ESI

Supporting Information

Linearly Bridging CO₂ in a Metal-organic Framework

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Materials and Methods

All reagents were obtained from commercial sources and used as received. H_6L was synthesized by a modified procedure previously documented.^{1,2}

Powder X-ray power diffraction (XRD) patterns were performed on a D8 Focus (Bruker) diffractometer with Cu K α radiation Field-emission ($\lambda = 0.15405$ nm, continuous, 40 kV, 40 mA, increment = 0.02°).

Thermogravimetric-mass spectra (**TG-MS**) were performed with a Thermal Analysis-Quadrupole Mass Spectrometer (STA449C-QMS 403 C) up to 800 C, and the heating rate was 10 °C min⁻¹ under a N_2 flow.

Gas chromatographic (GC) analysis was conducted on a GC7900 Gas Chromatograph (Shanghai Techcomp Instrument Ltd, China), equipped with a thermal conductivity detector (TCD) and a TDX-01 column (2 m, 3 mm, 2mm). Experimental conditions were as follows: Ar₂ (99.99%) as Carrier gas; column temperature, 50 °C; injector temperature, 100 °C; TCD temperature, 100 °C; carbon dioxide (99.5%) and air as quantitive analysis standard.

MS spectra for air, pure DMF, DMF with $Zn(NO_3)_2 \cdot 2H_2O$, and DMF with Zn^{2+} and H_6L was performed on a Thermo Fisher Scientific Mass spectrometer under a Ar flow.

Synthesis of the [Zn₃(L)(H₂O)]₂(CO₂) (1)

Zn(NO₃)₂•6H₂O (0.12 mmol, 35.7 mg) and H₆L (0.04 mmol, 39.0 mg) in mixed dimethyl formamide (DMF, 6 mL)/ distilled water (H₂O, 1 mL) solvent were placed in a Teflon-lined stainless steel vessel (20 mL) and heated to 115 °C in 300 min; maintained at this temperature for three days; and then cooled to room-temperature at a rate of 0.2 °C/min. The resulting colorless crystals were obtained, after washed by distilled water, yield 46.7 mg (68% based on Zn²⁺). Its purity was confirmed by X-ray power diffraction (XRD) (Fig. S8). Anal. Calcd (%) for 1 C₁₃₆H₁₆₇N₁₁O₅₄Zn₆ (Mr = 3212.03): C, 50.85; H, 5.24; N, 4.80. Found: C, 50.40; H, 5.28; N, 5.01.

X-ray crystal structure determination.

Four (1-A, 1-B, 1-C, and 1-D) suitable single crystals for 1 were selected for singlecrystal X-ray diffraction analyses. All single crystals for compound 1 were carefully selected under an optical microscope. 1-A was directly glued to thin glass fibers, whereas, 1-B, 1-C and 1-D were sealed into the glass tube filling with resultant solution. Crystallographic data were collected at 273 K for 1-A and 293 K for 1-B-D on three types of CCD diffractometers (Bruker Apex II CCD diffractometer for 1-A with graphite monochromated Mo-Ka radiation, Saturn70 (Confocal) CCD for 1-B and 1-C with graphite monochromated Mo-Ka radiation, an Agilent Technologies SuperNova Dual Wavelength CCD diffractometer for 1-D with Cu Ka radiation). Data processing was accomplished with the SAINT program. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL-97.³ All non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. The distributions of peaks in the channels of 1 were chemically featureless to refine using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining water molecule was removed by the SQUEEZE routine in PLATON.⁴ The numbers of free solvent DMF and water molecules in **1** were obtained by element analyses and thermogravinetric analysis. In order to eliminate the effect of pseudo-symmetrical centre, the structure of **1-D** was also solved by selecting the non-centrosymmetrical space group (*P*nc2) (**1-E**). A summary of the crystallographic data for complexes **1-A**, **B**, **C**, **D** is listed in Table S1 and S2. Selected bond distances and angles are given in Table S3.

Compound	1-A
CCDC	898424
chemical formula	$C_{136}H_{167}N_{11}O_{54}Zn_6$
structural formula	$[Zn_3(OH)(L)]_2(CO_2) \cdot 2[NH_2(CH_3)_2] \cdot 3H_2O \cdot 9DMF$
fw	3212.03
Temperature (K)	273(2)
<i>a</i> /Å	19.792(2)
b/Å	17.759(1)
c /Å	28.543(2)
α /°	90
eta /°	90
γ /°	90
$V/\text{\AA}^3$	10033.0(14)
Ζ	2
space group	Pmna
$2\theta \max (\deg)$	52.18
μ (Mo-K α) mm ⁻¹	0.773
D, g/cm ³	1.063
F(000)	3344
Reflections collected/unique	$54530/10246 [R_{int} = 0.0784]$
$R_1^{a}, w R_2^{b} [I > 2\sigma(I)]$	$R_1 = 0.0536, wR_2 = 0.1271$
R_1^a , wR_2^b (all data)	$R_1 = 0.1025, wR_2 = 0.1358$
GOF	0.962

Table S1. Summary of Crystal Data and Structure Results for 1-A.

 ${}^{a}\overline{R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|, {}^{b}wR_{2}} = \{\sum w[(F_{o})^{2} - (F_{c})^{2}]^{2} / \sum w[(F_{o})^{2}]^{2}\}^{1/2}}$

Table S2. Summary of Crystal Data and Structure Results for 1-B, 1-C and 1-D.

Compound	1-B	1-C	1-D	1-E
measurement	Saturn70 (Confocal)	Saturn70	SuperNova (Cu) X-	
device	CCD	(Confocal) CCD	ray Source	
Exp time	20s	30s	4s (low angle)/25s (high angle)	
mean (I/sigma)	8.0	9.58	11.26	
chemical formula	$C_{105}H_{82}O_{42}Zn_6$			
structural formula	[Zn ₃ (OH)(L)] ₂ (CO ₂)			
fw	2407.93			
Temperature (K)	293(2)			
λ (Mo/Cu K <i>α</i>), Å	0.71073 (Mo)		1.54178 (Cu)	
<i>a</i> /Å	19.824(5)	19.8637(9)	19.8520(2)	17.76660(10)
b /Å	17.832(4)	17.7960(7)	17.76660(10)	28.6399(3)
c /Å	28.585(6)	28.6162(12)	28.6399(3)	19.8520(2)
α /°	90	90	90	90
β /°	90	90	90	90
γ /°	90	90	90	90
$V/Å^3$	10105(4)	10115.7(7)	10101.37(16)	10101.37(16)
Ζ	2			
space group	Pmna			Pnc2
$2\theta \max (\deg)$	54.96	54.98	148.68	148.68
μ (Mo-K α) mm ⁻¹	0.748	0.747	1.188	1.188
D, g/cm^3	0.791	0.791	0.792	0.792
F(000)	2456	2456	2456	2456
Reflections collected	79031	78707	72787	72807
$R_1^a \left[I > 2\sigma(I) \right]$	0.0617	0.0606	0.0584	0.1074
$wR_2^b [I > 2\sigma(I)]$	0.1710	0.1881	0.1865	0.3337
GOF	0.979	0.994	1.072	1.492
Bond lengths [Å] for C=O	1.104(3)	1.095(3)	1.106(3)	1.097(5)
Bond angles (°) for O=C=O	180(4)	180(4)	180(4)	172(3)

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|, {}^{b}wR_{2} = \{\sum w[(F_{o})^{2} - (F_{c})^{2}]^{2} / \sum w[(F_{o})^{2}]^{2}\}^{1/2}$

Zn(1)-O(1)	2.008(4)	Zn(1)-O(12)	2.139(3)
Zn(1)-O(8)#1	2.080(2)	Zn(1)-O(8)#2	2.080(2)
Zn(1)-O(6)	2.119(3)	Zn(1)-O(6)#3	2.119(3)
Zn(2)-O(7)	1.943(2)	Zn(2)-O(9)#2	1.964(2)
Zn(2)-O(11)#4	1.954(5)	Zn(2)-O(12)	1.9859(11)
O(12)-Zn(2)#3	1.9859(11)	O(8)-Zn(1)#5	2.080(2)
O(9)-Zn(2)#5	1.964(2)	O(11)-Zn(2)#6	1.954(5)
C(1)-O(1)#7	1.107(4)		
O(1)-Zn(1)-O(8)#1	88.92(11)	O(1)-Zn(1)-O(8)#2	88.92(11)
O(1)-Zn(1)-O(6)	88.19(12)	O(1)-Zn(1)-O(6)#3	88.19(11)
O(8)#1-Zn(1)-O(8)#2	96.44(14)	O(8)#1-Zn(1)-O(6)	172.92(11)
O(8)#2-Zn(1)-O(6)	89.97(11)	O(8)#1-Zn(1)-O(6)#3	89.97(11)
O(8)#2-Zn(1)-O(6)#3	172.92(11)	O(6)-Zn(1)-O(6)#3	83.48(16)
O(1)-Zn(1)-O(12)	177.54(14)	O(8)#1-Zn(1)-O(12)	89.45(8)
O(8)#2-Zn(1)-O(12)	89.45(8)	O(6)-Zn(1)-O(12)	93.64(9)
O(6)#3-Zn(1)-O(12)	93.64(9)	O(7)-Zn(2)-O(11)#4	104.2(2)
O(7)-Zn(2)-O(9)#2	112.28(12)	O(7)-Zn(2)-O(12)	108.46(12)
O(9)#2-Zn(2)-O(12)	99.77(11)	O(11)#4-Zn(2)-O(12)	107.8(2)
O(11)#4-Zn(2)-O(9)#2	123.6(3)	Zn(2)-O(12)-Zn(2)#3	135.63(15)
Zn(2)-O(12)-Zn(1)	103.58(8)	Zn(2)#3-O(12)-Zn(1)	103.58(8)
C(1)-O(1)-Zn(1)	162.1(3)		

Table S3. Selected bond lengths (Å) and angles (°) for 1-A.

Symmetry transformations used to generate equivalent atoms: #1 x-1/2, -y+1, z-1/2; #2 -x+1/2, y+1, z-1/2; #3 -x, y, z; #4 x, y-1, z; #5 -x+1/2, -y+1, z+1/2; #6 x, y+1, z; #7 -x, -y+1, -z+1.



Fig. S1 ORTEP representation of the asymmetric unit of **1**. Thermal ellipsoids are drawn at the 50% probability level (Zn, green; oxygen, red; carbon, gray). The hydrogen atoms and free solvent molecules are omitted for clarity. Symmetry codes: A x-1/2, -y+1, z-1/2; B -x+1/2, -y+1, z-1/2; C -x, y, z; D x, y-1, z; E -x+1/2, -y+1, z+1/2; F x, y+1, z; G -x, -y+1, -z+1.





Fig. S2 The coordination mode of Zn1 and Zn2 (a), carboxylate ligand (b) and Zn^{II}₃ SBU (c). In (a) and (b), Zn, O and C atoms are shown as green, red, and grey balls. In (c), all C and O atoms are drawn in bricks.



(a)



(b)

(c)



Fig. S3 (a) View the 2-fold interpenetrating 3D framework along *a*-axis, in which all atoms are drawn as sticks. (b and c) The 3D single network viewed along *a*- (b) and *b*-axis (c) of compound 1 omitting CO₂ bridgers. C, O atoms are drawn in stick. ZnO₄ tetrahedra are shade in green. (d, e and f) The simplified single network along *a*-, *b*-, *c*-axis.



(a)

(b)



Fig. S4 View the 3D framework of 1 along [100] (a) and [010] (b) direction. (c) Projection of compound 1 in the <111> direction. Hydrogen atoms and solvent molecules are omitted for clarity. (d) Schematic representation of the 4,8-*c* net.



Fig. S5 The IR spectra of compound 1.

In order the eliminate the effect of CO_2 molecules in air, fourier-transform infrared (FT-IR) spectra for compound **1** was measured under **vacuum condition**, and recorded in the 4000-500 cm⁻¹ region on an Bruker FT-IR infrared spectrophotometer VERTEX70 (66V/S) with the KBr pellet technique. Thus the infrared absorption peak around 2336 cm⁻¹ that belong to the free CO₂ molecules in air is not amolst observed.



Fig. S6 The samples of ZnMOF (1) immersed in water with concentrated H_2SO_4 (40 μ L).



Fig. S7 MS analysis for samples of air (black), pure DMF, DMF with $Zn(NO_3)_2 \cdot 2H_2O$, and DMF with Zn^{2+} and H_6L for after heating at 80 °C for 24 h.



Fig. S8 The TGA diagram of compound 1.

The TGA analysis of compound 1 was carried out, shown in Fig. S8. The TGA diagram shows two main weight losses in the curves. The first step (53-260 °C) corresponds to the release of free solvent molecules and protonated dimethyl amines as well as CO_2 ligand. The observed weight loss of 24.8% is very close to the calculated values (25.0%). The second weight loss of 55.3% between 350 °C and 508 °C is attributed to the loss of ligand composite. The total observed weight loss is 83.2% at 508 °C. The final residuals for all compounds were not characterized due to their corrosive reactions with the TGA buckets made of Al_2O_3 , however it is expected that they are mainly zinc(II) oxide (84.7%).



Fig. S9 Simulated and measured XRD powder pattern for 1 and 1 after heating treatment at 120 °C.

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