

Poly[[μ_4 -3-[(1*H*-1,2,4-triazol-1-yl)-methyl]benzoato}zinc(II)] hemi-hydrate]: a novel two-dimensional framework formed by self-association of zinc(II) sulfate with 3-[(1*H*-1,2,4-triazol-1-yl)methyl]benzoic acid

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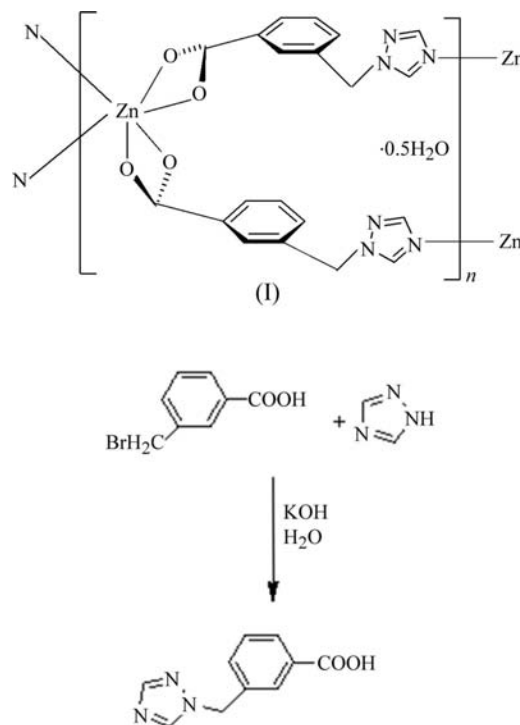
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The title novel two-dimensional coordination polymer, $\{[\text{Zn}_2(\text{C}_{10}\text{H}_8\text{N}_3\text{O}_2)_4 \cdot \text{H}_2\text{O}]_n\}$, features a $\{\text{Zn}_2L_2\}$ bimetallic ring repeat unit $\{L$ is the 3-[(1*H*-1,2,4-triazol-1-yl)methyl]benzoate ligand}. Each Zn^{II} cation of the bimetallic ring is further bonded to two other L ligands, resulting in a novel infinite two-dimensional network structure with two channels of different sizes. The crystallographically unique Zn^{II} atom is thus six-coordinated in a distorted octahedral environment of four carboxylate O atoms and two triazole N atoms. Two of these networks interpenetrate in an orthogonal arrangement to form the full three-dimensional framework, with disordered water molecules located in the channels.

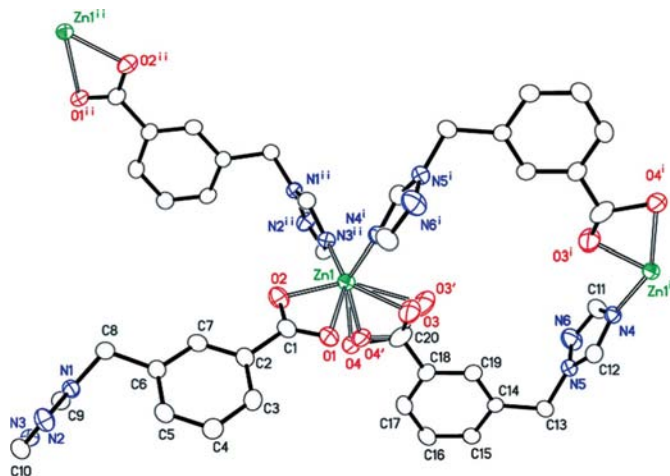
Comment

The construction of supramolecular complexes with novel structures and topologies has received considerable attention over the past decade for their potential applications in many fields, such as gas storage (Chen *et al.*, 2006), catalysis (Pan *et al.*, 2003), anion/guest exchange (Jung *et al.*, 2002), separation (Li *et al.*, 2008), magnetism (Halder *et al.*, 2002) and luminescent materials (Dong *et al.*, 2007). In the reported literature, 1,2,4-triazole, pyrazole, imidazole and their derivatives have been recognized as one of the most useful classes of organic building blocks in the construction of metal-organic frameworks (MOFs) (Zhang *et al.*, 2008), due to their ability to link metal ions together to afford diverse supramolecular complexes. Triazoles with an alkyl, aryl or amino substituent on the 4-position acting as bridging ligands have been particularly well studied (Bradford *et al.*, 2004; Klingele & Brooker,

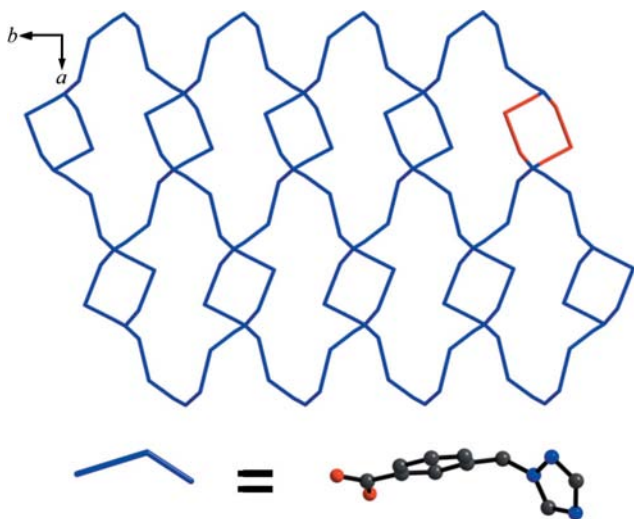
2003; Shakir *et al.*, 2003; Wang *et al.*, 2007; Huang *et al.*, 2006). A number of one-, two- and three-dimensional architectures have been obtained by self-assembly of 1,2,4-triazole, pyrazole, imidazole and their derivatives with transition metal salts. The specific structures obtained demonstrate that the nature of the MOF depends strongly on the properties of the organic ligands used in constructing the supramolecular complexes. Supramolecular complexes based on bent unsymmetric ligands containing 1,2,4-triazole and carboxylic acid groups have been less extensively studied (Ding *et al.*, 2008), so these bent unsymmetric ligands offer great potential for creating novel frameworks. Previously, we have reported the M^{II} ($M = \text{Co}$, Cd and Zn) coordination chemistry of the carboxylate-substituted 1,2,4-triazole 4-[(1*H*-1,2,4-triazol-1-yl)methyl]benzoic acid (Zhao *et al.*, 2007; Qin *et al.*, 2009). In the present work, the new isomeric bent organic ligand 3-[(1*H*-1,2,4-triazol-1-yl)methyl]benzoic acid (HL) was employed in a self-assembly reaction with zinc sulfate under hydrothermal conditions to create the title novel supramolecular complex, $\{[\text{Zn}_2L_4] \cdot \text{H}_2\text{O}\}_n$ (I).



Compound (I) crystallizes with one unique six-coordinated Zn^{II} centre in a distorted octahedral $\{\text{ZnN}_2\text{O}_4\}$ environment (Table 1) involving O atoms (O1, O2, O3 and O4) from the carboxylate groups of two L^- ligands and N atoms [N4ⁱ and N3ⁱⁱ; symmetry codes: (i) $-x, -y, -z$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$] from two other L^- ligands (Fig. 1). The coordinated carboxylate group involving atoms O3 and O4 was found to be disordered over two positions, with refined site-occupancy factors of 0.734 (7) (primed atom labels) and 0.266 (7) (unprimed). Neighbouring Zn^{II} ions are bound together by the carboxylate groups and terminal triazole N-atom donors of two L^- ligands to form a $\{\text{Zn}_2L_2\}$ bimetallic ring in which the diagonal $\text{Zn} \cdots \text{Zn}$ separation is 8.793 (1) Å. Each Zn^{II} centre


Figure 1

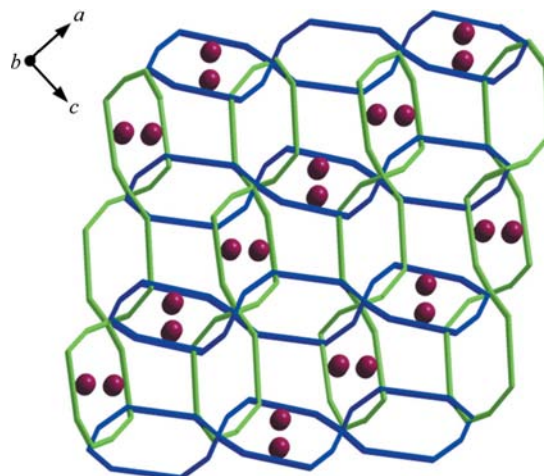
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. Both positions of disordered carboxylate atoms O3 and O4 are shown. [Symmetry codes: (i) $-x, -y, -z$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$]


Figure 2

A schematic representation of the two-dimensional supramolecular framework of (I), viewed down the c axis.

of the bimetallic ring is further bonded to two other bridging ligands, resulting in a novel infinite two-dimensional network structure in the ab plane (Fig. 2). The shortest $\text{Zn} \cdots \text{Zn}$ distance between adjacent bimetallic rings is 11.188 (2) Å.

When viewed down the crystallographic b axis, chains consisting of alternating symmetric ellipse-like cavities of different sizes are found (Fig. 3). The cavities are stacked to form channels. When the centres of the surrounding atoms are taken, these channels have dimensions of approximately 11.1×7.8 Å and 8.8×6.8 Å, but the accessible dimensions of the cavities are much smaller when the van der Waals radii of the surrounding atoms are taken into account. The chains repeat in an interpenetrating orthogonal arrangement. The water molecules occupy the smaller channels, where they are statistically disordered between two symmetry-related posi-


Figure 3

A schematic representation of the crystal packing of (I), viewed down the crystallographic b axis. The two interpenetrating orthogonal networks are shown; green (light) and blue (dark) in the electronic version of the paper. Water molecules are located in the channels. Two disordered positions for the water O atoms, each at 0.50 occupancy, are shown as dark spheres.

tions. The water molecules do not appear to interact strongly with the framework. The cavities in this structure are smaller than similar cavities composed of two Cd^{II} centres and two similar bent 4-[(1*H*-1,2,4-triazol-1-yl)methyl]benzoate ligands, in which the $\text{Cd} \cdots \text{Cd}$ separation is 12.40 (4) Å (Qin *et al.*, 2009). The smaller cavity size in (I) may be caused by the 3-substituted ligand being shorter than the 4-substituted ligand in terms of the distance from the carboxylate O atoms to the triazole N atom. Specifically, the longest $\text{N} \cdots \text{O}$ separations in the 3- and 4-substituted ligands are 7.816 (4) and 8.653 (31) Å, respectively. It is worth noting that the Cd compound of the 4-substituted ligand is a 1:1 salt with an additional chloride counter-ion, while (I) is a 1:2 salt with no other counter-ions. In addition, the Cd^{II} coordination polymer structure is also different in that no guest molecules are located in the channels. The structure of (I) further demonstrates the important role the bridging ligand plays in determining the specific nature of the resulting framework, and emphasizes the practically limitless potential for structural diversity in these systems.

Experimental

A mixture of 3-methylbenzoic acid (1.36 g, 10.0 mmol), succinbromimide (1.78 g, 10.0 mmol), benzoyl peroxide (0.025 g, 0.103 mmol) and tetrachloromethane (40 ml) was refluxed for 5 h. After cooling to room temperature, a pink precipitate was obtained by filtration and subsequently washed with tetrachloromethane and water. Recrystallization from dichloromethane provided 3-bromomethylbenzoic acid as a white solid in 80.3% yield.

KOH (2.8 g, 50.0 mmol) was added with stirring to a solution of 3-bromomethylbenzoic acid (2.15 g, 10.0 mmol) and 1*H*-1,2,4-triazole (0.69 g, 10.0 mmol) in water (60 ml). The mixture was stirred for 12 h and then acidified with hydrochloric acid to adjust the pH to 2. The white precipitate which formed was filtered off and recrystallized from methanol to give the product, HL (yield 81.3%). ^1H NMR

(300 MHz, DMSO- d_6): δ 12.99 (s, 1H, COOH), 8.71 (s, 1H, CH), 8.01 (s, 1H, CH), 7.89–7.50 (m, 4H, *m*-C₆H₄), 5.50 (s, 2H, CH₂); IR (KBr, cm⁻¹): 3450, 3108, 2767, 2516, 1925, 1694, 1611, 1518, 1454, 1276, 1201, 1136, 1019, 980, 891, 783, 742, 679, 656, 590.

A mixture of HL (20.3 mg, 0.10 mmol), ZnSO₄·7H₂O (28.7 mg, 0.10 mmol) and deionized water (2 ml) was sealed in a 5 ml test tube, heated at 453 K for 40 h and cooled slowly to room temperature over a period of 50 h. Colourless crystals of the title compound, (I), were isolated in 80% yield (based on HL). IR (KBr, cm⁻¹): 3450, 3132, 1694, 1518, 1348, 1276, 1203, 1131, 982, 931, 742, 678, 653; elemental analysis calculated for C₄₀H₃₄N₁₂O₉Zn₂: C 50.17, H 3.55, N 17.56%; found: C 50.14, H 3.57, N 17.58%.

Crystal data

[Zn ₂ (C ₁₀ H ₈ N ₃ O ₂) ₄ ·H ₂ O]	$V = 4041.9 (13) \text{ \AA}^3$
$M_r = 957.53$	$Z = 4$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation
$a = 13.875 (3) \text{ \AA}$	$\mu = 1.26 \text{ mm}^{-1}$
$b = 13.142 (3) \text{ \AA}$	$T = 298 \text{ K}$
$c = 22.166 (4) \text{ \AA}$	$0.52 \times 0.16 \times 0.08 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	19051 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3572 independent reflections
$T_{\min} = 0.560$, $T_{\max} = 0.906$	2598 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	13 restraints
$wR(F^2) = 0.118$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$
3572 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
296 parameters	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Zn1–O4	2.434 (2)	Zn1–O4'	2.436 (3)
Zn1–O3	2.081 (3)	Zn1–N4 ⁱ	2.033 (3)
Zn1–O3'	2.062 (2)	Zn1–N3 ⁱⁱ	2.043 (3)
N4 ⁱ –Zn1–N3 ⁱⁱ	101.80 (11)	N4 ⁱ –Zn1–O3	91.06 (11)
N4 ⁱ –Zn1–O2	110.52 (11)	N3 ⁱⁱ –Zn1–O3	110.99 (11)
N3 ⁱⁱ –Zn1–O2	94.87 (11)	O2–Zn1–O3	142.34 (11)

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

H atoms attached to C atoms were placed in geometrically idealized positions and included as riding atoms, with C–H = 0.93 (aromatic) or 0.97 Å (methylene) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The O atoms of one coordinated carboxylate group were disordered over two positions; the site-occupancy factors are 0.734 (7) (atoms O3' and O4') and 0.266 (7) (atoms O3 and O4). The anisotropic displacement parameters of atoms O3 and O4 were restrained to be similar to those of O3' and O4' within a standard deviation of 0.005 Å². A rigid bond

restraint with a standard deviation of 0.001 Å was applied to atoms Zn1 and O1. The disordered water molecule was modelled as half-occupied. H atoms of the water molecule were located in a difference map and refined as riding, with O–H = 0.85 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Data collection: SMART (Bruker, 2003); cell refinement: SMART; data reduction: SAINT (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3238). Services for accessing these data are described at the back of the journal.

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