Tris(μ-1,4-benzenedicarboxylate)tetrakis(dimethyl sulfoxide)di-μ₃-hydroxo-tetrazinc dihydrate

Ruihu Wang, Maochun Hong,* Yucang Liang and Rong Cao

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou, Fujian 350002, People's Republic of China

Correspondence e-mail: hmc@ms.fjirsm.ac.cn

The title compound, $[Zn_4(OH)_2(C_8H_4O_4)_3(C_2H_6OS)_4]\cdot 2H_2O$, has been prepared from the self-assembly reaction of $Zn(ClO_4)_2$, NaOMe and H_2bdc in dimethyl sulfoxide. The polymer exhibits a zeotype structure with microporous layers of ca 10.22×12.29 Å.

Comment

Microporous materials based on metal-organic polymers are a new field of great current interest in inorganic and new materials chemistry. A current goal in this area is to build a genuinely stable and useful metal–organic zeotype by selecting appropriate building blocks and organic ligands (Schnebeck *et al.*, 1999; Scherer *et al.*, 1999; Gardner *et al.*, 1995; Hennigar *et al.*, 1997). In the last few years, much effort has been devoted to the use of transition metal ions with *exo*-bidentate ligands, such as polypyridyl or pyrazines and 1,4-benzenedicarboxylate, to generate polymeric metal–organic coordination polymers with two- or three-dimensional networks. Very recently, Goodgame and Williams reported a new type of metal–organic large-pore zeotype [Zn(dim-to)₂]ₙ(dmf)ₙ [dimto is 2,4,6-tri(1-imidazolyl)-1,3,5-triazin-2-one and dmf is *N,N*-dimethylformamide], which was generated from zinc bromide and 2,4,6-tri(1-imidazolyl)-1,3,5-triazine (timt) (Goodgame *et al.*, 1999). Li reported a porous polymer [{Zn₄O(bdc)₃}(dmf)₈(C₆H₅Cl)]ₙ, which could absorb and desorb nitrogen gas (Li *et al.*, 1999).
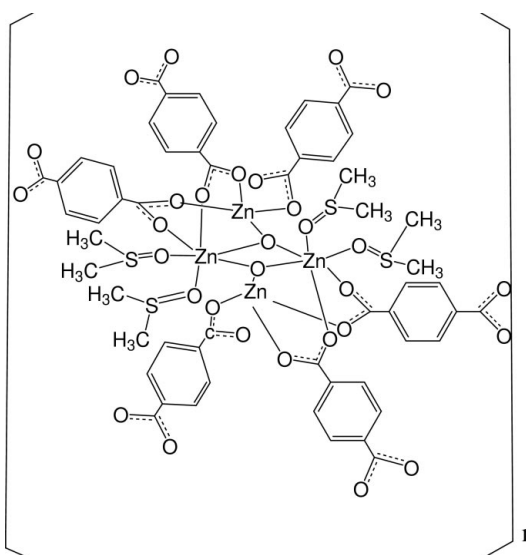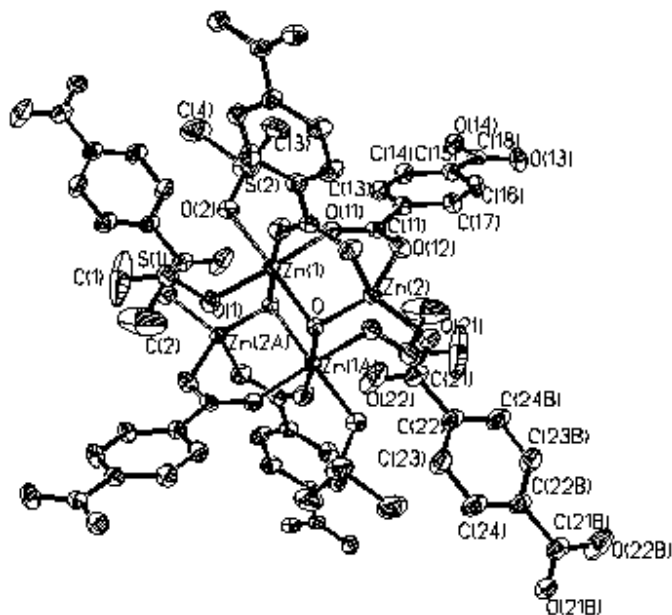

(I)

Figure 1
The structure of (I). Displacement ellipsoids are plotted at the 40% probability level.

Herein we report a coordination polymer with a porous zeotype structure $[\{Zn_4(OH)_2(bdc)_3(dmso)_4\}2H_2O]_n$, (I), which is built from a $[Zn_4(OH)_2]^{6+}$ rhombic cluster unit and 1,4-benzenedicarboxylate. The four Zn atoms are connected by two hydroxide groups forming a tetranuclear $[Zn_4(OH)_2]$ cluster unit (Fig. 1). Such cluster units are linked by bdc ligand through μ and μ_4 bridges to form a two-dimensional microporous layers with the dimensions of 10.22×12.29 Å. Four dimethyl sulfoxide (DMSO) solvent molecules are weakly coordinated, one to each zinc(II) center.

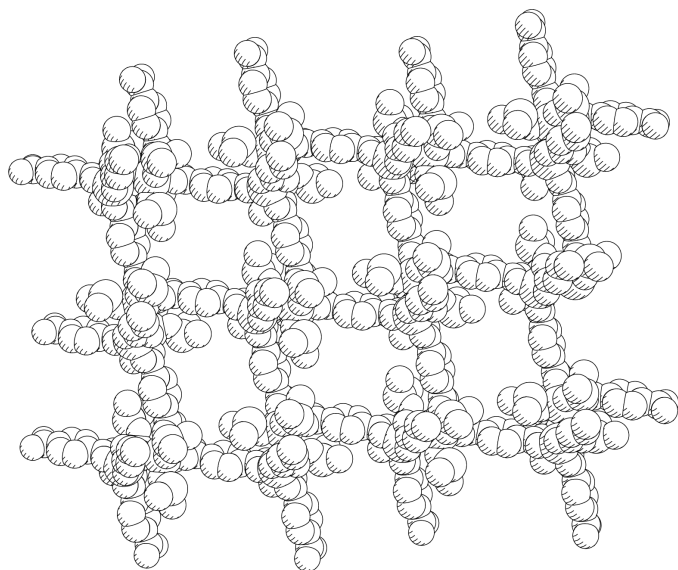Bdc ligands link metal–hydroxide clusters of $Zn_4(OH)_2$ forming a three-dimensional network with microporous structure. Such a three-dimensional coordination polymer with metal cluster and hydroxide bridges is quite rare in metal–organic polymers (Li *et al.*, 1999). As shown in Fig. 1, Zn^{II} atoms adopt two different coordination environments. One is tetracoordinated, ZnO_4, in a distorted tetrahedral fashion, with three O atoms from different bdc ligands and one O atom from hydroxyl. The other is hexacoordinated, ZnO_6, in a distorted octahedral fashion of six O atoms, two from different hydroxyls, two from bdc ligands and the others from two DMSO molecules. Zn—O bonds fall in the range of 2.079 (4)–2.107 (4) Å. There are two different kinds of coordination modes of the bdc ligand; one acts as a μ_4-bridge linking four Zn atoms, the other acts as a μ bridge linking two Zn atoms.

Experimental

A mixture of 1,4-benzene dicarboxylic acid (H_2bdc) (0.166 g, 1 mmol) and NaOMe (0.055 g, 1 mmol) in 25 ml of DMSO was stirred for 30 min. To the reaction mixture, solid $Zn(ClO_4)_2 \cdot 6H_2O$ (0.372 g, 1 mmol) was added. After stirring for 8 h at 323 K, the reaction mixture was filtered to give a colorless solution. Slow diffusion of diethyl ether containing triethylamine (0.025 ml) into the filtrate and natural evaporation of the filtrate in air yielded a large amount of colorless block crystals of the title compound.

Crystal data

$[Zn_4(OH)_2(C_8H_4O_4)_3(C_2H_6OS)_4]\cdot 2H_2O$	$D_x = 1.671$ Mg m^{-3}
$M_r = 1136.38$	Mo $K\alpha$ radiation
Orthorhombic, $Pbca$	Cell parameters from 145 reflections
$a = 14.4988$ (2) Å	$\theta = 2.2$–$25.0°$
$b = 17.1659$ (1) Å	$\mu = 2.36$ mm^{-1}
$c = 18.1536$ (5) Å	$T = 293$ (2) K
$V = 4518.16$ (14) Å^3	Plate, colorless
$Z = 4$	$0.36 \times 0.32 \times 0.26$ mm

Data collection

Smart CCD diffractometer	2600 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.058$
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 25.0°$
$T_{min} = 0.445$, $T_{max} = 0.542$	$h = -10 \rightarrow 17$
12 140 measured reflections	$k = -20 \rightarrow 8$
3986 independent reflections	$l = -21 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0691P)^2 + 17.1727P]$
$R[F^2 > 2\sigma(F^2)] = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.128$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.05$	$\Delta\rho_{max} = 1.88$ e Å^{-3}
3986 reflections	$\Delta\rho_{min} = -0.62$ e Å^{-3}
276 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Figure 2
Packing diagram of (I).

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	2.058 (4)	Zn1—Zn1^i	3.1582 (13)
Zn1—O^i	2.079 (4)	Zn2—O	1.947 (4)
Zn1—O13^{ii}	2.104 (4)	Zn2—O21	1.953 (4)
Zn1—O	2.107 (4)	Zn2—O12	1.969 (4)
Zn1—O2	2.108 (5)	Zn2—O14^{ii}	1.986 (4)
Zn1—O11	2.117 (4)		
O1—Zn1—O^i	92.62 (17)	O1—Zn1—Zn1^i	91.84 (13)
O1—Zn1—O13^{ii}	90.02 (19)	O^i—Zn1—Zn1^i	41.35 (10)
O^i—Zn1—O13^{ii}	173.89 (17)	O13^{ii}—Zn1—Zn1^i	133.08 (13)
O1—Zn1—O	90.18 (17)	O—Zn1—Zn1^i	40.69 (10)
O^i—Zn1—O	82.04 (15)	O2—Zn1—Zn1^i	138.18 (15)
O13^{ii}—Zn1—O	92.45 (16)	O11—Zn1—Zn1^i	89.26 (12)
O1—Zn1—O2	89.72 (19)	O—Zn2—O21	115.80 (18)
O^i—Zn1—O2	96.83 (18)	O—Zn2—O12	109.58 (17)
O13^{ii}—Zn1—O2	88.69 (19)	O21—Zn2—O12	101.6 (2)
O—Zn1—O2	178.86 (18)	O—Zn2—O14^{ii}	111.29 (18)
O1—Zn1—O11	176.95 (19)	O21—Zn2—O14^{ii}	115.8 (2)
O^i—Zn1—O11	86.34 (16)	O12—Zn2—O14^{ii}	100.96 (19)
O13^{ii}—Zn1—O11	91.30 (18)	Zn2—O—Zn1^i	129.5 (2)
O—Zn1—O11	92.51 (16)	Zn2—O—Zn1	103.31 (17)
O2—Zn1—O11	87.56 (17)	Zn1^i—O—Zn1	97.96 (15)

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1OW$\cdots$O22	0.98	1.84	2.731 (16)	150
O1W—H2OW$\cdots$S1^i	0.94	2.85	3.636 (14)	142

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.

The positions of the H atoms were generated geometrically (C—H bond fixed at 0.96 Å) and assigned isotropic displacement parameters, and allowed to ride on their respective parent C atoms before the final cycle of least-squares refinement. Hydroxo and water H atoms were placed in calculated positions (Nardelli, 1995, 1999).

Data collection: *SMART* (Siemens, 1994); cell refinement: *SMART*; data reduction: *SMART*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Gardner, G. B., Venkataraman, D., Moore, J. S. & Lee, S. (1995). *Nature*, **374**, 792–793.
Goodgame, D. M. L., Grachvogel, D. A. & Williams, D. J. (1999). *Angew. Chem. Int. Ed.* **38**, 153–156.
Hennigar, T. J., MacQuarrie, D. C., Losier, P., Rogers, R. D. & Zaworotko, M. J. (1997). *Angew. Chem. Int. Ed. Engl* **36**, 972–973.
Li, H., Eddaoudi, M. O. & Yaghi, O. M. (1999). *Nature*, **402**, 276.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Nardelli, M. (1999). *J. Appl. Cryst.* **32**, 563–571.
Schnebeck, R.-D., Freisinger, E. & Lippert, D. (1999). *Angew. Chem. Int. Ed.* **38**, 168–172.
Scherer, M., Caulder, D. L., Johnson, D. W. & Raymond, K. N. (1999). *Angew. Chem. Int. Ed.* **38**, 1587–1292.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.