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Bis(4,4′-bipyridine-*κN*)bis(hydrogen phthalato)-*κ*²*O*,*O*′;*κO*-zinc(II)

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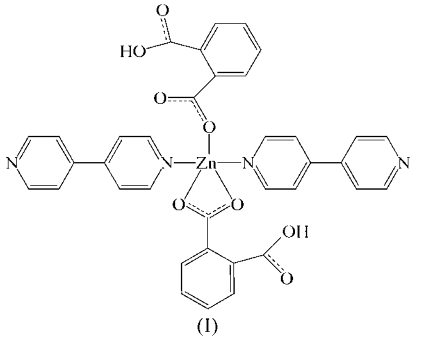
The title compound, $[Zn(C_8H_5O_4)_2(C_{10}H_8N_2)_2]$, was obtained by the hydrothermal reaction of $ZnSO_4·7H_2O$ with phthalic acid (H_2pht) and 4,4′-bipyridine (4,4′-bipy). Crystallographic analysis shows that it has a one-dimensional double-chain structure *via* hydrogen-bonding interactions. Each Zn^{II} atom, adopting a distorted tetrahedral geometry, is coordinated by two N atoms from two 4,4′-bipy ligands, with Zn—N distances of 2.054 (4) and 2.104 (4) Å, and by two O atoms from symmetry-related Hpht$^-$ ligands, with Zn—O distances of 1.921 (4) and 2.019 (4) Å.

Comment

The design and construction of novel coordination polymers based on covalent interactions (Fujita *et al.*, 1994) or supramolecular contacts, such as hydrogen bonds and π–π stacking interactions (Desiraju, 1995), is a rapidly developing research area, due not only to their fascinating structures (Blake *et al.*, 1999; Batten & Robson, 1998) but also to their unexpected properties for potential applications (Matsumoto *et al.*, 1999; Chui *et al.*, 1999). The design of coordination polymers is greatly influenced by factors such as the coordination nature of the metal ion, the structural characteristics of the polydentate organic ligand, the metal–ligand ratio, and the possible counter-ion. We report here the title novel metal–organic coordination polymer, (I), obtained by the hydrothermal reaction of 4,4′-bipy, H_2pht and $ZnSO_4·7H_2O$.



(I)

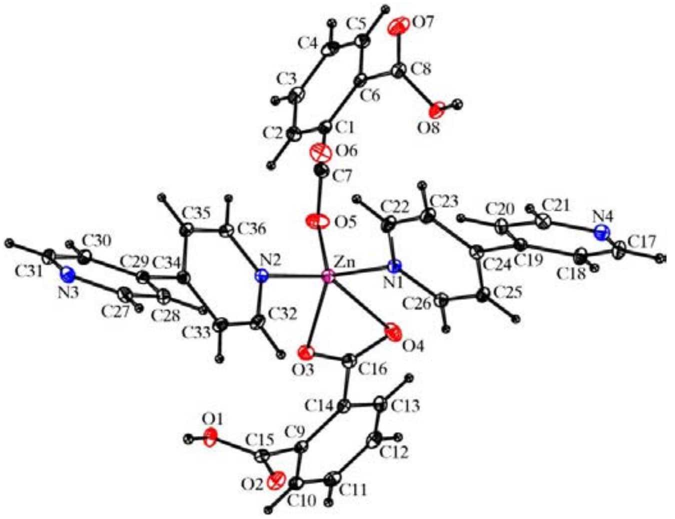


Figure 1
A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The present X-ray single-crystal diffraction study reveals that compound (I) consists of one Zn^{II} atom, two Hpht$^-$ ligands and two 4,4′-bipy ligands. As shown in Fig. 1, each Zn^{II} atom is four-coordinated tetrahedrally by two O atoms from two Hpht$^-$ ligands, with Zn—O bond lengths of 1.921 (4) and 2.019 (4) Å, and by two N atoms of two 4,4′-bipy ligands, with Zn—N bond distances of 2.054 (4) and 2.104 (4) Å. However, the Zn—O4 distance of 2.496 (4) Å suggests a non-negligible interaction with the uncoordinated O atom, which may be described as a semi-chelating coordination mode (Guilera & Steed, 1999). Hence, the Zn^{II} atom may also be regarded as having a trigonal–bipyramidal geometry. The aforementioned bond lengths agree with those observed in similar Zn complexes (Wu *et al.*, 2002). Each 4,4′-bipy ligand acts as a terminal ligand to link to one Zn^{II} atom. Within each 4,4′-bipy molecule, the two pyridine rings are twisted by 33.61 and 44.88° relative to one another.

As each Hpht$^-$ and 4,4′-bipy ligand acts as a terminal ligand, the uncoordinated carboxylic acid groups from the Hpht$^-$ ligands link to the uncoordinated N atoms from the 4,4′-bipy ligands *via* hydrogen bonding. The O1···N3 and O8···N4 distances are 2.643 (5) and 2.665 (6) Å, respectively, indicating strong hydrogen bonds. The two C═O bonds, *viz*. C15—O2 and C8—O7, are 1.191 (6) and 1.218 (7) Å, respectively; these are much shorter than the other C—O bonds.

It is interesting to note that two Zn^{II} atoms, two 4,4′-bipy molecules and two Hpht$^-$ anions produce a 30-membered grid, with a Zn···Zn distance of 14.024 (7) Å, *via* coordination covalent bonds and hydrogen bonds. These grids, by sharing Zn^{II} atoms, extend to form double zigzag chains propagating along the *c* axis (Fig. 2).

In contrast with other metal–organic frameworks constructed with 4,4′-bipy ligands and H_2pht (Ma *et al.*, 2003; Lightfoot & Sneddon, 1999; Suresh *et al.*, 2001), 4,4′-bipy acts as a terminal ligand in (I) instead of as a μ_2-bridging ligand

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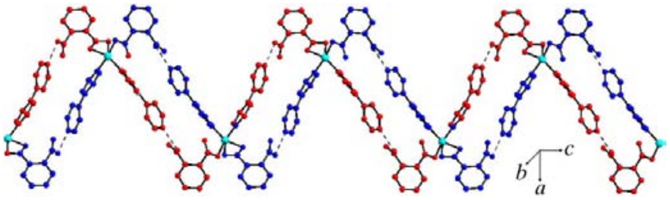

Figure 2
The double zigzag chains formed along the *c* axis of the crystal of (I), with hydrogen bonds shown as dotted lines.

Table 1
Selected geometric parameters (Å, °).

Zn—O5	1.921 (4)	Zn—N2	2.104 (4)
Zn—O3	2.019 (4)	Zn—O4	2.496 (5)
Zn—N1	2.054 (4)		
O5—Zn—O3	106.29 (19)	N1—Zn—N2	94.83 (16)
O5—Zn—N1	120.43 (19)	O5—Zn—O4	90.3 (2)
O3—Zn—N1	123.09 (16)	O3—Zn—O4	57.19 (14)
O5—Zn—N2	113.3 (2)	N1—Zn—O4	90.31 (15)
O3—Zn—N2	94.71 (15)	N2—Zn—O4	148.40 (16)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···N3^{i}	0.83 (6)	1.82 (6)	2.643 (5)	175 (7)
O8—H8O···N4^{ii}	0.83 (6)	1.84 (6)	2.665 (6)	172 (8)

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

and this results in a different structural topology. This also suggests that the combination of coordination covalent bonds and hydrogen bonds is an important tool for the construction of supramolecular architectures.

Experimental

A mixture of $ZnSO_4\cdot7H_2O$ (0.144 g, 0.5 mmol), 4,4′-bipy (0.080 g, 0.5 mmol) and H_2pht (0.166 g, 0.5 mmol) in EtOH–H_2O (1:8 *v*/*v*, 18 ml) was sealed in a Teflon-lined stainless steel vessel and heated at 438 K for 36 h under autogeneous pressure. A large quantity of colourless crystals of (I) (yield 56%) was obtained after the solution had cooled to room temperature.

Crystal data

$[Zn(C_8H_5O_4)_2(C_{10}H_8N_2)_2]$
$M_r = 708.00$
Triclinic, $P\overline{1}$
$a = 7.5100$ (3) Å
$b = 10.0003$ (4) Å
$c = 22.0821$ (6) Å
$\alpha = 84.307$ (1)°
$\beta = 88.084$ (1)°
$\gamma = 71.020$ (1)°
$V = 1560.52$ (10) Å^3
$Z = 2$
$D_x = 1.507$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3960 reflections
$\theta = 0.9$–25.0°
$\mu = 0.85$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.56 × 0.26 × 0.18 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.767$, $T_{max} = 0.858$
8036 measured reflections
5502 independent reflections
4273 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 25.0°$
$h = -5 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -23 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.177$
$S = 1.07$
5390 reflections
448 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0795P)^2 + 3.685P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}

H atoms bonded to C atoms were positioned geometrically and refined using a riding model [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. The hydroxy H atoms were located from difference maps. Their coordinates were refined subject to O—H distance restraints of 0.83 (6) Å and with the U_{iso} values fixed at $1.5U_{eq}(O)$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL* (Siemens, 1994); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL* (Bruker, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1166). Services for accessing these data are described at the back of the journal.

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