Poly[bis[μ₂-1,3-bis(pyridin-4-yl)urea-κ²N⁴:N⁴']-bis(μ₂-5-methylisophthalato-κ²O¹::O³)dizinc(II)], a parallel interpenetrated slab-like coordination polymer with {3.6⁴⁸}{3²6.⁷²⁸} 4,4-connected binodal topology

Jason Jia and Robert L. LaDuca*

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In the title compound, [Zn₂(C₈H₆O₄)₂(C₁₁H₁₀N₄O₂)₂]n, diperiodic coordination polymer slabs with {3.6⁴⁸}{3²6.⁷²⁸} 4,4-connected binodal topology are held into a parallel interpenetrated triperiodic crystal structure by means of N—H···O hydrogen-bonding patterns.

Structure description

The title compound was isolated during an exploratory synthetic effort aiming to produce a zinc coordination polymer containing both 5-methylisophthalate (mip) and 4,4'-dipyridylurea (dpu) ligands. Previously our group had isolated a zinc mip coordination polymer featuring 3-pyridylnicotinamide coligands; this phase manifested a mono-periodic ribbon structure (Kraft et al., 2015).

The asymmetric unit of the title compound contains two divalent Zn atoms on special positions in space group Pbcn, half of one methylisophthalate ligand, all of whose C and O atoms are situated on a horizontal crystallographic mirror plane (mip-A), half of a second methylisophthalate ligand bisected vertically by another crystallographic mirror plane cutting through atoms C12, C14, and C15 (mip-B), and a complete dpu ligand. The Zn1 atoms are located on a crystallographic mirror plane (Wyckoff position d), while the Zn2 atoms are located on a crystallographic twofold rotation axis (Wyckoff position e). The Zn1 atoms display a five-coordinate [N₂O₃] environment intermediate between idealized trigonal–bipyramidal and square-pyramidal arrangements, as indicated by the trigonality factor τ of 0.471 (Addison & Rao, 1984). The Zn2 atoms show a pseudo-
tetradehal [N₂O₂] environment. A depiction of the different coordination environments and full ligand set is shown in Fig. 1; numerical details are collated in Table 1.

The Zn1 atoms and chelating/monodentate mip-A ligands form \([\text{Zn(mip)}]_n\) coordination polymer chains with a Zn1·Zn1 distance of 10.361 (1) Å; these chain motifs are oriented along the b axis (Fig. 2). The Zn2 atoms and bis(monodentate) mip-B ligands form \([\text{Zn(mip)}]_n\) coordination polymer chains with a Zn2·Zn2 distance of 8.746 (1) Å; these chain motifs are oriented along the c axis (Fig. 3). The Zn1-based \([\text{Zn(mip)}]_n\) chains and Zn2-based \([\text{Zn(mip)}]_n\) chains are oriented orthogonally to each other. In turn, these chain motifs are pillared into \([\text{Zn(mip)(bpu)}]_n\) coordination polymer slabs by tethering bpu ligands (Fig. 4). The bpu ligands span a Zn·Zn distance of 13.803 (1) Å. Treating each of the Zn1 and Zn2 atoms as 4-connected nodes reveals an unprecedented \([3,6]^{28}[3,6,7]^{28}\) 4,4-connected binodal topology (Fig. 5) as determined by TOPOS software (Blatov et al., 2014).

Parallel interpenetration of the slab motifs occurs within the title compound (Fig. 6). N—H···O hydrogen-bonding patterns between the central N3—H3 and N4—H4 groups of the dpu ligands and unligated mip-B carboxylate O6 atoms stabilize the entangled triperiodic crystal structure. Details

### Table 1

| Zn1—O1  | 1.952 (3) |
| Zn1—O3  | 2.272 (3) |
| Zn1—O4  | 2.060 (3) |
| Zn1—N1  | 2.077 (3) |
| Zn1—Ni  | 2.077 (3) |

| O1—Zn1—O3  | 154.66 (12) |
| O1—Zn1—O4  | 94.69 (13) |
| O1—Zn1—Ni  | 105.72 (9)  |
| O4—Zn1—O3  | 59.97 (12)  |
| O4—Zn1—Ni  | 126.42 (8) |

Symmetry codes: (1) x+1/2, y+1/2, z; (2) x, y, z; (3) x+1/2, y+1/2, z; (4) x, y, z+1.

### Table 2

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Symmetry code: (iv) x, y+1, z+1/2.

---

**Figure 1**
Distinct coordination environments in the title compound with full ligand sets. Displacement ellipsoids are drawn at the 50% probability level. Color code: Zn, gray; O, red; N, light blue; C, black. H atom positions are shown as sticks. Symmetry codes are as listed in Table 1.

**Figure 2**
\([\text{Zn(mip)}]_n\) coordination polymer chain in the title compound, based on Zn1 atoms and chelating/monodentate mip-A ligands.

**Figure 3**
\([\text{Zn(mip)}]_n\) coordination polymer chain in the title compound, based on Zn2 atoms and bis(monodentate) mip-B ligands.

**Figure 4**
\([\text{Zn2(mip)2(bpu)2}]_n\) coordination polymer slab motif in the title compound. \([\text{Zn(mip)}]_n\) chains based on Zn1 and mip-A ligands are in the interior of the slab and drawn in red. \([\text{Zn(mip)}]_n\) chains based on Zn2 and mip-B ligands are on the exterior of the slab and drawn in orange.

**Figure 5**
Topological perspective of a single \([\text{Zn2(mip)2(bpu)2}]_n\) coordination polymer slab with \([3,6]^{28}[3,6,7]^{28}\) 4,4-connected binodal topology in the title compound. The 4-connected zinc atom nodes are shown as spheres. The mip and bpu ligands are rendered as rods.
regarding the hydrogen bonding patterns in the title compound are listed in Table 2.

Synthesis and crystallization

Zn(NO$_3$)$_2$·6H$_2$O (110 mg, 0.37 mmol), 5-methylisophthalic acid (mipH$_2$) (66 mg, 0.37 mmol), 4,4'-dipyridylurea (dpu) (79 mg, 0.37 mmol), and 0.75 ml of a 1.0 M NaOH solution were placed into 10 ml of distilled water in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 393 K for 48 h, and then cooled slowly to 273 K. Colorless crystals of the title complex were obtained in 59% yield.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

Funding information

Funding for this work was provided by the Lyman Briggs College of Science at Michigan State University.

Table 3

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<tr>
<th>Crystal data</th>
<th>Chemical formula</th>
<th>[Zn$_2$(C$_9$H$_6$O$<em>4$)$<em>2$(C$</em>{11}$H$</em>{10}$N$_4$O)$_2$]</th>
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Data collection

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<td>$\Delta p_{max}$, $\Delta p_{min}$ (e Å$^{-3}$) 0.88, −0.34</td>
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Computer programs: COSMO (Bruker, 2009), SAINT (Bruker, 2014), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b), Crystal Maker X (Palmer, 2020), and OLEX2 (Dolomanov et al., 2009).

References


Poly[bis[µ₂⁻¹,3-bis(pyridin-4-yl)urea⁻²N⁴⁻N⁴]bis(µ₂⁻5-methylisophthalato⁻κ²O¹⁻O³)dizinc(II)], a parallel interpenetrated slab-like coordination polymer with {3.6⁴8}{3²6.7²8} 4,4-connected binodal topology

Jason Jia and Robert L. LaDuca

Crystal data

\[\text{[Zn}_2(C_9H_6O_4)\text{]}(C_{11}H_{10}N_4O)_2\]  
Mr = 915.47  
Orthorhombic, \(Pbcn\)  
a = 12.0755 (11) Å  
b = 17.7239 (16) Å  
c = 17.4919 (16) Å  
\(V = 3743.7 \text{(6) Å}^3\)  
Z = 4  
\(F(000) = 1872\)

Data collection

Bruker APEXII CCD diffractometer  
Radiation source: sealed tube  
Graphite monochromator  
Detector resolution: 8.36 pixels mm⁻¹  
\(\omega\) scans  
Absorption correction: multi-scan  
\(\text{(SADABS; Krause et al., 2015)}\)

\(T_{\min} = 0.654, \ T_{\max} = 0.745\)

Refinement

Refinement on \(F^2\)  
Least-squares matrix: full  
\(R[F^2 > 2\sigma(F^2)] = 0.038\)  
\(wR(F^2) = 0.096\)  
\(S = 1.04\)  
3546 reflections  
299 parameters  
0 restraints  
Primary atom site location: dual  
Hydrogen site location: inferred from neighbouring sites  
\(H\)-atom parameters constrained

\(\Delta\sigma)_{\text{max}} = 0.001\)  
\(\Delta\rho_{\text{max}} = 0.88 \text{ e Å}^{-3}\)  
\(\Delta\rho_{\text{min}} = -0.34 \text{ e Å}^{-3}\)
Special details

Experimental. Data were collected using a BRUKER CCD (charge coupled device) based diffractometer equipped with an Oxford low-temperature apparatus operating at 173 K. A suitable crystal was chosen and mounted on a nylon loop using Paratone oil. Data were measured using omega scans of 0.5° per frame for 30 s. The total number of images were based on results from the program COSMO where redundancy was expected to be 4 and completeness to 0.83Å to 100%. Cell parameters were retrieved using APEX II software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software which corrects for Lp. Scaling and absorption corrections were applied using SADABS multi-scan technique, supplied by George Sheldrick. The structure was solved by the direct method using the SHELXT program and refined by least squares method on F2, SHELXL, incorporated in OLEX2.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The structure was refined by Least Squares using version 2018/3 of SHELXL (Sheldrick, 2015b) incorporated in OLEX2 (Dolomanov et al., 2009). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model, except for the Hydrogen atom on the nitrogen atom which was found by difference Fourier methods and refined isotropically.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

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Atom displacement parameters (Å²)
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C2 0.023 (2) 0.021 (2) 0.018 (2) −0.0049 (18) 0.000 0.000
C3 0.025 (2) 0.023 (2) 0.022 (2) −0.0022 (19) 0.000 0.000
C4 0.029 (2) 0.020 (2) 0.022 (2) −0.0045 (19) 0.000 0.000
C5 0.023 (2) 0.023 (3) 0.037 (3) −0.0068 (19) 0.000 0.000
C6 0.021 (2) 0.028 (3) 0.036 (3) 0.001 (2) 0.000 0.000
C7 0.023 (2) 0.017 (2) 0.029 (2) −0.0037 (18) 0.000 0.000
C8 0.028 (2) 0.026 (3) 0.021 (2) −0.005 (2) 0.000 0.000
C9 0.023 (3) 0.031 (3) 0.067 (4) 0.001 (2) 0.000 0.000
C10 0.0242 (16) 0.0190 (16) 0.0237 (17) −0.0008 (13) 0.0014 (13) 0.0003 (13)
C11 0.0194 (15) 0.0186 (16) 0.0190 (15) −0.0021 (12) −0.0011 (12) −0.0024 (12)
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C13 0.0239 (16) 0.0192 (16) 0.0221 (16) 0.0002 (13) 0.0028 (13) −0.0007 (13)
C14 0.018 (2) 0.021 (2) 0.030 (2) 0.0011 (18) 0.000 0.000
C15 0.031 (3) 0.037 (3) 0.028 (3) 0.014 (2) 0.000 0.000
C16 0.0245 (17) 0.0278 (19) 0.0327 (18) −0.0048 (14) −0.0017 (14) 0.0039 (15)
C17 0.0270 (18) 0.0270 (18) 0.0335 (19) −0.0026 (14) −0.0053 (15) 0.0034 (15)
C18 0.0243 (16) 0.0272 (18) 0.0206 (15) 0.0014 (14) −0.0014 (13) −0.0022 (13)
C19 0.0250 (17) 0.0260 (18) 0.0344 (19) 0.0002 (14) −0.0105 (15) −0.0662 (15)
C20 0.0290 (18) 0.0217 (18) 0.037 (2) 0.0013 (14) −0.0022 (15) −0.0044 (14)
C21 0.0314 (18) 0.031 (2) 0.024 (2) 0.0037 (15) −0.0047 (15) 0.0031 (15)
C22 0.045 (2) 0.030 (2) 0.0277 (18) 0.0054 (16) −0.0134 (16) −0.0094 (15)
C23 0.0356 (19) 0.035 (2) 0.0265 (18) 0.0082 (15) −0.0113 (15) −0.0035 (15)
C24 0.0233 (16) 0.0253 (17) 0.0238 (16) −0.0002 (13) −0.0016 (13) 0.0028 (14)
C25 0.0273 (17) 0.0286 (19) 0.0230 (17) −0.0019 (14) −0.0041 (13) −0.0037 (14)
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**Geometric parameters (Å, °)**

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C3—C4—C8—O3  
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Symmetry codes: (i) -x, y+1/2, -z+1/2; (ii) x, y, -z+1/2; (iii) x, -y+1/2, -z+1; (iv) -x, y-1/2, -z+1/2; (v) x, y, -z+3/2.

| Hydrogen-bond geometry (Å, °) |  |
|---|---|---|---|---|
| D—H···A | D—H | H···A | D···A | D—H···A |
| N2—H2···O6vi | 0.88 | 2.12 | 2.919 (3) | 151 |
| N3—H3···O6vi | 0.88 | 1.91 | 2.751 (3) | 159 |
| C5—H5···O3 | 0.95 | 2.42 | 2.754 (5) | 101 |
| C7—H7···O1 | 0.95 | 2.41 | 2.741 (5) | 100 |
| C17—H17···O7 | 0.95 | 2.24 | 2.805 (4) | 117 |
| C23—H23···O7 | 0.95 | 2.27 | 2.846 (4) | 118 |

Symmetry code: (vi) -x+2, y+1/2, z.