

Hydrothermal Synthesis, Structure and Thermal Property of a New 3D Zinc Framework Containing 1,3,5-triazine-2,4,6-tricarboxylate

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Recently, synthetic engineering of the coordination polymers or metal-organic frameworks (MOFs) has been highlighted with their potential applications in the fields of functional materials, such as ion-exchange, sorption, catalysis and nonlinear optics.¹ It can be anticipative that the organic ligands can provide the assistance in the formation of the desired MOFs, and the inorganic components are a resource to impart a particular physical property.² An investigation of the literatures revealed that the well-characterized compounds of triazine are very limited.³ However, the compounds of triazine derivatives⁴ are familiar with the subjects on photochemistry, analytical chemistry, biochemistry and magnetism.⁵ For example, 2,4,6-tris(pyridyl)-1,3,5-triazine has been attracted much interest for its applications.⁶ The triazine derivative, 1,3,5-triazine-2,4,6-tricarboxylate (TTA³⁻), as a multi-functional chelating and/or bridging ligand, contains many merits that the triazine ring itself is an excellent bridge with its 1-, 3- and 5-positioned nitrogen atoms and three carboxylic groups as short bridges to offer the possibilities for fabricating functional MOFs. The survey on Cambridge Structural Data gave only one example of 1-D chain K{Fe(TTA)(H₂O)₂}·2H₂O from diffusion method.⁷ The rare situation is in accord with our systematic experiments that most experiments only gave powder products in related with the difficulties in crystallizations of TTA³⁻ compounds and dissolution in water and other common solvents. Hydrothermal method may effectively cover the solubility problem. The hydrothermal reaction of ZnCl₂ with TTA³⁻ in water at 120 °C yielded a new 3D MOF, [Zn₄(HTTA)₂(μ₄-O)Cl₂] (1), which was presented with the synthesis, crystal structure and thermal property.

Experimental

Materials and Physical Measurements. All chemicals were obtained from commercial sources and used without further purification. The IR spectrum was recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellet in the range 4000-400 cm⁻¹ and elemental analysis of C, H and N was carried out on a Vario EL III elemental analyzer. Thermogravimetric (TG) analysis was performed at a heating

rate of 10 °C·min⁻¹ in nitrogen atmosphere on a TA4000/SDT 2960 thermoanalyzer.

Synthesis of [Zn₄(HTTA)₂(μ₄-O)Cl₂] (1). A suspension of 0.1 mmol triethyl 1,3,5-triazine-2,4,6-tricarboxylate was treated with 0.3 mmol NaOH in 10 mL water stirring at 0 °C for 1 h, then mixed with ZnCl₂·6H₂O (0.1 mmol, 29.7 mg) in a 25 mL Teflon-lined stainless-steel autoclave. The mixture was heated at 120 °C for 5 days in a furnace and then naturally cooled to obtain colorless crystals of 1. Yield based on Zn: 24.7 mg, 5.8%. Elemental analysis found (calcd): C, 18.63 (18.74); H, 0.31 (0.24); N, 10.82 (10.91). IR data (in KBr, cm⁻¹): 3428 (br, s), 2977 (w), 2892 (w), 1638 (m), 1461 (w), 1388 (w), 1090 (w), 1047 (m), 870 (w), 761 (w), 718 (w), 554 (w), 469 (w).

Structural Determination and Refinement. Data were collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 298(2) K. The intensity data were collected by the ω scan technique. The intensity data were reduced using CrystalClear program.⁸ The structure was solved by direct method using SHELXTLTM package of crystallographic software⁹ and refined by full-matrix least-squares technique on F². All non-hydrogen atoms were refined anisotropically, and the hydrogen atom bearing on N12 was located in the difference Fourier maps and was not refined. A summary of the structural determination and refinement for the title compound is listed in Table 1. Selected bond distances and angles are shown in Table 2.

Results and Discussion

Structural Description of 1. The structure of [Zn₄(HTTA)₂(μ₄-O)Cl₂] (1) features a 3D framework in which HTTA²⁻ exhibits a μ₆-tri-bidentate connection mode. As shown in Figure 1, Zn1 is located in a trigonal bipyramid constructed by three carboxylic oxygen atoms, O14A, O16 and O1 in the base plane, and O11B and O13C in the axial position. Zn2 center is coordinated by Cl1, O1, O12B and O15D to form a distorted tetrahedral geometry. The Zn-Cl distance of 2.363(2) Å is comparative to those reported in the normal range 2.2-2.4 Å. The bond-valence sum (BVS) of O1 is

Table 1. Crystallographic and experimental data for **1**.

Empirical formula	C ₂₄ H ₄ Cl ₄ N ₁₂ O ₂₆ Zn ₈
Color and Habit	colorless block
Crystal Size (mm)	0.13 × 0.13 × 0.09
Crystal system	Orthorhombic
Space group	C222 ₁
<i>a</i> (Å)	12.971(2)
<i>b</i> (Å)	16.715(3)
<i>c</i> (Å)	15.828(3)
<i>V</i> (Å ³)	3431.7(11)
<i>Z</i>	2
Fw	1541.15
D _{calc} (Mgm ⁻³)	1.491
μ (mm ⁻¹)	2.969
<i>F</i> (000)	1496
θ (°)	2.44 to 28.32
Reflections measured	11998
Independent refs	4209 (<i>R</i> _{int} = 0.1814)
Observed Refs [<i>I</i> > 2σ(<i>I</i>)]	1917
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0787, 0.1485
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1944, 0.1788
<i>S</i>	1.010
(Δ/σ) _{max/min}	0.004, 0.000
Δσ _{max/min} (eÅ ⁻³)	1.115, 0.884

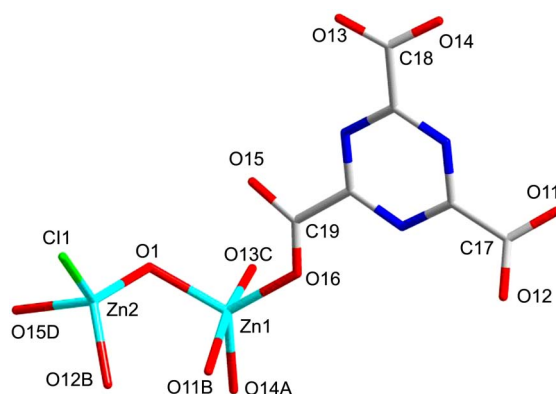
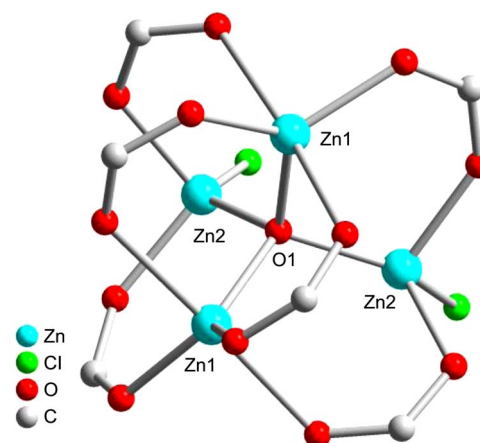
$$R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|). \quad wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w|F_o^2|)]^{1/2}$$

Table 2. Selected bond distance (Å) and bond angle (°) for **1**

Zn1-O16	1.959(4)	Zn1-Zn2D	3.149(1)
Zn1-O1	1.957(4)	Zn2-O12B	1.931(5)
Zn1-O14A	1.985(5)	Zn2-O1	1.945(4)
Zn1-O11B	2.234(5)	Zn2-O15D	1.968(5)
Zn1-O13C	2.253(5)	Zn2-Cl1	2.363(2)
Zn1-Zn1D	3.013(1)		
O16-Zn1-O1	116.65(17)	O1-Zn1-Zn2D	36.08(7)
O16-Zn1-O14A	122.72(18)	O14A-Zn1-Zn2D	149.96(14)
O1-Zn1-O14A	120.64(17)	O11B-Zn1-Zn2D	111.76(13)
O16-Zn1-O11B	91.10(17)	O13C-Zn1-Zn2D	79.23(11)
O1-Zn1-O11B	95.43(14)	Zn1D-Zn1-Zn2D	63.71(2)
O14A-Zn1-O11B	84.04(19)	O12B-Zn2-O1	115.5(2)
O16-Zn1-O13C	93.39(16)	O12B-Zn2-O15D	100.5(2)
O1-Zn1-O13C	91.97(14)	O1-Zn2-O15D	103.63(15)
O14A-Zn1-O13C	84.67(18)	O12B-Zn2-Cl1	101.64(17)
O11B-Zn1-O13C	168.55(16)	O1-Zn2-Cl1	127.92(16)
O16-Zn1-Zn1D	144.15(13)	O15D-Zn2-Cl1	104.00(17)
O1-Zn1-Zn1D	39.67(14)	O12B-Zn2-Zn1D	109.52(16)
O14A-Zn1-Zn1D	86.73(14)	O1-Zn2-Zn1D	36.34(9)
O11B-Zn1-Zn1D	113.82(11)	O15D-Zn2-Zn1D	69.46(15)
O13C-Zn1-Zn1D	67.36(10)	Cl1-Zn2-Zn1D	148.80(7)
O16-Zn1-Zn2D	83.69(13)		

Symmetry code: *A* = *x* + 1/2, *y* - 1/2, *z*; *B* = -*x* + 3/2, *y* - 1/2, -*z* + 1/2; *C* = *x* + 1/2, -*y* + 1/2, -*z*; *D* = *x*, -*y*, -*z*.

2.052 calculated by valence-sum calculation, close to -2, showing O1 should be O²⁻ anion. The calculation result also accords with the short Zn-O distances (Zn1-O1 = 1.957(4) Å; Zn2-O1 = 1.945(3) Å). To keep charge balance, the TTA³⁻

**Figure 1.** The coordination spheres of Zn centers in **1** (Symmetry codes: *A* = *x* + 1/2, *y* - 1/2, *z*; *B* = -*x* + 3/2, *y* - 1/2, -*z* + 1/2; *C* = *x* + 1/2, -*y* + 1/2, -*z*; *D* = *x*, -*y*, -*z*).**Figure 2.** The structural motif of the [Zn₄(μ₄-O)(COO)₆Cl₂]²⁻ subunit.

ligand should be protonated to HTTA²⁻. The position of H atom carried on N12 is determined by the calculation with difference Fourier maps. O1 adopts μ₄-mode to bridge two Zn1 centers and two Zn2 centers with Zn...Zn interactions (Zn1...Zn1D = 3.013(1) Å; Zn1...Zn2D = 3.149(1) Å). The Zn1...Zn1 edge is further stabilized by two COO⁻ bridges, and two Zn1...Zn2 edges are respectively connected by two groups of COO⁻ bridges; while no COO⁻ bridge locates between Zn2...Zn2 edge, thus to form a [Zn₄(μ₄-O)(COO)₆Cl₂]²⁻ subunit (Figure 2). With O12 and O15, Four HTTA²⁻ ligands alternately bond two Zn2 nodes and two [Zn(2)₂(μ₂-O)] subunits at diagonal positions to form a 36-membered [Zn₆(HTTA)₄(μ₂-O)₂] ring. The expansion of such rings produces a wave-like layer along the *bc* plane (Figure 3). The 2D layer is further connected to the neighboring ones through [Zn(1)O₅] trigonal pyramidal bridges to form a 3D framework structure (Figure 4) containing cavities with the size of 7.178 × 8.446 Å². Taking the van der Waals radii of O and N (1.52 and 1.55 Å, respectively) into account, the effective aperture of the cavity is 4.138 × 5.376 Å². The total solvent-accessible volume of the channels in the unit is 1547.9 Å³ accounting for 45.1% calculated by PLATON.¹⁰ In the crystal structure of triethyl-1,3,5-triazine-2,4,6-tricarboxylate, all dihedral angles between three carboxylic

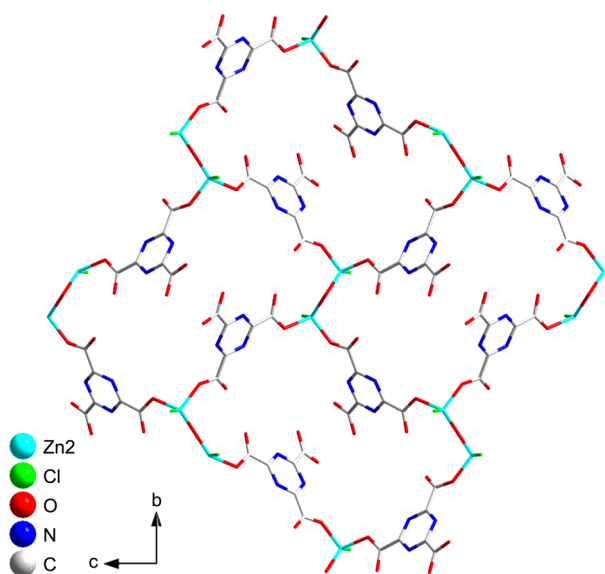


Figure 3. The 2D layer along the *bc* plane.

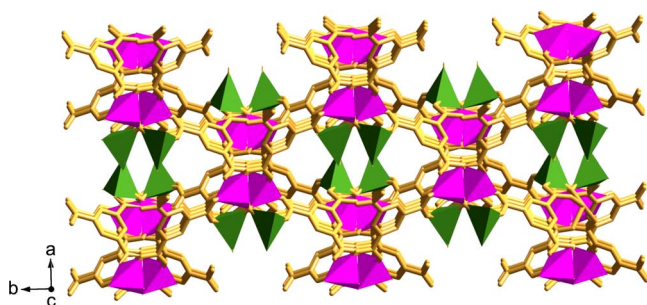


Figure 4. The 3D framework constructed by the linkage of $[Zn(1)O_5]$ (purple polyhedron) with the 2D layers with (Zn2 polyhedron: green polyhedron).

groups and triazine ring are 0° ,¹¹ indicating carboxylic groups and triazine ring in the same plane without steric hindrance. While in the title compound, the dihedral angles are 22.36° , 22.35° , and 5.90° , which are larger than those in $K\{Fe(TTA)(H_2O)_2\} \cdot 2H_2O$ (5.43° , 5.43° , and 0.95°).⁷ The larger dihedral angles in **1** are in accord with the degree of spatial crowdedness, indicating COO^- groups revolve to decreasing the steric hindrance.

Unexpected, in the framework structure of **1**, none of nitrogen atoms in the triazine ring coordinates with metal centers, different from those in the $K\{Fe(TTA)(H_2O)_2\} \cdot 2H_2O$ with nitrogen atom and COO^- chelating one Fe^{2+} center.⁷ This situation should be related with low $n_M : n_{TTA}$, the coordination capabilities of nitrogen atom and COO^- , and the nature of protonated $HTTA^{2-}$. In the low $n_M : n_{TTA}$ condition, the metal center prefers to coordinate with the stronger COO^- groups. In addition, under the basic condition, the triazine ring is apt to be relatively positive and to be protonated to some degree, thus to decrease the electronic density of the triazine ring. Consequently, the coordination capabilities of the nitrogen atoms will be restrained, causing the coordination behavior of TTA similar to 1,3,5-benzene-

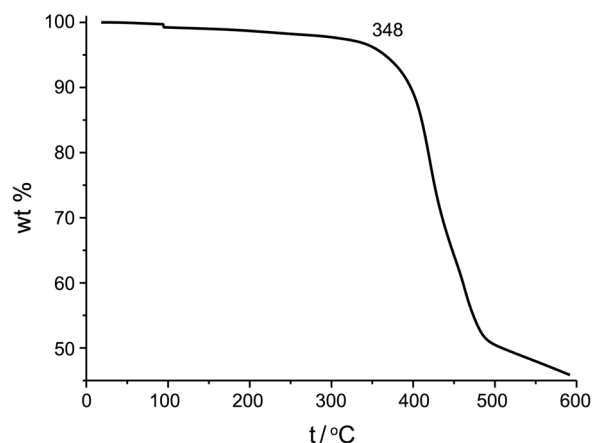


Figure 5. The TGA analysis of **1**.

tricarboxylic acid (H_3BTC).

Characterization. In the FT-IR spectra, the characteristic absorption peaks of the main functional groups for **1** are in accord with the crystallographic analysis. The asymmetric stretching vibration $\nu_{as}(COO^-)$ was observed at 1638 cm^{-1} and symmetric stretching vibration $\nu_s(COO^-)$ at 1461 cm^{-1} . The differences $\Delta(\nu_{as}(COO^-) - \nu_s(COO^-))$ were 177 , around 200 cm^{-1} , characteristic for coordinated carboxylic groups.¹² Thermogravimetric (TG) analysis of the crystal sample shows that **1** has a high thermal stability (Figure 5). The weight loss in **1** occurs in one step. The framework of **1** decomposed at 348°C , indicating the component parts of the 3D architecture decomposing synchronously.

Supplementary Material. Crystallographic data for the structure reported here has been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-675915). That data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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