Zn(4)–O(5)	1.956(3)		
O(20)–Zn(1)–O(10)#1	106.65(14)	O(14)–Zn(4)–O(19)	108.8(2)
O(20)–Zn(1)–O(10)	106.65(14)	O(5)–Zn(4)–O(19)	109.8(2)
O(10)#1–Zn(1)–O(10)	83.3(2)	O(14)–Zn(4)–O(12)	104.41(18)
O(20)–Zn(1)–O(1)#1	103.60(13)	O(5)–Zn(4)–O(12)	112.0(2)
O(10)#1–Zn(1)–O(1)#1	149.74(15)	O(19)–Zn(4)–O(12)	100.0(2)
O(10)–Zn(1)–O(1)#1	88.85(18)	O(11)#1–Zn(5)–O(11)	88.0(2)
O(20)–Zn(1)–O(1)	103.60(13)	O(11)#1–Zn(5)–O(25)	88.81(15)
O(10)#1–Zn(1)–O(1)	88.85(18)	O(11)–Zn(5)–O(25)	88.81(15)
O(10)–Zn(1)–O(1)	149.74(15)	O(11)#1–Zn(5)–O(6)#1	92.40(18)
O(1)#1–Zn(1)–O(1)	83.3(3)	O(11)–Zn(5)–O(6)#1	176.11(15)
O(20)–Zn(2)–O(2A)	116.6(4)	O(25)–Zn(5)–O(6)#1	87.32(15)
O(20)–Zn(2)–O(23)	109.66(18)	O(11)#1–Zn(5)–O(6)	176.11(15)
O(2A)–Zn(2)–O(23)	96.4(4)	O(11)–Zn(5)–O(6)	92.40(18)
O(20)–Zn(2)–O(16A)	114.7(2)	O(25)–Zn(5)–O(6)	87.32(15)
O(2A)–Zn(2)–O(16A)	112.3(4)	O(6)#1–Zn(5)–O(6)	86.9(3)
O(23)–Zn(2)–O(16A)	104.7(3)	O(11)#1–Zn(5)–O(19)	89.78(16)
O(20)–Zn(2)–O(2)	106.79(17)	O(11)–Zn(5)–O(19)	89.78(16)
O(2A)–Zn(2)–O(2)	20.7(3)	O(25)–Zn(5)–O(19)	178.0(2)
O(23)–Zn(2)–O(2)	117.1(3)	O(6)#1–Zn(5)–O(19)	94.10(16)
O(16A)–Zn(2)–O(2)	104.0(3)	O(6)–Zn(5)–O(19)	94.10(16)
O(20)–Zn(2)–O(16)	109.28(19)	O(22)–Zn(6)–O(8)#2	99.41(11)
O(2A)–Zn(2)–O(16)	100.4(4)	O(22)–Zn(6)–O(8)	99.41(11)
O(23)–Zn(2)–O(16)	124.0(3)	O(8)#2–Zn(6)–O(8)	161.2(2)
O(16A)–Zn(2)–O(16)	20.6(2)	O(22)–Zn(6)–O(7)#2	101.05(11)
O(2)–Zn(2)–O(16)	87.5(2)	O(8)#2–Zn(6)–O(7)#2	87.94(18)
O(24)–Zn(3)–O(20)	148.3(4)	O(8)–Zn(6)–O(7)#2	88.47(18)
O(24)–Zn(3)–O(15)	102.3(3)	O(22)–Zn(6)–O(7)	101.05(11)
O(20)–Zn(3)–O(15)	100.67(14)	O(8)#2–Zn(6)–O(7)	88.47(18)
O(24)–Zn(3)–O(15)#1	102.3(3)	O(8)–Zn(6)–O(7)	87.94(18)
O(20)–Zn(3)–O(15)#1	100.67(14)	O(7)#2–Zn(6)–O(7)	157.9(2)
O(15)–Zn(3)–O(15)#1	86.7(3)	O(21)–Zn(7)–O(18)	97.89(14)
O(24)–Zn(3)–O(9)#1	74.4(3)	O(21)–Zn(7)–O(4)	103.47(14)
O(20)–Zn(3)–O(9)#1	87.2(2)	O(18)–Zn(7)–O(4)	158.50(14)
O(15)–Zn(3)–O(9)#1	167.8(2)	O(21)–Zn(7)–O(3)	94.48(16)
O(15)#1–Zn(3)–O(9)#1	82.6(2)	O(18)–Zn(7)–O(3)	87.50(16)
O(24)–Zn(3)–O(9)	74.4(3)	O(4)–Zn(7)–O(3)	88.46(17)
O(20)–Zn(3)–O(9)	87.2(2)	O(21)–Zn(7)–O(17)	105.76(15)
O(15)–Zn(3)–O(9)	82.6(2)	O(18)–Zn(7)–O(17)	88.11(16)
O(15)#1–Zn(3)–O(9)	167.8(2)	O(4)–Zn(7)–O(17)	88.40(15)
O(9)#1–Zn(3)–O(9)	107.3(4)	O(3)–Zn(7)–O(17)	159.69(13)
O(14)–Zn(4)–O(5)	119.90(16)		

Symmetry transformations used to generate equivalent atoms: #1 *x*, *y*, –*z*+1; #2 *x*+0, –*y*+0, –*z*+3/2.