metal-organic compounds

Poly[[[(1,10-phenanthroline-$\kappa^2 N,N'$)-zinc(II)]-μ_3-5-hydroxyisophthalato-$\kappa^4 O,O':O'':O'''$] monohydrate]

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In the title compound, $\{[Zn(C_8H_4O_5)(C_{12}H_8N_2)]\cdot H_2O\}_n$ or $\{[Zn(OH\text{-}BDC)(phen)]\cdot H_2O\}_n$ (where OH-H$_2$BDC is 5-hydroxyisophthalic acid and phen is 1,10-phenanthroline), the Zn atoms are coordinated by two N atoms from the phen ligands and by four O atoms from hydroxyisophthalate ligands in a highly distorted octahedral geometry, with Zn—O distances in the range 2.042 (4)–2.085 (5) Å and Zn—N distances of 2.133 (5) and 2.137 (5) Å. The $\{[Zn(OH\text{-}BDC)(phen)]\cdot H_2O\}_n$ infinite zigzag polymer forms a helical chain of $[Zn_2(OH\text{-}BDC)_2]_n$ units. Face-to-face π–π interactions (3.60–3.75 Å) occur between two phen rings belonging to the same helical chain. Consolidation of the packing structure is achieved by O—H$\cdots$O hydrogen-bonding interactions between the carboxylate O atoms, the hydroxyl group and the water molecule, forming two-dimensional sheets.

Comment

Helical structures have attracted increasing attention in coordination and materials chemistry, being an essential element of living structures and important also in advanced materials, such as optical devices and asymmetric catalysis (Lehn, 1995). The design and synthesis of supramolecular coordination polymer networks, especially those constructed *via* hydrogen-bonding and π–π stacking interactions, has been a field of rapid growth because of their special physical properties and potential application in functional materials (Atwood *et al.*, 1996; Barton *et al.*, 1999). The coordination chemistry of aromatic polycarboxylate transition metal complexes has received considerable attention due to the variety of bridging abilities of polycarboxylates in the formation of porous frameworks (Mori *et al.*, 1997; Chui *et al.*, 1999; Lo *et al.*, 2000). 5-Hydroxyisophthalic acid, OH-H$_2$BDC, like benzene-1,3,5-tricarboxylic acid, has two carboxylic acid groups arranged *meta* to each other, but with a phenol hydroxy group *meta* to both (Plate *et al.*, 2001). This phenol hydroxy group was intended as a mimic for the third carboxy group, which remains protonated in other reported layered polymers (Foreman *et al.*, 1999), as well as in the title compound. As part of our research interest in new polycarboxylic acid-bridged polymeric complexes, the title complex, (I), was obtained by the hydrothermal reaction of OH-H$_2$BDC with zinc acetate and 1,10-phenanthroline (phen), as a colourless solid in 67.3% yield.
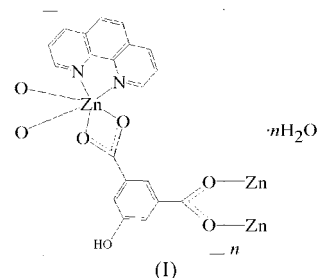

As shown in Fig. 1, the Zn atoms in (I) are six-coordinated *via* two N atoms from the phen ligand and four O atoms from hydroxyisophthalate ligands in a highly distorted octahedral geometry, with Zn—O distances in the range 2.042 (4)–2.085 (5) Å and Zn—N distances of 2.133 (5) and 2.137 (5) Å. These values are similar to those found in [Zn(phen)MoO$_4$] (Hagrman & Zubieta, 1999), [Zn$_2$(bpy)$_2$(MeCO$_2$)$_3$]ClO$_4$ (bpy is bipyridine; Chen & Tong, 1994) and in the closest relative *catena*-[(μ_2-adipato-O,O',O'',O''')(μ_2-adipato-O,O')diaqua-bis(1,10-phenanthroline)dizinc(II)] (Zheng *et al.*, 2002). The closest Zn$\cdots$Zn distance is 3.989 (4) Å, indicating no direct metal–metal interaction. The 5-hydroxyisophthalate acts as a tetradentate ligand in this structure, with one carboxylate group as bidentate to one Zn atom and the two remaining O atoms as monodentate to two further Zn atoms. The asymmetric unit thus consists of one Zn atom, one phen ligand bound in a bidentate manner, one hydroxyisophthalate ligand and one water molecule. One-dimensional chains are formed by the Zn cations and the carboxylate ligands, so that (I) contains a $[Zn_2(OH\text{-}BDC)_2]_n$ helical structure which is composed of eight- and sixteen-membered rings (Fig. 2). The phen ligands are at approximately 90° to these latter rings. The smallest repeat distance of the helical chain is 17.451 (2) Å.

The chains of (I) are linked by an O—H$\cdots$O hydrogen-bonding network consisting of carboxylate and hydroxy O atoms interacting with the H atoms of the water molecule, resulting in two-dimensional sheets (Table 2). Additionally, there are face-to-face π–π interactions between phen ligands belonging to the same helical chain (Fig. 2a), with phen–phen distances in the range 3.595 (4)–3.748 (3) Å, close to the sum of the van der Waals radii of two C atoms (Bondi, 1964). The usual π–π interaction is offset or slipped stacking, *i.e.* the rings are parallel displaced; the face-to-face π–π alignment seen in (I), where most of the ring-plane area overlaps, is a rare phenomenon (Janiak, 2000).
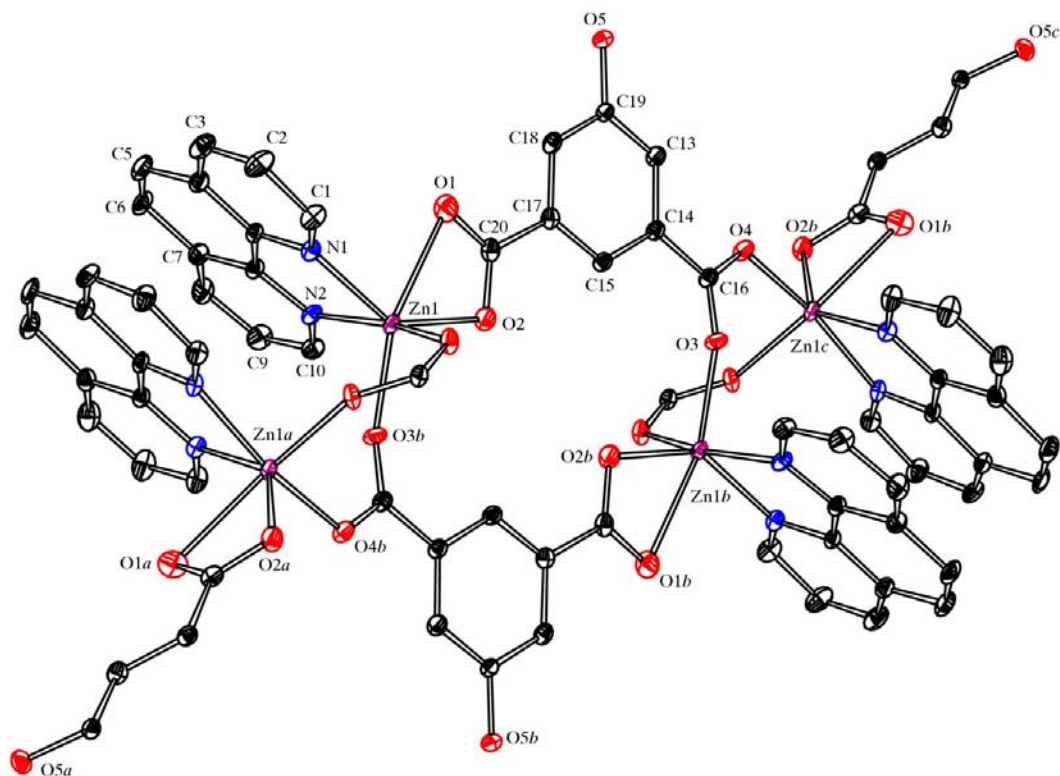
Figure 1
Part of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 60% probability level. H atoms and solvent water molecules have been omitted for clarity. Atoms labelled with the suffixes *a*, *b* and *c* are at the symmetry positions ($\frac{3}{2} - x, y, \frac{3}{2} - z$), ($2 - x, 1 - y, 2 - z$) and ($\frac{1}{2} + x, 1 - y, \frac{1}{2} + z$), respectively.
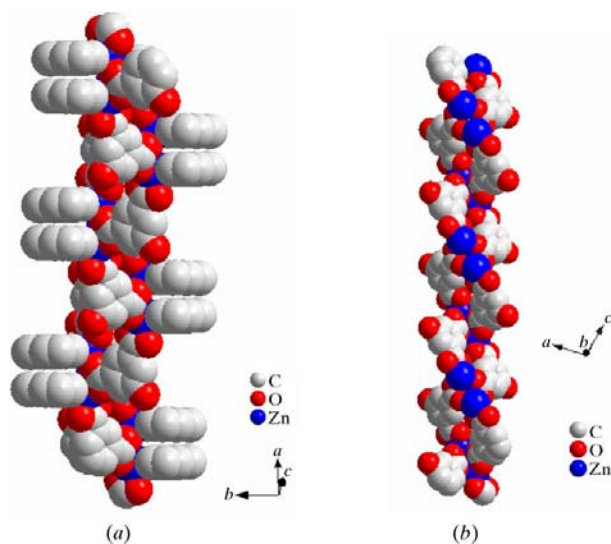
Figure 2
(*a*) A space-filling atomic diagram showing the zigzag chain of (I). (*b*) A space-filling plot of the $[Zn_2(OH\text{-}BDC)_2]_n$ double helix. H atoms have been omitted for clarity.

Experimental

A mixture of $Zn(CH_3CO_2)_2\cdot 2H_2O$ (0.5 mmol), OH-H_2BDC (0.5 mmol), phen (0.5 mmol), Na_2CO_3 (0.5 mmol) and water (16 ml) was sealed in a 25 ml stainless-steel reactor with a Teflon liner. The reaction system was heated at 433 K for 60 h. Slow cooling of the system to room temperature yielded colourless crystals of the title complex, which were collected by filtration.

Crystal data

$[Zn(C_8H_4O_5)(C_{12}H_8N_2)]\cdot H_2O$	$D_x = 1.665$ Mg m^{-3}
$M_r = 443.70$	Mo $K\alpha$ radiation
Monoclinic, $P2/n$	Cell parameters from 3603
$a = 8.7640\ (4)$ Å	reflections
$b = 12.1090\ (6)$ Å	$\theta = 1.7\text{–}25.0°$
$c = 17.0440\ (8)$ Å	$\mu = 1.43$ mm^{-1}
$\beta = 101.8460\ (10)°$	$T = 293\ (2)$ K
$V = 1770.24\ (15)$ Å^3	Prism, colourless
$Z = 4$	$0.40 \times 0.30 \times 0.20$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	3087 independent reflections
	2512 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.039$
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 25.0°$
	$h = -10 \rightarrow 9$
$T_{min} = 0.578$, $T_{max} = 0.751$	$k = -11 \rightarrow 14$
6008 measured reflections	$l = -20 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$+ 7.1455P]$
$wR(F^2) = 0.156$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{max} = 0.004$
3087 reflections	$\Delta\rho_{max} = 0.46$ e Å^{-3}
268 parameters	$\Delta\rho_{min} = -0.45$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

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Table 1
Selected geometric parameters (Å, °).

Zn1—O4^i	2.043 (4)	Zn1—N1	2.133 (4)
Zn1—O3^{ii}	2.071 (4)	Zn1—N2	2.137 (4)
Zn1—O2	2.086 (4)	Zn1—O1	2.429 (5)
O4^i—Zn1—O3^{ii}	92.45 (16)	O2—Zn1—N1	138.97 (17)
O4^i—Zn1—O2	95.16 (16)	O4^i—Zn1—N2	166.96 (17)
O3^{ii}—Zn1—O2	94.69 (16)	O3^{ii}—Zn1—N2	82.96 (16)
O4^i—Zn1—N1	95.53 (16)	O2—Zn1—N2	97.37 (17)
O3^{ii}—Zn1—N1	124.22 (16)	N1—Zn1—N2	77.27 (17)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$WB\cdots$O2	0.82 (6)	2.36 (8)	2.883 (6)	122 (8)
O1W—H1$WA\cdots$O4^i	0.82 (6)	2.01 (3)	2.817 (6)	169 (9)
O5—H5O$\cdots$O1W^{ii}	0.82	1.82	2.642 (7)	178.0

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

All H atoms, except water atoms H1WA and H1WB, were positioned geometrically and refined using a riding model [C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C), and O—H = 0.82 Å and U_{iso}(H) = 1.5U_{eq}(O)]. Atoms H1WA and H1WB were located from difference maps and refined isotropically, with O—H distances fixed at 0.82 Å and with U_{iso}(H) = 1.5U_{eq}(O).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1996); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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