

A novel threefold-interpenetrating primitive cubic network based on a dinuclear Zn₂ node

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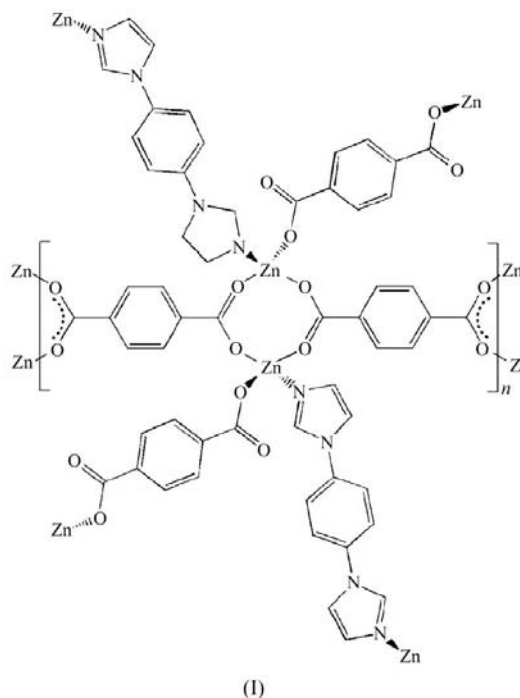
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In the mixed-ligand metal–organic polymeric compound poly[[μ_2 -1,4-bis(imidazol-1-yl)benzene](μ_2 -terephthalato)di-zinc(II)], $[\text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_{12}\text{H}_{10}\text{N}_4)]_n$ or $[\text{Zn}_2(\text{bdc})_2(\text{bib})]_n$ [H_2bdc is terephthalic acid and bib is 1,4-bis(imidazol-1-yl)-benzene], the asymmetric unit contains one Zn^{II} ion, with two half bdc anions and one half bib molecule lying around inversion centers. The Zn^{II} ion is in a slightly distorted tetrahedral environment, coordinated by three carboxylate O atoms from three different bdc anions and by one bib N atom. The crystal structure is constructed from the secondary building unit (SBU) $[\text{Zn}_2(\text{CO}_2)_2\text{N}_2\text{O}_2]$, in which the two metal centers are held together by two bdc linkers with bis(*syn,syn*-bridging bidentate) bonding modes. The SBU is connected by bdc bridges to form a two-dimensional grid-like (4,4)-layer, which is further pillared by the bib ligand. Topologically, the dinuclear SBU can be considered to be a six-connected node, and the extended structure exhibits an elongated primitive approximately cubic framework. The three-dimensional framework possesses a large cavity with dimensions of approximately $10 \times 13 \times 17 \text{ \AA}$ in cross-section. The potential porosity is filled with mutual interpenetration of two identical equivalent frameworks, generating a novel threefold interpenetrating network with an α -polonium topology [Abrahams, Hoskins, Robson & Slizys (2002). *CrystEngComm*, **4**, 478–482].

Comment

Metal–organic frameworks (MOFs) are hybrid materials where metal ions or small clusters are bridged by multi-functional organic linkers into one-dimensional chains, two-dimensional layers or three-dimensional nets. During the past decade, the construction of MOFs through crystal engineering has attracted considerable attention owing to the various

intriguing architectures of these frameworks and their potential applications as functional materials (Kitaura *et al.*, 2003; Eddaoudi *et al.*, 2000; Kepert *et al.*, 2001). As nature abhors a vacuum, mutual interpenetration is a common phenomenon in supramolecular chemistry and provides a unique class of robust framework (Carlucci *et al.*, 2000). Comprehensive reviews of interpenetration, which has been the most investigated type of entanglement, are given by Batten (2001) and Blatov *et al.* (2004). Much effort has been devoted to the synthesis of novel interpenetrating networks with interesting topologies. The most commonly used synthetic strategy is to select appropriate long-chain ligands, which bridge metal ions to afford infinite networks. Recently, the synthetic strategy utilizing secondary building units (SBUs) has achieved stable highly porous open frameworks; two efficient SBUs are the tetrameric $M_4\text{O}(\text{COO})_6$ clusters and the paddle-wheel dimeric $M_2(\text{COO})_4$ clusters formed by carboxylate ligands (Chae *et al.*, 2004; Sun *et al.*, 2006; Han *et al.*, 2008; Chen, Che *et al.*, 2007). There are many inorganic–organic hybrid complexes composed of polyoxometalates (POMs) associated with various metal–ligand systems (Tian *et al.*, 2008). A large number of attractive MOFs of ingenious design based on flexible bis(imidazole) ligands have been crystallographically characterized (Jin *et al.*, 2006; Li *et al.*, 2006; Fan *et al.*, 2006). In order to enrich the coordination chemistry of interpenetrating MOFs based on POMs as nodes, we describe the synthesis and crystal structure of a novel threefold-interpenetrating primitive cubic network constructed from terephthalic acid (H_2bdc), 1,4-bis(imidazol-1-yl)-benzene (bib) and Zn^{II}, namely $[\text{Zn}_2(\text{bdc})_2(\text{bib})]_\infty$ (I).



As shown in Fig. 1, the Zn^{II} center is four-coordinated by one N atom from the bib ligand and by three O atoms from individual bdc anions to form a slightly distorted tetrahedral

configuration. The Zn–O/N bond lengths are in the range 1.927 (3)–1.990 (3) Å (Table 1), comparable to those observed in related Zn^{II} polymeric structures (Li *et al.*, 2008; Chen, Che *et al.*, 2007; Wang *et al.*, 2006). The bdc and bib ligands lie about centers of symmetry. In the bdc anion, the two carboxylate groups show different bridging modes, *viz.* monodentate and *syn–syn* bidentate (Fig. 2). The bib ligand is *trans* coordinated to the Zn^{II} center and keeps its rigid conformation in the self-assembly of the coordination polymer. As depicted in Fig. 2, two crystallographically equivalent Zn^{II} atoms, *i.e.* Zn1 and Zn1(–*x* + 2, –*y*, –*z* + 1), are bridged by two *syn–syn*-connecting carboxylates with a Zn···Zn distance of 3.706 (1) Å. This arrangement constitutes a relatively rare dinuclear SBU, *viz.* [Zn₂(CO₂)₂N₂O₂], in which two Zn^{II} centers are encompassed by two *syn–syn*-bridging and two monodentate carboxylate groups, respec-

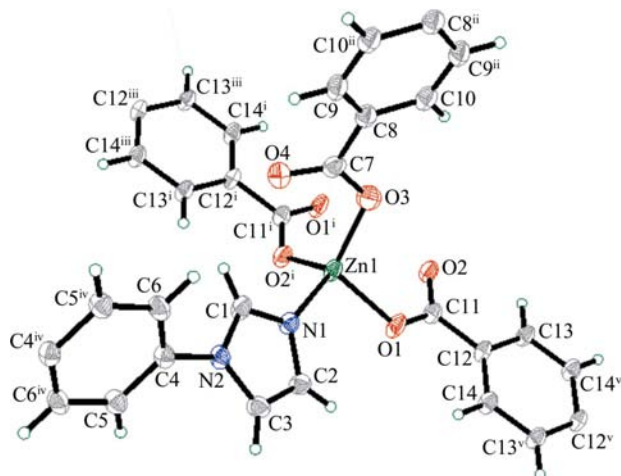


Figure 1

A view of the coordination environment of the Zn^{II} cation in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii. [Symmetry codes: (i) –*x* + 2, –*y*, –*z* + 1; (ii) –*x* + 2, –*y* – 1, –*z*; (iii) *x* – 1, *y* – 1, *z*; (iv) –*x*, –*y*, –*z*; (v) –*x* + 3, –*y* + 1, –*z* + 1.]

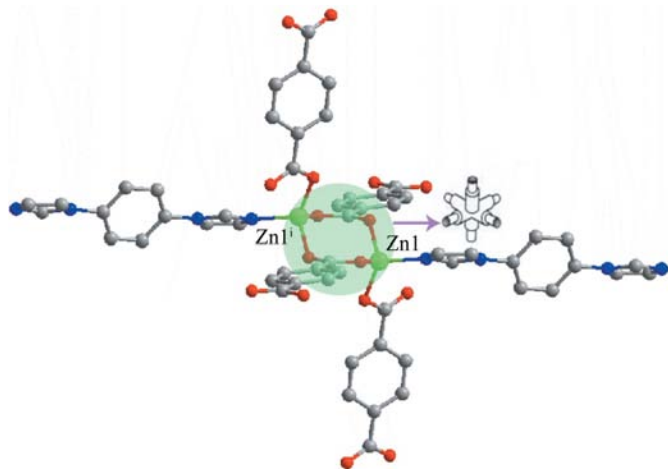


Figure 2

The dinuclear Zn₂ SBU of (I), showing an *O_h* symmetry node. Zn1 and Zn1' are linked by two *syn–syn*-connecting carboxylate groups. The insert shows an ideal octahedral node. [Symmetry code: (i) –*x* + 2, –*y*, –*z* + 1.]

tively. Thus, it is quite different from the common paddle-wheel dimeric unit, which is bridged by four *syn–syn*-connecting carboxylate groups. Some similar zinc-based SBUs linked by this carboxylate bridging mode are found in coordination polymers, but there are minor differences from the present compound in the coordination environments of the Zn^{II} ions (Dietzel *et al.*, 2006; Wang *et al.*, 2006). One closely related structure was reported by Chen, Zhang & Lu (2007), with the dinuclear Zn^{II} unit also connected by two bdc ligands; however, the Zn···Zn distances within this unit are 3.522 (1) and 3.564 (1) Å, somewhat shorter than here. Furthermore, the Zn···Zn separations in paddle-wheel SBUs are generally around 2.9 Å, and two intra-unit Zn^{II} centers are typically much closer (Ma *et al.*, 2005; Zhou *et al.*, 2000; Li *et al.*, 2004; Chun *et al.*, 2005).

A better insight into this fascinating structure can be achieved by the application of topology analysis. Although each Zn^{II} center sits in a tetrahedral coordination environment, the dinuclear SBU is octahedrally connected by four bdc anions and two bib molecules (Fig. 2). Each six-connected SBU is linked to four equivalent units through four bdc anions to generate a neutral two-dimensional square-grid (4,4)-layer, *viz.* [Zn₂(bdc)₂]_∞. As shown in Fig. 3, the two-dimensional layer is further pillared by the long bib ligand to afford an extended three-dimensional framework, *viz.* [Zn₂(bdc)₂(bib)]_∞, with a cube-like structure, which is also found in the two-dimensional parallel catenation of bilayered [Zn₂(bdc)₂(bpp)]_∞ [bpp is 1,3-bis(4-pyridyl)propane; Chen, Zhang & Lu, 2007]. If the dinuclear SBU is simplified to a six-connected node and, accordingly, the bdc and bib ligands act as two-connected linkers, the overall topology can be

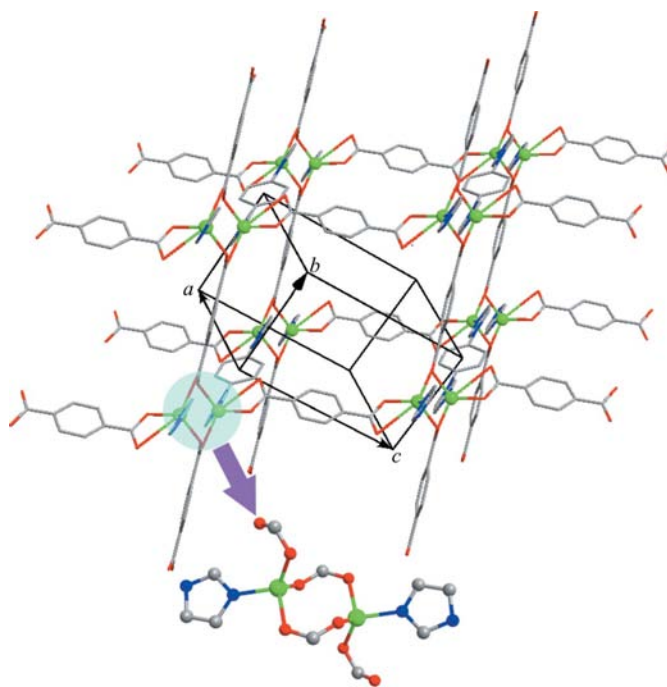


Figure 3

A schematic representation of the cube-like structure of (I), based on dinuclear Zn₂ clusters. The insert shows the Zn^{II} coordination environment.

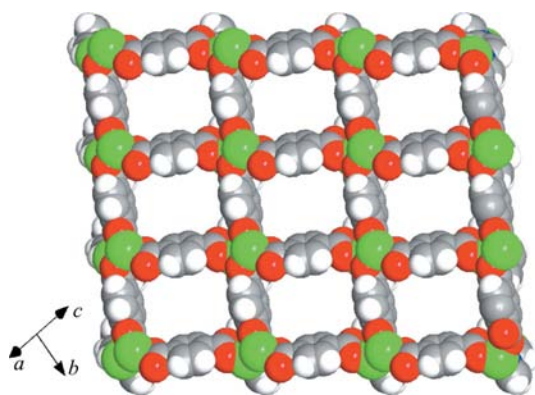


Figure 4
The large channel of one single α -polonium framework in (I), with dimensions of $10 \times 13 \times 17 \text{ \AA}$ (see *Comment*).

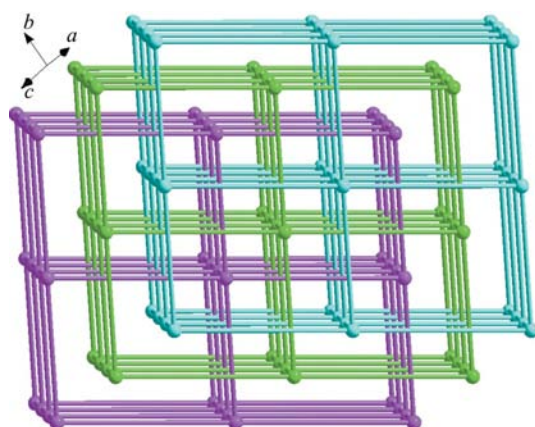


Figure 5
A view of the threefold-interpenetrating α -polonium network of (I). The dinuclear Zn_2 SBU acts as a node, while bridging bdc and bib ligands act as linkers. (These alternating frameworks are shown in turquoise, pink and blue, respectively, in the electronic version of the paper.)

described as an α -polonium framework (Abrahams *et al.*, 2002), which possesses large cubic cavities of approximately $10 \times 13 \times 17 \text{ \AA}$ (Fig. 4). The large voids formed by a single three-dimensional framework allow the incorporation of two identical frameworks, thus giving a threefold-interpenetrating α -polonium-related network, as shown in Fig. 5. The nodes of the second and third nets are located, equally spaced, along the cubic diagonal of the first net, and each square window has a rod from each of the two adjacent nets passing through it, giving a complicated interpenetration. We recognize, as did previous workers, that among the currently known examples of α -polonium topology, the majority are twofold (Niel *et al.*, 2002; Jensen *et al.*, 2002; Yang *et al.*, 2002), and only a few threefold-interpenetrated frameworks have been identified (Abrahams *et al.*, 2002; Wang *et al.*, 2006).

In summary, a novel threefold-interpenetrating network with an α -polonium topology has been synthesized; this is another interpenetrating MOF based on a POM as the node.

Experimental

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (149 mg, 0.5 mmol), H_2bdc (83 mg, 0.5 mmol), bib (78 mg, 0.25 mmol), water (6 ml) and ethanol (8 ml)

was placed in a Teflon reactor (23 ml). The mixture was heated at 413 K for 3 d, and then cooled to room temperature at a rate of 5 K h^{-1} . Colorless block-shaped crystals of (I) were obtained (yield 37%, based on Zn). Analysis calculated for $\text{C}_{14}\text{H}_9\text{N}_2\text{O}_4\text{Zn}$: C 50.25, H 2.71, N 8.37%; found: C 49.99, H 2.64, N 8.53%.

Crystal data

$[\text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_{12}\text{H}_{10}\text{N}_4)]$	$\gamma = 96.32 (3)^\circ$
$M_r = 334.60$	$V = 637.1 (2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 6.9711 (14) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.0784 (16) \text{ \AA}$	$\mu = 1.95 \text{ mm}^{-1}$
$c = 11.903 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\alpha = 102.68 (3)^\circ$	$0.20 \times 0.20 \times 0.20 \text{ mm}$
$\beta = 99.68 (3)^\circ$	

Data collection

Bruker SMART 1000 CCD diffractometer	2244 independent reflections
5445 measured reflections	1952 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	190 parameters
$wR(F^2) = 0.103$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{\text{max}} = 0.45 \text{ e \AA}^{-3}$
2244 reflections	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$

Table 1

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

Zn1—O3	1.927 (3)	Zn1—O1	1.978 (3)
Zn1—O2 ⁱ	1.955 (3)	Zn1—N1	1.990 (3)
O3—Zn1—O2 ⁱ	112.06 (12)	O3—Zn1—N1	118.46 (12)
O3—Zn1—O1	107.96 (12)	O2 ⁱ —Zn1—N1	107.67 (11)
O2 ⁱ —Zn1—O1	113.91 (11)	O1—Zn1—N1	95.96 (11)

Symmetry code: (i) $-x + 2, -y, -z + 1$.

All H atoms were positioned geometrically and refined using a riding model [$\text{C—H} = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; 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: GA3114). Services for accessing these data are described at the back of the journal.

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