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Polymeric diaquabis[μ_4-1,3,5-benzenetricarboxylato(3–)](μ-4,4′-bipyridine)trizinc(II)

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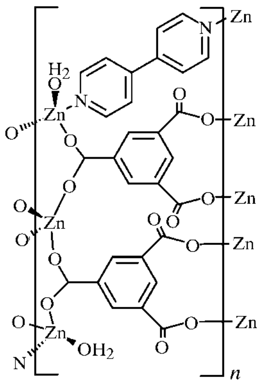
The solvothermal reaction of zinc(II) acetate with 1,3,5-benzenetricarboxylic acid and 4,4′-bipyridine in 1-butanol and acetic acid solution gives the title complex, $[Zn_3(C_9H_3O_6)_2(C_{10}H_8N_2)(H_2O)_2]_n$. There are two different coordination environments for the Zn atom, namely $ZnNO_2(H_2O)$ and ZnO_4; in the latter case, the Zn atom lies on a twofold symmetry axis. Carboxylate-bridged $Zn_3(O_2C)_6$ clusters are connected through 1,3,5-benzenetricarboxylate and 4,4′-bipyridine ligands (which lie about inversion centers), yielding a three-dimensional framework.

Comment

In recent years, studies of the synthesis of metal-organic frameworks from transition metals and organic ligands have been developed extensively because of the crystallographic diversity of these frameworks and their potential applications in catalysis, non-linear optics, magnetism and molecular recognition (Eddaoudi *et al.*, 2001; Zaworotko, 2001; Evans & Lin, 2002). Ligands with pyridyl or carboxylate groups are employed the most often in the design and synthesis of novel metal-organic frameworks; for instance, 1,3,5-benzenetricarboxylic acid (H_3btc) and 4,4′-bipyridine (4,4′-bipy) have been applied widely to the construction of frameworks (Yaghi *et al.*, 1997; Chui *et al.*, 1999; Livage *et al.*, 2001). Recent efforts in this field have focused largely on the combination of pyridyl and carboxylate ligands (Suresh *et al.*, 2001; Karanovic *et al.*, 2002). Huh *et al.* (2002) reported a one-dimensional metal-organic framework with a formula of $Cu(H_2btc)_2$(4,4′-bipy) synthesized by a hydrothermal reaction, which is the only example of mixed ligands of H_3btc and 4,4′-bipy. We report here the solvothermal synthesis and crystal structure of a three-dimensional zinc(II)-based metal-organic framework, namely $[Zn_3(btc)_2(4,4'\text{-bipy})(H_2O)_2]_n$, (I).

The asymmetric unit and labeling scheme are shown in Fig. 1. There are two different coordination environments for the Zn atoms, namely Zn1 and Zn2, both having tetrahedral geometry (Table 1). Atom Zn1 is coordinated to two carboxylate O atoms of two btc ligands, one N atom of a 4,4′-bipy ligand and one coordinated water O atom. In the environment of atom Zn2 (which lies on a twofold axis), four O atoms from four different carboxylate groups occupy the coordinated positions. The three btc carboxylate groups have two different coordination modes, *viz.* as a monodentate ligand with either atom Zn1 or atom Zn2, and as a bidentate ligand with both Zn1 and Zn2. In the structure of (I), two Zn1 centers and one Zn2 center linked by six carboxylate groups from six separate btc ligands produce a trinuclear $Zn_3(O_2C)_6$ secondary building unit, which forms an '*S*' helical configuration. The 4,4′-bipy ligand lies about an inversion center and these ligands link the '*S*' units into one-dimensional zigzag chains, which lie on the (204) Miller planes, as shown in Fig. 2. Each btc ligand links three zigzag chains through its three



(I)

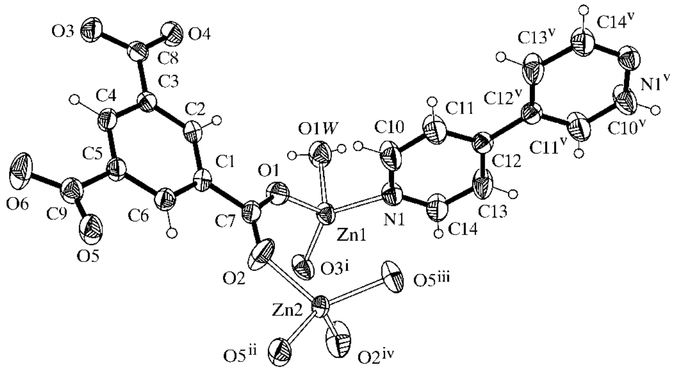


Figure 1
A view of the structure of (I), showing displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x, -y, z-\frac{1}{2}$; (iii) $-x, -y, -z+2$; (iv) $-x, y, -z+\frac{3}{2}$; (v) $-x+1, -y, -z+1$.]

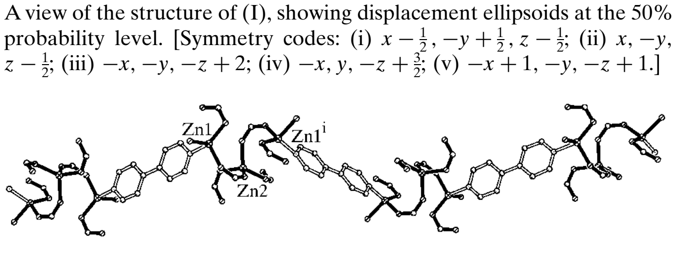


Figure 2
A view of the one-dimensional zigzag chain constructed from 4,4′-bipy ligands (open lines) linking the $Zn_3(O_2C)_6$ secondary building unit (filled lines). [Symmetry code: (i) $-x, y, \frac{3}{2}-z$.]

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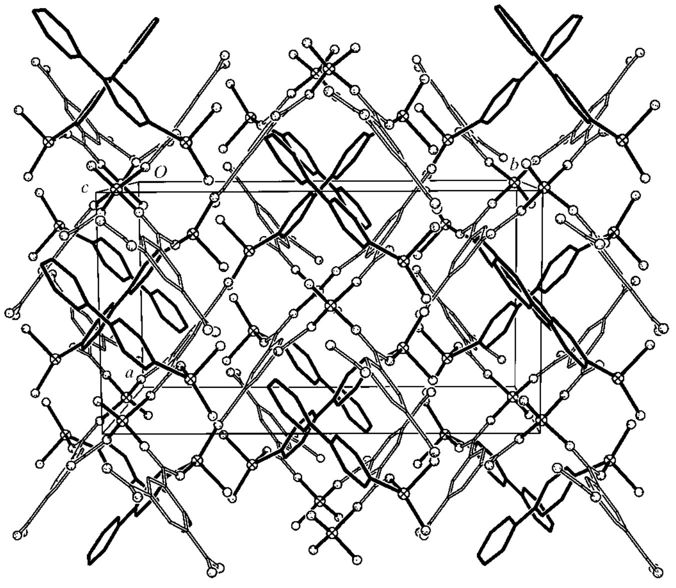

Figure 3
A view of the three-dimensional structure of (I) along the *c* axis (open lines denote btc and filled lines denote 4,4′-bipy).

carboxyl groups, thus yielding a three-dimensional framework (Fig. 3).

Experimental

In a typical synthetic procedure, $Zn(CH_3COO)_2\cdot 2H_2O$ (0.220 g), H_3btc (0.105 g), 4,4′-bipy·$2H_2O$ (0.096 g), 1-butanol (2 ml) and acetic acid (3 ml) were mixed, sealed in a Teflon-lined steel autoclave and allowed to crystallize at 433 K for 120 h. The resulting colorless crystals were washed with deionized water, filtered and dried in air at room temperature.

Crystal data

$[Zn_3(C_9H_3O_6)_2(C_{10}H_8N_2)(H_2O)_2]$
$M_r = 802.55$
Monoclinic, $C2/c$
$a = 10.3816\ (3)$ Å
$b = 18.6749\ (6)$ Å
$c = 14.8264\ (4)$ Å
$\beta = 94.517\ (2)°$
$V = 2865.55\ (15)$ Å^3
$Z = 4$

$D_x = 1.860$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4171 reflections
$\theta = 2.2–30.0°$
$\mu = 2.57$ mm^{-1}
$T = 293\ (2)$ K
Block, colorless
0.29 × 0.22 × 0.14 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.478$, $T_{\max} = 0.695$
11 594 measured reflections

4171 independent reflections
2817 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 30.0°$
$h = -14 \rightarrow 9$
$k = -22 \rightarrow 26$
$l = -20 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.068$
$S = 0.91$
4171 reflections
221 parameters

H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O3^{i}	1.8880 (15)	Zn2—O5^{ii}	1.9195 (14)
Zn1—O1	1.9428 (14)	Zn2—O5^{iii}	1.9195 (14)
Zn1—N1	2.0031 (17)	Zn2—O2	1.9592 (16)
Zn1—O1*W*	2.013 (2)	Zn2—O2^{iv}	1.9592 (16)
O3^{i}—Zn1—O1	112.45 (7)	O5^{iii}—Zn2—O2	94.66 (7)
O3^{i}—Zn1—N1	135.84 (8)	O5^{ii}—Zn2—O2^{iv}	94.66 (7)
O1—Zn1—N1	99.99 (7)	O5^{iii}—Zn2—O2^{iv}	117.04 (8)
O3^{i}—Zn1—O1*W*	106.49 (9)	O2—Zn2—O2^{iv}	109.43 (12)
O1—Zn1—O1*W*	99.12 (8)	C7—O1—Zn1	140.94 (15)
N1—Zn1—O1*W*	96.58 (9)	C7—O2—Zn2	142.43 (16)
O5^{ii}—Zn2—O5^{iii}	124.73 (10)	C8—O3—Zn1^{v}	112.84 (13)
O5^{ii}—Zn2—O2	117.04 (8)	C9—O5—Zn2^{iii}	122.69 (14)

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

H atoms attached to C atoms were refined as riding, with C—H distances of 0.93 Å, and water H atoms were refined freely, giving O—H distances of 0.75 (3) and 0.79 (3) Å.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXP*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1022). Services for accessing these data are described at the back of the journal.

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