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Aqua(dipicolinato-κ^3O,N,O')(1,10-phenanthroline-κ^2N,N')zinc(II) monohydrate

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Key indicators

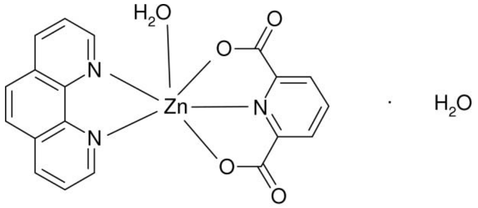
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.031
wR factor = 0.080
Data-to-parameter ratio = 24.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Zn(C_7H_3NO_4)(C_{12}H_8N_2)(H_2O)]\cdot H_2O$, is isostructural with the manganese(II) analogue. The Zn atom is coordinated by a tridentate dipicolinate dianion, a bidentate 1,10-phenanthroline molecule and a water molecule, resulting in a substantially distorted ZnO_3N_3 octahedral grouping. The crystal packing is consolidated by O—H···O hydrogen bonds and probable π–π stacking.

Comment

The title compound, (I), arose during our exploratory synthetic studies of coordination polymers containing divalent cations, the dipicolinate (dipic) dianion and multi-functional nitrogen-containing ligands such as 4,4-bipyridine (bipy) and 1,10-phenanthroline (phen). Compound (I) is isostructural with the manganese(II) analogue (Ma *et al.*, 2002).



(I)

The asymmetric unit of (I) contains a neutral aqua(dipicolinato)(1,10-phenanthroline)zinc(II) molecule accompanied by one water molecule of crystallization (Fig. 1). The dipic dianion bonds to zinc in an O,N,O'-tridentate mode and the phen is N,N'-bidentate. The distorted octahedral ZnO_3N_3 coordination (Table 1) is completed by a water molecule. The substantial deviations of the bond angles from ideal octa-

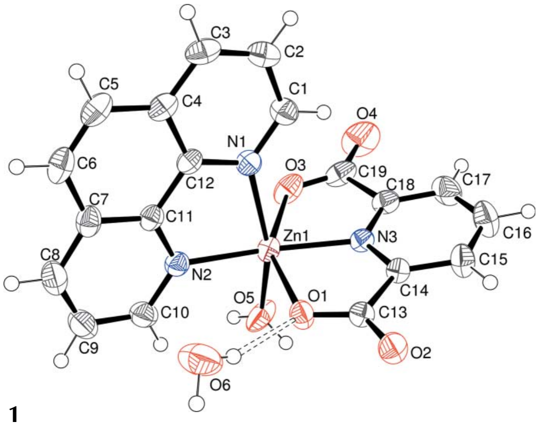


Figure 1
View of (I), showing 50% displacement ellipsoids and arbitrary spheres for the H atoms. The hydrogen bond is indicated by a dashed line.

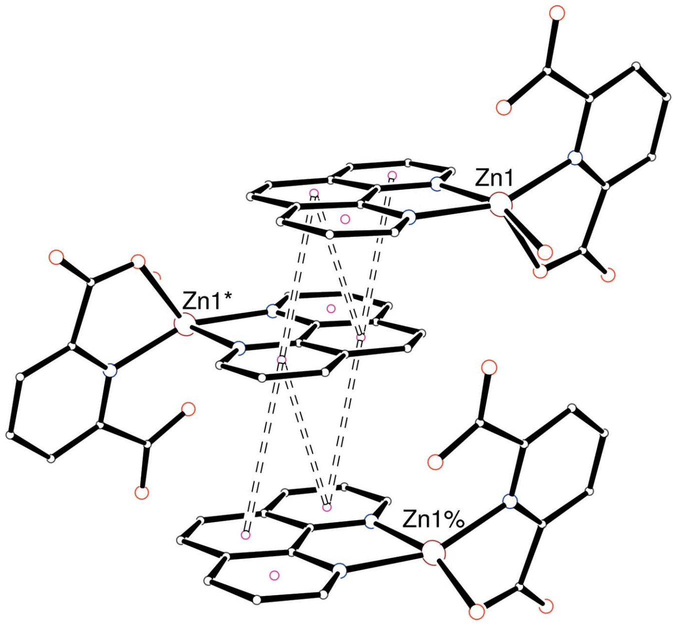


Figure 2
Detail of (I) showing probable π–π stacking interactions shorter than 3.8 Å (as dashed lines) linking the centroids (pink circles) of the phen rings. The Zn1* molecule is generated by the symmetry operation $(1 - x, 1 - y, z)$ and Zn1% by $(1 + x, y, z)$. H atoms have been omitted.

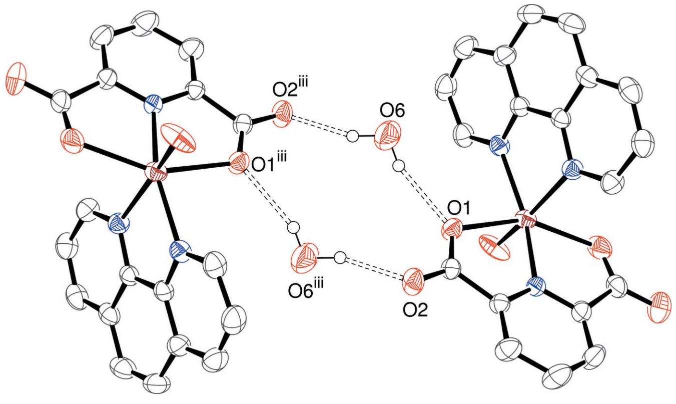


Figure 3
Detail of (I) showing the water-bridged dimeric entity. All H atoms except those of the non-coordinated water molecule have been omitted for clarity. The symmetry code is as in Table 2. Dashed lines indicate hydrogen bonds.

hedral values [range of *cis* angles = 73.99 (4)–122.56 (4)° and range of *trans* angles = 150.12 (4)–161.00 (5)°] may be correlated with the geometrical constraints imposed by the chelating ligands. The Zn—O$_d$ (d = dipic) bond lengths are distinctly different; both are substantially longer than the Zn—O$_w$ (w = water) bond. Very similar equivalent geometric values arose for the isostructural manganese complex (Ma *et al.*, 2002). Considered in isolation, the ZnO_3N_3 grouping in (I) adopts the *mer* geometric isomer. The dipic dianion is close to planar (for the non-H atoms, r.m.s. deviation from the mean plane = 0.028 Å) and the bipy molecule, as expected, is essentially flat (r.m.s. deviation from the mean plane = 0.036 Å). The zinc cation deviates from the dipic and bipy mean planes by 0.0828 (9) and 0.0232 (11) Å, respectively. The dihedral angle between the dipic and bipy planes is 80.08 (2)° [equivalent value for the Mn congener = 81.5 (1)°].

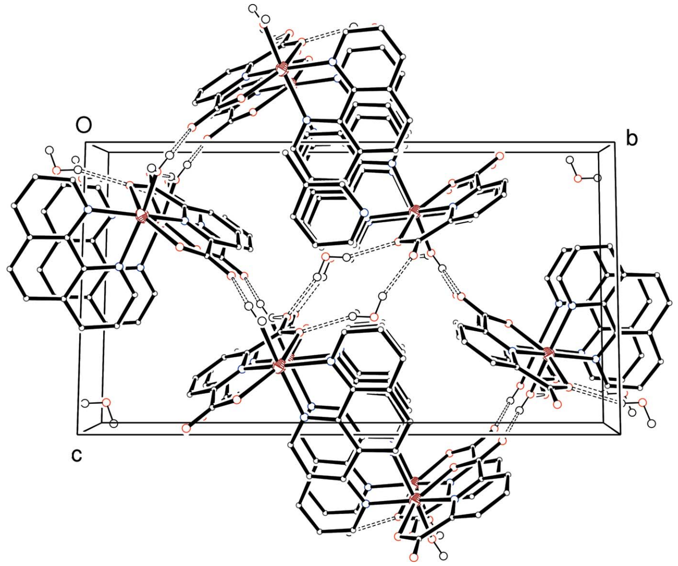


Figure 4
The packing of (I), viewed along [100]. Only H atoms involved in hydrogen bonds (dashed lines) are shown.

The packing in (I) involves a network of O—H⋯O hydrogen bonds (Table 2) and probable π–π stacking interactions (Fig. 2) involving the phen ring systems. The shortest π–π ring-centroid separation of 3.4981 (9) Å involves the centroid, *Cg*1, of the N1/C1–C4/C12 phen ring and its inversion-generated partner, $Cg1^{\mathrm{i}}$ [symmetry code: (i) $1 - x, 1 - y, z$]. In the crystal structure, the solvent water molecules connect complex molecules *via* O—H⋯O hydrogen bonds, forming centrosymmetric clusters (Fig. 3). In addition, intermolecular O—H⋯O hydrogen bonds involving the coordinated water molecules connect these clusters into a three-dimensional network (Fig. 4 and Table 2), as in the Mn analogue (Ma *et al.*, 2002).

Compound (I) complements a number of previously described dipicolinate complexes of zinc which show a wide variety of metal–ligand binding modes. For example, in $(C_3H_5N_2)_2[Zn(dipic)_2]\cdot 2H_2O$ (MacDonald *et al.*, 2000), two dipic dianions bond to zinc and the resulting overall dianion is charge-balanced by two imidazolinium cations. In $Zn(Hdipic)_2\cdot 3H_2O$ (Håkansson *et al.*, 1993), two Hdipic monoanions chelate the zinc cation, resulting in a neutral molecule. In $Zn_2(dipic)_2(H_2O)_5\cdot 2H_2O$ (Håkansson *et al.*, 1993), a dipic ligand acts as a bridge between two Zn centres (one coordinated by two tridentate dipic anions and one coordinated by a monodentate dipic O atom and five water molecules). In $(C_5H_8N_3)[Zn(dipic)(Hdipic)]\cdot 3H_2O$ (Ranjbar *et al.*, 2002), one dipic dianion and one Hdipic anion bind to zinc, with 2,6-diaminopyridinium serving as the charge-balancing cation. The complex formula of $[Zn(phen)_3]_4(NO_3)_7\cdot Hdipic\cdot 26H_2O$ (Moghimi *et al.*, 2005) corresponds to a crystal structure in which the Hdipic anion does not bond to Zn. Finally, a novel variant to (I) is provided by $[Zn(bipy)_2(H_2O)_2][Zn(dipic)_2]\cdot 7H_2O$ (Moghimi *et al.*, 2005), in which the bipy mol-

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ecules and dipic dianions complex separate zinc centres, resulting in a molecular salt.

Experimental

A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (27 mg), pyridine-2,6-dicarboxylic acid (20 mg), 1,10-phenanthroline monohydrate (24 mg) and water (2.0 ml) (molar ratio = *ca* 1:1:1:9300) was sealed in a 23 ml Teflon-lined stainless steel bomb and kept at 423 K under autogenous pressure for 72 h. After slowly cooling ($10\ K\ h^{-1}$) to room temperature, needle-shaped colourless crystals of (I) were obtained by filtration and rinsing with water and diethyl ether (yield 72%). Analysis calculated for $C_{19}H_{17}N_3O_7Zn$: C 49.6, H 2.71, N 9.16%; found: C 50.71, H 2.72, N 9.46%. Thermogravimetric analysis for (I) (ramp at $10\ K\ min^{-1}$ under N_2) revealed a weight loss of 6.7% between 463 and 468 K, probably corresponding to the loss of both coordinated and non-coordinated water molecules (calculated 8.5%). The dipic and phen ligands decompose slowly (weight loss = 44.8%) over the broad temperature range 493–1173 K. IR (KBr, cm^{-1}): 3445, 1637, 1583, 640, 430.

Crystal data

$[Zn(C_7H_3NO_4)(C_{12}H_8N_2)(H_2O)] \cdot H_2O$
$M_r = 446.71$
Monoclinic, $P2_1/c$
$a = 7.5199\ (3)$ Å
$b = 20.9079\ (8)$ Å
$c = 11.5755\ (4)$ Å
$\beta = 100.135\ (1)^\circ$
$V = 1791.56\ (12)$ Å^3
$Z = 4$
$D_x = 1.656$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7488 reflections
$\theta = 2.7$–32.0°
$\mu = 1.42$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.21 × 0.20 × 0.20 mm

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{min} = 0.747$, $T_{max} = 0.757$
21156 measured reflections
6439 independent reflections
4678 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 32.5^\circ$
$h = -10 \rightarrow 11$
$k = -31 \rightarrow 31$
$l = -13 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.080$
$S = 0.97$
6439 reflections
263 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0020 (5)

Table 1
Selected bond lengths (Å).

Zn1—O5	2.0513 (11)	Zn1—O3	2.1941 (11)
Zn1—N3	2.0540 (11)	Zn1—N1	2.2071 (12)
Zn1—N2	2.1168 (11)	Zn1—O1	2.2651 (10)

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H51···O4^{i}	0.84	1.79	2.6058 (17)	162
O5—H52···O2^{ii}	0.83	1.90	2.7162 (15)	167
O6—H61···O2^{iii}	0.90	1.98	2.8461 (18)	161
O6—H62···O1	0.83	2.14	2.9356 (16)	160

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

The water H atoms were located in difference maps and refined as riding in their as-found relative positions. The C-bound H atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) was applied in all cases.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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