

Aqua(benzene-1,3-dicarboxylato)-zinc(II)

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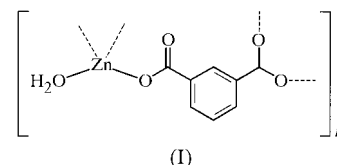
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The title compound, poly[[aquazinc(II)]- μ -benzene-1,3-dicarboxylato- $O^1:O^1':O^2$], $[Zn(C_8H_4O_4)(H_2O)]_n$, forms a metal-organic coordination network that consists of tetrahedral Zn atoms bonded to one water molecule and three carboxylate groups. Isophthalate groups bridge the four-coordinate Zn centers to generate two-dimensional architectures in the *ac* plane. These planar zinc isophthalate motifs are linked by infinite $C=O \cdots H-O-H$ interactions along the *a* axis to form a chiral framework. The observed polar structural pattern originates due to the distorted tetrahedral Zn centers [$O-Zn-O$ 100.7 (2)–136.0 (1)°] and the alignment of the water molecules. Bridging isophthalate groups align to form approximate centrosymmetric motifs.

Comment

A considerable number of reports based on metal-organic coordination polymers have appeared over the past few decades. Constructed of catenary ligands bonded to metal centers, these materials have successfully been used to generate desired crystalline architectures with bulk functions (Biradha *et al.*, 1999; Evans & Lin, 2000; Mori & Takamizawa, 2000). The use of metal centers with relatively robust coordination environments and conformationally rigid ligands often produces frameworks with structural preferences. Zn^{II} carboxylates are one such example that form predictable metal-center geometries which can be linked through multi-dentate bridging ligands (Li *et al.*, 1998; Lin *et al.*, 1999; Robl, 1987*a*). The development of new materials based on metal-organic frameworks requires an understanding of structural biases resulting from the self-assembly of the fundamental components. While many of the principles responsible for the construction of coordination polymers have been exposed (Aakeröy *et al.*, 2000; Guilera & Steed, 1999; Saalfrank *et al.*, 1999), a unified set of criteria that describes specific crystal-packing arrangements remains relatively undiscovered. Since steps towards clarifying structural principles often follow a rational study of the extant crystallographic data, the addition of new structures to this database serves to support or challenge existing structural principles. Here, we describe the synthetic and structural chemistry of the title compound, (I), a

coordination polymer comprised of an isophthalic acid complex of Zn^{II} .



The asymmetric unit of (I) contains a Zn atom, one isophthalate group, and one coordinated water molecule. Fig. 1 shows the local coordination environment around the Zn center as a distorted tetrahedron (Table 1) comprised of one water molecule and three bridging isophthalate carboxylate O atoms. This geometric pattern is consistent with other Zn^{II} coordination frameworks reported in the literature (Mehrota & Bohra, 1983; Robl, 1987*b*). Each Zn atom coordinates to six adjacent Zn centers [shortest distance is $Zn \cdots Zn^{vi} = 4.3323$ (3) Å; symmetry code: (vi) $\frac{1}{2} + x, 1 - y, z$] through the bridging isophthalate atoms O1, O2, and O3 to give a planar polymeric network in the *ac* plane (Fig. 2). The two-dimensional architecture is constructed of Zn atoms linked by bidentate carboxylate groups, O1 and O2, along the *a* axis. This motif is extended along the *c* axis by monodentate chelation of the remaining carboxylate group to adjacent Zn centers *via* O3–Zn interactions.

A noteworthy feature is that the non-coordinated carboxylate O4 atom forms infinite chains of undulating $O5-H \cdots O4$ hydrogen bonds with neighboring chelated water molecules (Fig. 2 and Table 2). This pattern extends along the *a* axis and links the two-dimensional isophthalate– Zn^{II} coordination networks. The resulting three-dimensional assemblage, constructed from polymeric Zn centers and catemeric hydrogen bonds, lacks residual solvent-accessible regions, as determined from an examination of the structure with PLATON (Spek, 1990).

The chiral framework of the structure originates from the distorted tetrahedral Zn centers and polar alignment of the chelated water molecules. Inspection of Table 1 reveals Zn–O bonds that differ by only 0.030 (3) Å, with significant variations in the O–Zn–O angles [100.7 (2)–136.0 (1)°]. The skewed coordination environment of each Zn atom generates a stereogenic metal center with vectorial properties that are not cancelled by the orientation of neighboring symmetry-

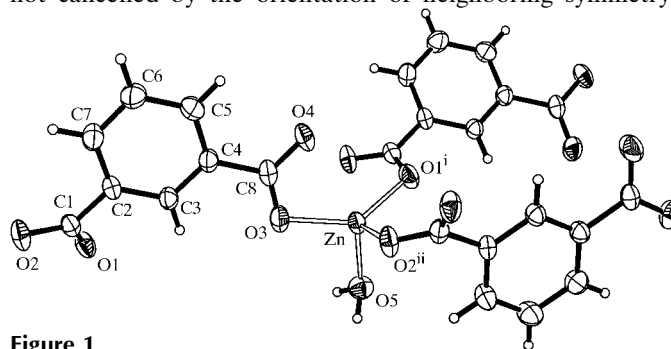


Figure 1
The Zn^{II} coordination environment in (I) and the atom-labeling scheme. Displacement ellipsoids are shown at the 60% probability level and H atoms are drawn as small spheres of arbitrary radii [symmetry codes: (i) $\frac{3}{2} - x, y, \frac{1}{2} + z$; (ii) $1 - x, 1 - y, \frac{1}{2} + z$].

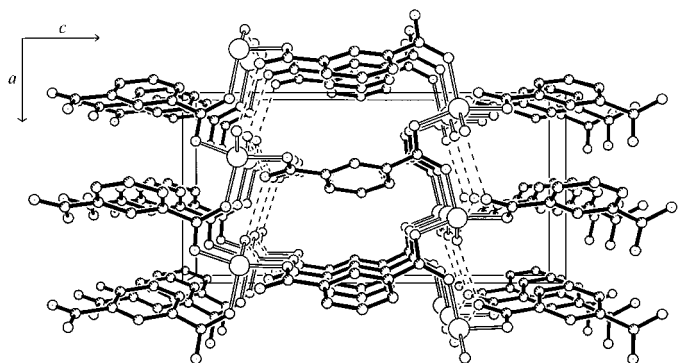


Figure 2

Projection of the structure of (I) down the *b* axis, showing the layered coordination polymer linked by infinite arrays of O5–H...O4 hydrogen-bond interactions.

related Zn centers. In contrast with these polar structural components, the assemblage of bridging isophthalate groups forms motifs that closely resemble centrosymmetric alignment.

Experimental

Compound (I) was prepared using a modification of the gel-assisted slow diffusion technique described by Robl (1987*b*) for the preparation of metal carboxylates. HNO₃ (2 *M*) was added dropwise to a solution of Na₂H₂SiO₄ (10 ml, 2 *M*) and disodium isophthalate (10 ml, 0.01 *M*). At the appropriate pH, typically 5.0–5.5, the viscosity of the mixture rapidly increased. The silicate mixture was promptly distributed into test tubes and allowed to stiffen to form translucent gels. Each gel was layered with Zn(NO₃)₂ (2 ml, 0.5 *M*) and allowed to stand. After 5–6 weeks, transparent colorless plates of (I) grew, with crystal dimensions of up to 2 mm. A crystal suitable for X-ray analysis was fixed to the tip of a glass fiber with cyanoacrylate adhesive.

Crystal data

[Zn(C ₈ H ₄ O ₄)(H ₂ O)]	Mo K α radiation
<i>M_r</i> = 247.50	Cell parameters from 37 reflections
Orthorhombic, <i>Pca</i> 2 ₁	θ = 20.8–25.0°
<i>a</i> = 8.3887 (6) Å	μ = 2.84 mm ⁻¹
<i>b</i> = 6.0883 (5) Å	<i>T</i> = 298 (2) K
<i>c</i> = 16.8795 (10) Å	Plate, colorless
<i>V</i> = 862.09 (11) Å ³	0.68 × 0.42 × 0.19 mm
<i>Z</i> = 4	
<i>D_x</i> = 1.907 Mg m ⁻³	

Data collection

Siemens P4 diffractometer	<i>R</i> _{int} = 0.016
$\theta/2\theta$ scans	θ_{\max} = 30°
Absorption correction: by integration (<i>SHELXTL</i> ; Bruker, 1998)	<i>h</i> = -1 → 11
<i>T</i> _{min} = 0.33, <i>T</i> _{max} = 0.59	<i>k</i> = -1 → 8
1797 measured reflections	<i>l</i> = -23 → 1
1377 independent reflections	3 standard reflections
1288 reflections with <i>I</i> > 2 σ (<i>I</i>)	every 97 reflections
	intensity decay: <2.5%

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.18	$\Delta\rho_{\max} = 0.44 \text{ e \AA}^{-3}$
1377 reflections	$\Delta\rho_{\min} = -1.07 \text{ e \AA}^{-3}$
135 parameters	Absolute structure: Flack (1983)
H atoms: see below	Flack parameter = 0.02 (2)

Water H-atom positions were located on a difference density map, and the aryl H-atom positions were calculated using a C–H distance

Table 1

Selected geometric parameters (Å, °).

Zn–O3	1.953 (3)	O1–C1	1.254 (5)
Zn–O1 ⁱ	1.955 (3)	O2–C1	1.264 (5)
Zn–O2 ⁱⁱ	1.978 (3)	O4–C8	1.255 (4)
Zn–O5	1.983 (3)	O3–C8	1.264 (5)
O3–Zn–O1 ⁱ	135.99 (14)	O1 ⁱ –Zn–O2 ⁱⁱ	102.09 (12)
O2 ⁱⁱⁱ –Zn–O5	106.27 (13)	O3–Zn–O5	100.71 (16)
O1 ⁱ –Zn–O5	105.13 (16)	C1–O2–Zn ⁱⁱⁱ	128.4 (2)
O3–Zn–O2 ⁱⁱ	104.04 (13)	C1–O1–Zn ^{iv}	112.9 (2)

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

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O5–HAO5...O4 ^v	0.88 (6)	1.83 (6)	2.708 (4)	173 (6)
O5–HBO5...O4 ^{vi}	0.92 (9)	1.90 (9)	2.711 (4)	145 (8)

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

of 0.93 Å. Water H atoms were refined isotropically and the remaining H atoms were refined using a riding model with fixed displacement parameters [$U_{ij} = 1.2U_{ij}(\text{eq})$ for the atom to which they were bonded]. The absolute configuration was determined by refinement of the *TWIN* and *BASF* commands in *SHELXL97* (Sheldrick, 1997) to give an estimated Flack (1983) parameter.

Data collection: *XSCANS* (Bruker, 1999); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*; molecular graphics: *SHELXTL/PC* (Bruker, 1994); software used to prepare material for publication: *X-SEED* (Barbour, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1593). Services for accessing these data are described at the back of the journal.

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