

A novel parallel interpenetrating two-dimensional (4,4) network: poly[[μ_2 -1,4-bis(imidazol-1-ylmethyl)benzene]-(μ_2 -naphthalene-1,4-dicarboxylato)-zinc(II)]

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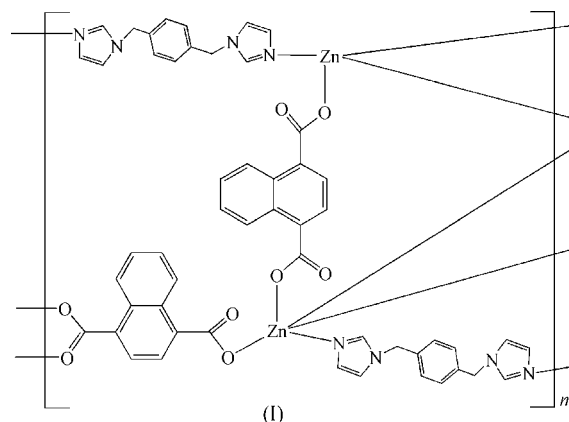
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In the title coordination compound, $[\text{Zn}(\text{C}_{12}\text{H}_6\text{O}_4)(\text{C}_{14}\text{H}_{14}\text{N}_4)]_n$, the two Zn^{II} centers exhibit different coordination environments. One Zn^{II} center is four-coordinated in a distorted tetrahedral environment surrounded by two carboxylate O atoms from two different naphthalene-1,4-dicarboxylate (1,4-ndc) anions and two N atoms from two distinct 1,4-bis(imidazol-1-ylmethyl)benzene (1,4-bix) ligands. The coordination of the second Zn^{II} center comprises two N atoms from two different 1,4-bix ligands and three carboxylate O atoms from two different 1,4-ndc ligands in a highly distorted square-pyramidal environment. The 1,4-bix ligand and the 1,4-ndc anion link adjacent Zn^{II} centers into a two-dimensional four-connected (4,4) network. The two (4,4) networks are interpenetrated in a parallel mode.

Comment

The current interest in polymeric coordination networks is rapidly expanding not only because of their potential applications in medical chemistry, host–guest chemistry, ion exchange, artificial eye lenses, gas storage and nonlinear optics, but also for their intriguing variety of topologies (Carlucci *et al.*, 2003; Eddaoudi *et al.*, 2001). It is well known that structural diversity in coordination polymers can occur as a result of various processes, including supramolecular isomerism and interpenetration. In this regard, interpenetrating networks, as an important subject in the area of entanglement, have provided a long-standing fascination for chemists (Batten & Robson, 1998; Ockwig *et al.*, 2005).

Generally, the topology of a coordination polymer can often be controlled and modified by selecting the coordination geometry preferred by the metal ion and the chemical structure of the organic ligand chosen (Batten, 2001). Flexible N-donor ligands are good candidates for the assembly of versatile entangled structures, owing to their propensity to form large voids; in particular, bis(imidazole) ligands are a good choice. Using these ligands, many intriguing varieties of interpenetrating architectures and topologies have been constructed (Sun *et al.*, 2009). Among the bis(imidazole) ligands, 1,4-bis(imidazol-1-ylmethyl)benzene (1,4-bix) is particularly interesting. For example, the flexible bridging 1,4-bix gives an unusual extended two-dimensional polyrotaxane network when it is reacted with $\text{Cd}(\text{SO}_4)\cdot 6\text{H}_2\text{O}$ (Carlucci *et al.*, 2005). An unusual triply interpenetrating α -polonium topology is produced when it is reacted with $\text{Cd}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Abrahams *et al.*, 2002). In the present study, 1,4-bix assembles with zinc naphthalene-1,4-dicarboxylate (1,4-ndc) to furnish a 1:1:1 adduct, $[\text{Zn}(1,4\text{-ndc})(1,4\text{-bix})]_{2n}$ (I), which exists as a twofold interpenetrating (4,4) topology.



The asymmetric unit of (I) (Fig. 1 and Table 1) contains two crystallographically independent Zn^{II} centers, two unique 1,4-ndc anions and two unique 1,4-bix ligands. The two Zn^{II} centers exhibit different coordination environments. $\text{Zn}1$ is four-coordinated in a distorted tetrahedral environment surrounded by two carboxylate O atoms from two different 1,4-ndc anions and two N atoms from two distinct 1,4-bix ligands. The coordination of atom $\text{Zn}2$ comprises two N atoms from two different 1,4-bix ligands and three carboxylate O atoms from two different 1,4-ndc ligands in a highly distorted square-pyramidal environment. One N atom (N5) and three O atoms (O1, O7ⁱⁱ and O8ⁱⁱⁱ) constitute the base of the square-pyramid, whereas one N atom (N8ⁱⁱⁱ) occupies the apical position with a $\text{Zn}-\text{N}8^{\text{iii}}$ distance of 2.046 (3) Å. The average $\text{Zn}-\text{O}$ and $\text{Zn}-\text{N}$ distances in (I) (Table 1) are comparable to those observed for $[\text{Zn}(\text{OAc})(\text{TITMB})](\text{OH})\cdot 8.5\text{H}_2\text{O}$ [TITMB is 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene and OAc is the acetate anion; Fan *et al.*, 2003]. As depicted in Fig. 2, each Zn^{II} center is bridged by the 1,4-ndc dianions and 1,4-bix ligands to give a two-dimensional four-connected (4,4) network. Along the *c* axis, adjacent Zn^{II} centers are linked *via* the two carboxylate groups of the 1,4-ndc ligands to form one-dimensional chains. The 1,4-bix

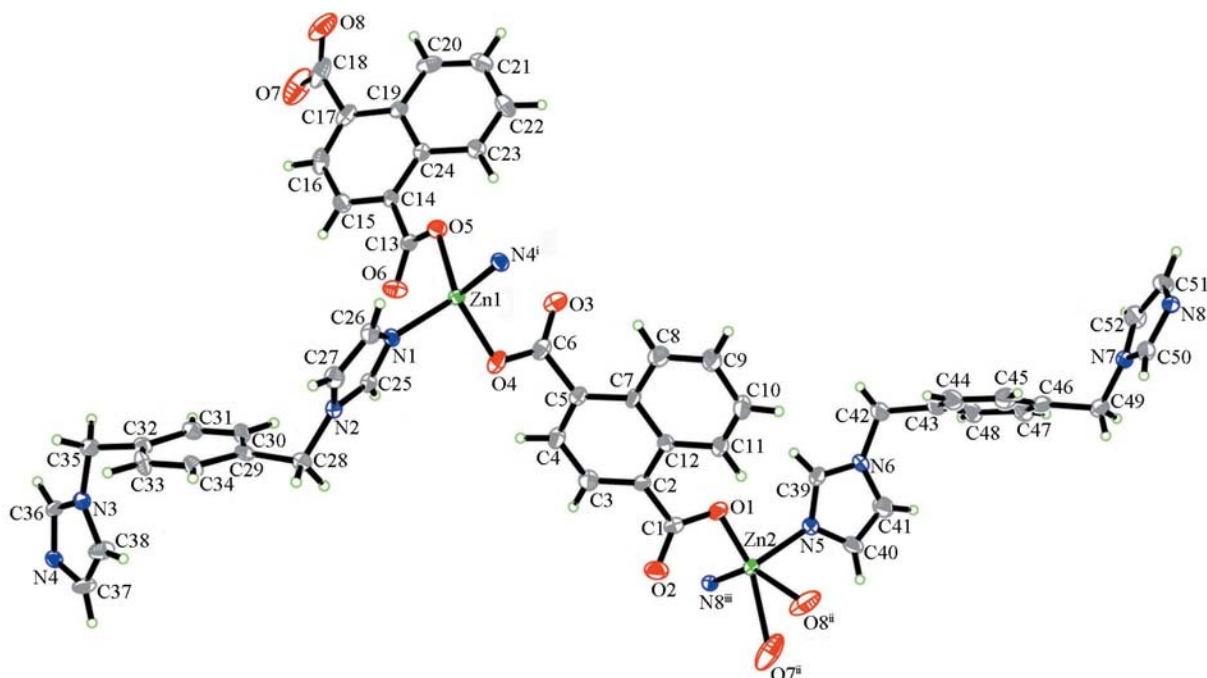


Figure 1

A view of the local coordination of the Zn^{II} cations in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. One of the H atoms on C42 is wholly obscured by its parent atom. [Symmetry codes: (i) $x - 1, y - 1, z$; (ii) $x, y, 1 + z$; (iii) $x + 1, y + 1, z$.]

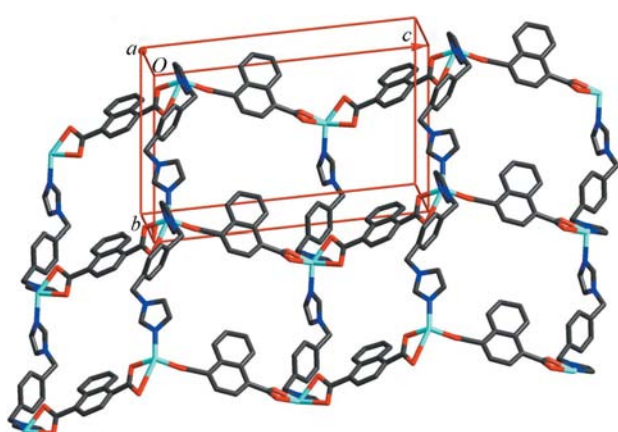


Figure 2

A view of the two-dimensional (4,4) network in the $(\bar{1}10)$ plane.

ligands further extend these chains along the b axis, yielding the final two-dimensional (4,4) network. Interestingly, the two (4,4) networks are interpenetrated in a parallel mode in the $(\bar{1}10)$ plane (Fig. 3). The two interpenetrating networks are individually generated by translation and they are related by inversion.

It is noteworthy that the structure of (I) is entirely different from those of the two related structures $[\text{Cu}(1,3\text{-bdc})_2(1,4\text{-bix})][\text{Cu}(1,4\text{-bix})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (1,3-bdc is benzene-1,3-dicarboxylate) and $[\text{Cu}(1,4\text{-ndc})(1,2\text{-bix})_2] \cdot 2\text{H}_2\text{O}$ (Yang *et al.*, 2008). The reported complex $[\text{Cu}(1,3\text{-bdc})_2(1,4\text{-bix})][\text{Cu}(1,4\text{-bix})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ consists of two types of coordination polymers, namely two-dimensional (4,4) grids of $[\text{Cu}(1,4\text{-bix})_2(\text{H}_2\text{O})_2]^{2+}$ and linear chains of $[\text{Cu}(1,3\text{-bdc})_2(1,4\text{-bix})]^{2-}$. The structure of $[\text{Cu}(1,4\text{-ndc})(1,2\text{-bix})_2] \cdot 2\text{H}_2\text{O}$ contains two-dimensional (4,4) networks. However, this structure does not

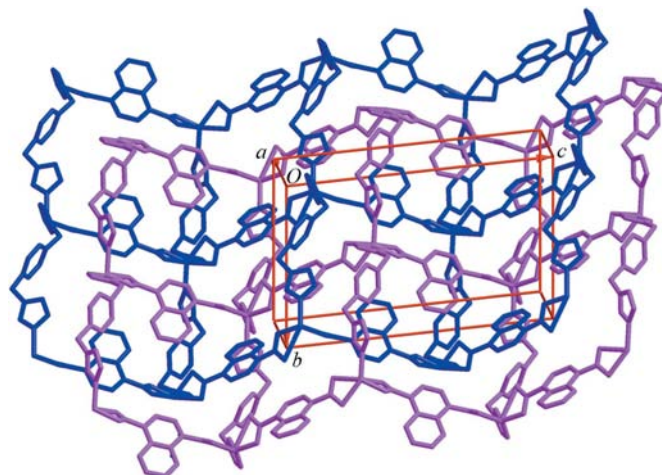


Figure 3

A view of the parallel interpenetrating (4,4) networks of (I) in the $(\bar{1}10)$ plane.

exhibit interpenetration. The structure of (I) is also entirely different from that of the related polymer $[\text{Zn}(\text{SO}_4)(\text{bis})_{1.5}(\text{H}_2\text{O})] \cdot 6\text{H}_2\text{O}$ [bis is 1,1'-(butane-1,4-diyl)bis(imidazole); Ma *et al.*, 2000]. In that structure, the networks are interpenetrated in an inclined mode by symmetry-related identical networks to give an interlocked three-dimensional structure. This compound may be a good candidate for artificial eye lenses.

Experimental

Zinc chloride (0.068 g, 0.5 mmol), naphthalene-1,4-dicarboxylic acid (0.108 g, 0.5 mmol) and 1,4-bix (0.119 g, 0.5 mmol) were placed in water (12 ml), and triethylamine was added until the pH value of the

solution was 5.8. The solution was heated in a 25 ml Teflon-lined stainless-steel autoclave at 450 K for 5 d. The autoclave was allowed to cool to room temperature over a period of several hours. Colorless blocks were isolated in about 42% yield.

Crystal data

$[\text{Zn}(\text{C}_{12}\text{H}_6\text{O}_4)(\text{C}_{14}\text{H}_{14}\text{N}_4)]$	$\gamma = 100.628 (4)^\circ$
$M_r = 517.83$	$V = 2249.95 (18) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 4$
$a = 10.4112 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 11.5745 (5) \text{ \AA}$	$\mu = 1.13 \text{ mm}^{-1}$
$c = 19.1907 (9) \text{ \AA}$	$T = 293 \text{ K}$
$\alpha = 96.319 (4)^\circ$	$0.33 \times 0.27 \times 0.22 \text{ mm}$
$\beta = 93.869 (5)^\circ$	

Data collection

Bruker APEX diffractometer	22060 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	9159 independent reflections
$T_{\min} = 0.680$, $T_{\max} = 0.775$	4749 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	631 parameters
$wR(F^2) = 0.096$	H-atom parameters constrained
$S = 0.83$	$\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$
9159 reflections	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$

H atoms were treated as riding atoms in geometrically idealized positions, with C—H distances of 0.93 (aromatic) and 0.97 Å (methylene), and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3296). Services for accessing these data are described at the back of the journal.

Table 1

Selected geometric parameters (Å, °).

Zn1—O4	1.960 (3)	Zn2—O7 ⁱⁱ	2.224 (4)
Zn1—O5	1.958 (2)	Zn2—O8 ⁱⁱ	2.256 (4)
Zn1—N1	2.038 (3)	Zn2—N5	2.053 (3)
Zn1—N4 ⁱ	2.035 (3)	Zn2—N8 ⁱⁱⁱ	2.046 (3)
Zn2—O1	1.950 (2)		
O5—Zn1—O4	131.58 (11)	N8 ⁱⁱⁱ —Zn2—N5	100.87 (13)
O5—Zn1—N4 ⁱ	98.42 (12)	O1—Zn2—O7 ⁱⁱ	140.89 (14)
O4—Zn1—N4 ⁱ	108.08 (12)	N8 ⁱⁱⁱ —Zn2—O7 ⁱⁱ	86.96 (15)
O5—Zn1—N1	115.50 (11)	N5—Zn2—O7 ⁱⁱ	111.53 (15)
O4—Zn1—N1	97.48 (12)	O1—Zn2—O8 ⁱⁱ	100.20 (14)
N4 ⁱ —Zn1—N1	102.78 (12)	N8 ⁱⁱⁱ —Zn2—O8 ⁱⁱ	143.68 (15)
O1—Zn2—N8 ⁱⁱⁱ	111.14 (12)	N5—Zn2—O8 ⁱⁱ	91.51 (14)
O1—Zn2—N5	99.11 (12)	O7 ⁱⁱ —Zn2—O8 ⁱⁱ	56.80 (15)

Symmetry codes: (i) $x - 1, y - 1, z$; (ii) $x, y, z + 1$; (iii) $x + 1, y + 1, z$.

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