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Poly[[aqua(μ_2-4,4′-bipyridine)(μ_5-4,4′-oxydibenzene-1,2-carboxylato)di-zinc(II)] 4,4′-bipyridine hemisolvate]

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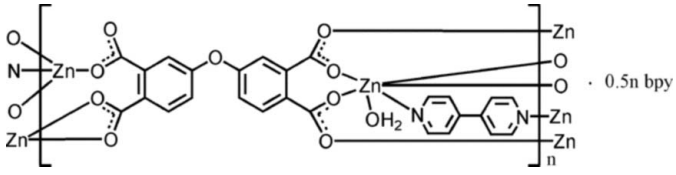
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.007 Å; R factor = 0.048; wR factor = 0.099; data-to-parameter ratio = 12.6.

A new three-dimensional metal–organic framework, $\{[Zn_2(C_{16}H_6O_9)(C_{10}H_8N_2)(H_2O)]\cdot 0.5C_{10}H_8N_2\}_n$, is a porous three-dimensional bipyridyl-pillared framework with rhombic channels built from two-dimensional helical double layers of Zn–DETA [DETA is 4,4′-oxydi(benzene-1,2- carboxylate)] with the 4,4′-bipyridyl guest molecules locked in the cavities through short O—H···N hydrogen bonds.

Related literature

For related literature, see: Cheng *et al.* (2006); Chui *et al.* (1999); Dietzel *et al.* (2006); Fujita *et al.* (1994); He *et al.* (2006); Hong (2005); Li *et al.* (1999); Sun *et al.* (2006); Wang *et al.* (2006); Xiao *et al.* (2006); Zheng *et al.* (2006); Tao *et al.* (2000).



Experimental

Crystal data

$[Zn_2(C_{16}H_6O_9)(C_{10}H_8N_2)(H_2O)]\cdot 0.5C_{10}H_8N_2$
M_r = 725.28
Monoclinic, $P2_1/n$
a = 10.9516 (4) Å
b = 15.1202 (5) Å
c = 16.5498 (4) Å
β = 92.0630 (10)°
V = 2738.71 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.82 mm^{-1}
T = 293 (2) K
0.28 × 0.25 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.606, T_{max} = 0.695
13598 measured reflections
5211 independent reflections
3672 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.099
S = 1.08
5211 reflections
415 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.63 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O6^{iv}	0.82	1.95	2.770 (4)	173
O1W—H1WB···N3	0.85	2.14	2.863 (6)	143

Symmetry code: (iv) $-x, -y, -z$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *XPREP* (Siemens, 1996); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GG3085).

References

Bruker (1997). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cheng, J. W., Zhang, J., Zheng, S. T., Zhang, M. B. & Yang, G. Y. (2006). *Angew. Chem. Int. Ed.* **45**, 73–77.
Chui, S. S.-Y., Lo, S. M.-F., Charmant, J. P. H., Orpen, A. G. & Williams, I. D. (1999). *Science*, **283**, 1148–1150.
Dietzel, P. D. C., Panella, B., Hirscher, M., Blom, R. & Fjellvag, H. (2006). *Chem. Commun.* pp. 959–961.
Fujita, M., Kwon, Y. J., Washizu, S. & Ogura, K. (1994). *J. Am. Chem. Soc.* **116**, 1151–1152.
He, J. R., Wang, Y. L., Bi, W. H., Zhu, X. D. & Cao, R. (2006). *J. Mol. Struct.* **787**, 63–68.
Hong, J. (2005). *J. Mol. Struct.* **752**, 166–169.
Li, H., Eddaoudi, M., Keeffe, M. & Yaghi, O. M. (1999). *Nature (London)*, **402**, 276–279.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Siemens (1996). *XPREP*, *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sun, H. L., Ma, B. Q., Gao, S. & Batten, S. R. (2006). *Cryst. Growth Des.* **6**, 1261–1263.
Tao, J., Tong, M. L., Shi, J. X., Chen, X. M. & Ng, S. W. (2000). *Chem. Commun.* pp. 2043–2044..
Wang, X. L., Qin, C., Wang, E. B. & Su, Z. M. (2006). *Chem. Eur. J.* **12**, 2680–2691.
Xiao, D. R., Wang, E. B., An, H. Y., Li, Y. G., Su, Z. M. & Sun, C. Y. (2006). *Chem. Eur. J.* **12**, 6528–6541.
Zheng, Y. Z., Tong, M. L., Zhang, W. X. & Chen, X. M. (2006). *Angew. Chem. Int. Ed.* **45**, 6310–6314

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supplementary materials

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Poly[[aqua(μ_2-4,4'-bipyridine)(μ_5-4,4'-oxydibenzene-1,2-carboxylato)dizinc(II)] 4,4'-bipyridine hemisolvate]

P.-X. Yin, Z.-J. Li, X.-Y. Cao, Y.-Y. Qin and Y.-G. Yao

Comment

The rational design and synthesis of extended metal-organic frameworks (MOFs) is important and amongst the new classes of solid functional materials has applications in magnetism, as optical materials, in catalysis and gas absorption/separation, but also by their novel diverse molecular architectures and topologies (Zheng *et al.*, 2006; Sun *et al.*, 2006; Fujita *et al.*, 1994; Dietzel *et al.*, 2006). In this family, metal carboxylates have attracted much attention: among the numerous ligands employed in this field, by far the most common are the rigid aromatic polycarboxylate ligands including 1,2-benzenedicarboxylate, 1,3,5-benzenetricarboxylate and 1,2,4,5-benzenetetracarboxylate, which have been extensively utilized in the fabrication of extended MOFs with interesting structures and desired properties (Cheng *et al.*, 2006; Chui *et al.*, 1999; Li *et al.*, 1999). However, reports on MOFs based on flexible polycarboxylate ligands have been relatively scarce. Against this background, we have selected a flexible divergent carboxylic acid 3,3',4,4'-diphenyl ether-tetracarboxylic acid (H_4DETA), to construct new complexes with the cooperativity of an auxiliary bpy ligand as a rigid organic spacer. The title compound, (I), was obtained under hydrothermal conditions as a pale yellow solid in good yield.

There are two crystallographically independent Zn centers in the asymmetric unit (Fig. 1). The Zn1 center has a distorted tetrahedral coordination geometry being defined by three carboxylate atoms from three different DETA ligands with Zn—O distances from 1.942 (3) to 1.975 (3) Å, and a N atom (Zn1—N = 2.045 (3) Å) from a bpy ligand occupying the 4t h site, whereas the Zn2 center is coordinated by four carboxylate atoms from two distinct DETA ligands Zn—O 2.008 (3) to 2.099 (3) Å, a longer Zn—O 2.373 (4) Å, Zn—O_{aqua} 2.180 (3) Å and one bipy N atom Zn—N at 2.086 (4) Å, providing a highly distorted octahedral coordination polyhedron (with two O sites at symmetry related positions). The Zn—O and Zn—N distances at Zn2 are slightly longer than those at Zn1 but all values are comparable with those reported for Zn related complexes (Tao *et al.*, 2000; Wang *et al.*, 2006; He *et al.*, 2006; Hong 2005). There is also a unique DETA ligand in the fundamental unit of (I), which is bent about the central ether bond with a dihedral angle between the two phenyl rings of 72.28 (2)°. The V-shaped DETA favors the formation of helices as authenticated by BTDC (where BTDC is 3,3',4,4'-benzophenone tetracarboxylate). (Hong 2005; Xiao *et al.*, 2006). It serves as a tetra-connector with its four carboxylate arms in three coordination modes, monodentate, bidentate and *syn*—anti bridging bidentate, linking Zn atoms into 2-D (two-dimensional) helical double layer subunit, (Fig. 2). There are no Zn···Zn interactions.

A feature of (I) is the two-dimensional helical double layers which are further pillared up by bpy ligands resulting in a 3-D host–guest structure: the neutral 3-D host architecture of Zn—DETA—bpy, which consists of one-dimensional rhombus channels along the [100] direction (Fig. 3), encapsulates the guest bpy ligands *via* hydrogen bonding interactions between the guest bpy ligands and the nearest coordinated water molecules (O_1W—H_1W···N3, 2.859 (6) Å).

Experimental

A mixture of $Zn(CH_3CO_2)_2·2H_2O$ (0.120 g, 0.55 mmol), 4,4'-oxyphthalic anhydride (0.081 g, 0.26 mmol), 4,4'-bpy (0.088 g, 0.56 mmol) in a molar ratio of about 2.1:1:2.1 and water (15 ml) were placed in a 25 ml Teflon-lined stainless steel reactor and heated to 453 K for 76 h. When the reactor was cooled to room temperature over a period of 3 d, yellow prismatic single crystals suitable for X-ray diffraction were obtained.

Refinement

All H atoms, except for the aqua H atoms, were positioned geometrically and refined using a riding model [C—H = 0.93 Å] and $U_{iso}(H) = 1.2U_{eq}(C)$. The water H atoms were located from difference maps and refined isotropically, with O—H distances fixed at 0.82/0.85 Å and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Figures

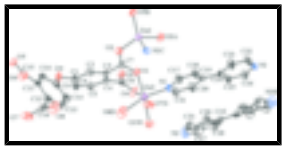


Fig. 1. *ORTEP* representation of the coordination environment around the Zn centers, showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level. H atoms have been omitted for clarity [Symmetry codes: (*a*) −*x*, 1 − *y*, −*z*; (*b*) 1/2 − *x*, 1/2 + *y*, 1/2 − *z*; (*c*) 1/2 − *x*, −1/2 + *y*, −1/2 − *z*; (*d*) −*x*, 1 − *y*, −*z*; e, −*x*, 1 − *y*, −1 − *z*].

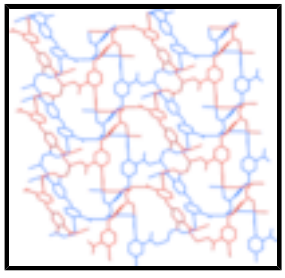


Fig. 2. View of the two-dimensional helical double layer in (I).

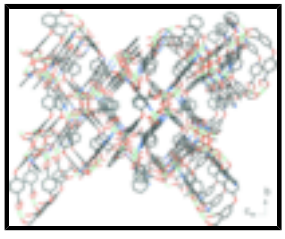


Fig. 3. Perspective view of the 3-D framework, highlighting the 1-D rhombus channels. Guest bpy molecules included in the channels are omitted for clarity.

Poly[[aqua(μ$_2$-4,4'-bipyridine)(μ$_4$-4,4'-oxydibenzene-1,2- carboxylato)dizinc(II)] 4,4'-bipyridine hemisolvate]

Crystal data

$[Zn_2(C_{16}H_6O_9)(C_{10}H_8N_2)(H_2O)]·0.5C_{10}H_8N_2$	F_{000} = 1468
M_r = 725.28	D_x = 1.759 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 4772 reflections
a = 10.9516 (4) Å	θ = 1.8–25.7°

b = 15.1202 (5) Å	μ = 1.82 mm^{-1}
c = 16.5498 (4) Å	T = 293 (2) K
β = 92.0630 (10)º	Prism, yellow
V = 2738.71 (15) Å^3	0.28 × 0.25 × 0.20 mm
Z = 4	

Data collection

Siemens SMART CCD area-detector diffractometer	5211 independent reflections
Radiation source: fine-focus sealed tube	3672 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.054
T = 293(2) K	θ_{max} = 25.7º
φ and ω scans	θ_{min} = 1.8º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −13→13
T_{min} = 0.606, T_{max} = 0.695	k = −18→18
13598 measured reflections	l = −20→11

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.048	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.099	$w = 1/[\sigma^2(F_o^2) + (0.0268P)^2 + 5.3897P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.08	$(\Delta/\sigma)_{max} < 0.001$
5211 reflections	$\Delta\rho_{max}$ = 0.50 e Å^{-3}
415 parameters	$\Delta\rho_{min}$ = −0.63 e Å^{-3}
2 restraints	Extinction correction: none

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}

Zn1	0.28659 (5)	0.39722 (3)	0.03206 (3)	0.02325 (14)
Zn2	−0.10394 (5)	0.35096 (3)	−0.13285 (3)	0.02633 (15)
O1W	−0.2490 (3)	0.3177 (2)	−0.22115 (19)	0.0378 (8)
H1WA	−0.2298	0.2733	−0.2462	0.057*
H1WB	−0.2648	0.3551	−0.2583	0.057*
O1	0.0277 (3)	0.3752 (2)	−0.04076 (17)	0.0335 (8)
O2	0.1330 (3)	0.3517 (2)	0.07326 (18)	0.0320 (7)
O3	−0.2645 (3)	0.49931 (19)	0.03977 (18)	0.0319 (8)
O4	−0.2214 (3)	0.4210 (2)	−0.06792 (18)	0.0374 (8)
O5	0.0825 (3)	−0.0796 (2)	0.38851 (18)	0.0323 (8)
O6	0.1656 (3)	−0.1681 (2)	0.29850 (19)	0.0379 (8)
O7	−0.0057 (3)	−0.2528 (2)	0.1830 (2)	0.0473 (10)
O8	0.1323 (4)	−0.1990 (3)	0.1029 (2)	0.0599 (11)
O9	−0.1372 (3)	0.1490 (2)	0.22898 (18)	0.0388 (8)
N1	−0.0411 (3)	0.4590 (2)	−0.1978 (2)	0.0270 (9)
N2	0.1499 (3)	0.8058 (2)	−0.4527 (2)	0.0266 (9)
N3	−0.2168 (5)	0.3922 (4)	−0.3780 (3)	0.0637 (14)
C1	−0.1547 (4)	0.2161 (3)	0.1711 (3)	0.0311 (11)
C2	−0.0578 (4)	0.2483 (3)	0.1292 (3)	0.0291 (11)
H2B	0.0197	0.2242	0.1377	0.035*
C3	−0.0761 (4)	0.3176 (3)	0.0734 (2)	0.0216 (9)
C4	−0.1928 (4)	0.3543 (3)	0.0637 (2)	0.0223 (9)
C5	−0.2867 (4)	0.3236 (3)	0.1104 (3)	0.0299 (11)
H5	−0.3627	0.3510	0.1062	0.036*
C6	−0.2696 (4)	0.2530 (3)	0.1631 (3)	0.0326 (11)
H6	−0.3340	0.2311	0.1923	0.039*
C7	0.0348 (4)	0.3511 (3)	0.0313 (3)	0.0235 (10)
C8	−0.2258 (4)	0.4302 (3)	0.0075 (3)	0.0225 (10)
C9	−0.0858 (4)	0.0700 (3)	0.2056 (3)	0.0280 (11)
C10	−0.0280 (4)	0.0212 (3)	0.2669 (3)	0.0296 (11)
H10	−0.0210	0.0444	0.3189	0.036*
C11	0.0193 (4)	−0.0620 (3)	0.2513 (3)	0.0236 (10)
C12	0.0088 (4)	−0.0963 (3)	0.1728 (3)	0.0273 (10)
C13	−0.0484 (5)	−0.0449 (3)	0.1119 (3)	0.0357 (12)
H13	−0.0554	−0.0673	0.0596	0.043*
C14	−0.0945 (4)	0.0380 (3)	0.1275 (3)	0.0345 (12)
H14	−0.1309	0.0716	0.0862	0.041*
C15	0.0944 (4)	−0.1088 (3)	0.3168 (3)	0.0263 (10)
C16	0.0501 (5)	−0.1880 (3)	0.1511 (3)	0.0389 (13)
C17	0.0756 (4)	0.4700 (3)	−0.2140 (3)	0.0367 (12)
H17	0.1326	0.4294	−0.1935	0.044*
C18	0.1155 (5)	0.5394 (3)	−0.2603 (3)	0.0410 (13)
H18	0.1983	0.5451	−0.2698	0.049*
C19	0.0339 (4)	0.6006 (3)	−0.2929 (2)	0.0241 (10)
C20	−0.0867 (4)	0.5901 (3)	−0.2732 (3)	0.0361 (12)
H20	−0.1453	0.6306	−0.2915	0.043*
C21	−0.1202 (5)	0.5192 (3)	−0.2263 (3)	0.0354 (12)
H21	−0.2019	0.5133	−0.2139	0.042*
C22	0.2286 (5)	0.7506 (3)	−0.4162 (3)	0.0451 (14)

H22	0.3112	0.7563	−0.4265	0.054*
C23	0.1937 (5)	0.6853 (3)	−0.3639 (3)	0.0460 (14)
H23	0.2527	0.6488	−0.3397	0.055*
C24	0.0727 (4)	0.6734 (3)	−0.3469 (3)	0.0268 (10)
C25	−0.0089 (4)	0.7326 (3)	−0.3832 (3)	0.0374 (12)
H25	−0.0918	0.7287	−0.3731	0.045*
C26	0.0329 (4)	0.7973 (3)	−0.4344 (3)	0.0358 (12)
H26	−0.0235	0.8369	−0.4573	0.043*
C27	−0.2418 (6)	0.4675 (5)	−0.4165 (4)	0.073 (2)
H27	−0.3186	0.4923	−0.4107	0.088*
C28	−0.1606 (6)	0.5114 (4)	−0.4650 (4)	0.0627 (18)
H28	−0.1836	0.5640	−0.4904	0.075*
C29	−0.0460 (5)	0.4770 (4)	−0.4753 (3)	0.0437 (14)
C30	−0.0191 (6)	0.3989 (4)	−0.4357 (4)	0.0646 (18)
H30	0.0573	0.3728	−0.4403	0.077*
C31	−0.1056 (7)	0.3594 (4)	−0.3892 (4)	0.074 (2)
H31	−0.0852	0.3062	−0.3640	0.089*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0235 (3)	0.0229 (3)	0.0233 (3)	0.0029 (2)	0.0008 (2)	−0.0003 (2)
Zn2	0.0308 (3)	0.0257 (3)	0.0228 (3)	0.0013 (2)	0.0042 (2)	0.0018 (2)
O1W	0.035 (2)	0.0387 (19)	0.040 (2)	0.0004 (15)	0.0028 (16)	−0.0032 (16)
O1	0.0298 (19)	0.051 (2)	0.0194 (17)	−0.0076 (15)	−0.0007 (14)	0.0065 (14)
O2	0.0225 (18)	0.0423 (19)	0.0310 (17)	−0.0011 (15)	−0.0006 (14)	0.0051 (15)
O3	0.044 (2)	0.0240 (17)	0.0278 (17)	0.0096 (15)	0.0028 (15)	0.0020 (14)
O4	0.046 (2)	0.046 (2)	0.0207 (17)	0.0228 (17)	0.0052 (15)	0.0053 (15)
O5	0.0323 (19)	0.0406 (19)	0.0237 (17)	0.0031 (15)	−0.0011 (14)	−0.0015 (14)
O6	0.037 (2)	0.0361 (19)	0.040 (2)	0.0130 (16)	−0.0106 (16)	−0.0065 (15)
O7	0.045 (2)	0.0231 (18)	0.073 (3)	0.0018 (16)	−0.020 (2)	−0.0029 (18)
O8	0.075 (3)	0.060 (3)	0.046 (2)	0.022 (2)	0.012 (2)	−0.007 (2)
O9	0.057 (2)	0.0313 (18)	0.0287 (18)	0.0116 (17)	0.0087 (16)	0.0111 (15)
N1	0.033 (2)	0.025 (2)	0.023 (2)	−0.0009 (17)	0.0020 (17)	0.0011 (16)
N2	0.026 (2)	0.026 (2)	0.029 (2)	−0.0028 (17)	0.0012 (17)	0.0047 (17)
N3	0.070 (4)	0.071 (4)	0.051 (3)	−0.008 (3)	0.010 (3)	0.000 (3)
C1	0.038 (3)	0.025 (2)	0.030 (3)	0.001 (2)	0.007 (2)	0.007 (2)
C2	0.025 (3)	0.025 (2)	0.037 (3)	0.007 (2)	0.002 (2)	0.004 (2)
C3	0.025 (3)	0.023 (2)	0.018 (2)	0.0019 (19)	0.0005 (18)	0.0011 (18)
C4	0.023 (2)	0.019 (2)	0.025 (2)	0.0032 (19)	0.0013 (18)	0.0013 (19)
C5	0.021 (3)	0.031 (3)	0.038 (3)	0.009 (2)	0.007 (2)	0.006 (2)
C6	0.025 (3)	0.032 (3)	0.041 (3)	0.000 (2)	0.009 (2)	0.007 (2)
C7	0.022 (2)	0.021 (2)	0.027 (3)	0.0039 (19)	0.002 (2)	−0.001 (2)
C8	0.012 (2)	0.026 (2)	0.029 (3)	0.0018 (18)	0.0020 (19)	0.0027 (19)
C9	0.026 (3)	0.017 (2)	0.041 (3)	0.0009 (19)	0.005 (2)	0.005 (2)
C10	0.034 (3)	0.024 (2)	0.031 (3)	−0.002 (2)	−0.003 (2)	0.001 (2)
C11	0.023 (2)	0.020 (2)	0.027 (2)	−0.0007 (19)	−0.0024 (19)	0.0027 (19)
C12	0.025 (3)	0.020 (2)	0.037 (3)	−0.0017 (19)	−0.002 (2)	0.002 (2)

C13	0.044 (3)	0.032 (3)	0.030 (3)	−0.001 (2)	−0.006 (2)	0.000 (2)
C14	0.040 (3)	0.026 (3)	0.037 (3)	−0.001 (2)	−0.004 (2)	0.007 (2)
C15	0.021 (2)	0.025 (2)	0.033 (3)	−0.007 (2)	−0.001 (2)	−0.002 (2)
C16	0.046 (3)	0.037 (3)	0.033 (3)	0.009 (3)	−0.020 (3)	−0.007 (2)
C17	0.026 (3)	0.038 (3)	0.046 (3)	0.006 (2)	−0.001 (2)	0.019 (2)
C18	0.026 (3)	0.044 (3)	0.053 (3)	−0.002 (2)	−0.001 (2)	0.020 (3)
C19	0.025 (3)	0.024 (2)	0.023 (2)	−0.001 (2)	0.0007 (19)	0.0003 (19)
C20	0.032 (3)	0.027 (3)	0.050 (3)	0.006 (2)	0.014 (2)	0.013 (2)
C21	0.030 (3)	0.033 (3)	0.044 (3)	0.008 (2)	0.012 (2)	0.008 (2)
C22	0.022 (3)	0.049 (3)	0.065 (4)	−0.002 (2)	0.006 (3)	0.028 (3)
C23	0.033 (3)	0.046 (3)	0.058 (4)	0.007 (3)	0.004 (3)	0.029 (3)
C24	0.032 (3)	0.022 (2)	0.026 (2)	−0.001 (2)	0.002 (2)	−0.0018 (19)
C25	0.026 (3)	0.042 (3)	0.045 (3)	−0.001 (2)	0.009 (2)	0.015 (2)
C26	0.030 (3)	0.034 (3)	0.043 (3)	0.008 (2)	0.005 (2)	0.012 (2)
C27	0.048 (4)	0.101 (6)	0.071 (5)	−0.001 (4)	−0.002 (4)	0.015 (4)
C28	0.053 (4)	0.079 (5)	0.055 (4)	0.003 (4)	−0.013 (3)	0.022 (3)
C29	0.055 (4)	0.050 (3)	0.025 (3)	−0.002 (3)	−0.004 (2)	−0.007 (2)
C30	0.082 (5)	0.050 (4)	0.064 (4)	0.012 (3)	0.024 (4)	0.008 (3)
C31	0.111 (6)	0.049 (4)	0.065 (4)	0.005 (4)	0.035 (4)	0.002 (3)

Geometric parameters (Å, °)

Zn1—O2	1.962 (3)	C5—C6	1.388 (6)
Zn1—O3^{i}	1.975 (3)	C5—H5	0.9300
Zn1—O5^{ii}	1.942 (3)	C6—H6	0.9300
Zn1—N2^{iii}	2.045 (3)	C9—C14	1.380 (6)
Zn2—N1	2.086 (3)	C9—C10	1.388 (6)
Zn2—O1	2.092 (3)	C10—C11	1.389 (6)
Zn2—O4	2.008 (3)	C10—H10	0.9300
Zn2—O7^{iv}	2.099 (3)	C11—C12	1.399 (6)
Zn2—O8^{iv}	2.373 (4)	C11—C15	1.513 (6)
Zn2—O1W	2.179 (3)	C12—C13	1.402 (6)
Zn2—C16^{iv}	2.554 (5)	C12—C16	1.506 (6)
O1W—H1WA	0.8200	C13—C14	1.379 (6)
O1W—H1WB	0.8486	C13—H13	0.9300
O1—C7	1.246 (5)	C14—H14	0.9300
O2—C7	1.260 (5)	C16—Zn2^{iv}	2.554 (5)
O3—C8	1.254 (5)	C17—C18	1.380 (6)
O3—Zn1^{i}	1.975 (3)	C17—H17	0.9300
O4—C8	1.258 (5)	C18—C19	1.383 (6)
O5—C15	1.278 (5)	C18—H18	0.9300
O5—Zn1^{v}	1.942 (3)	C19—C20	1.381 (6)
O6—C15	1.233 (5)	C19—C24	1.489 (6)
O7—C16	1.278 (6)	C20—C21	1.381 (6)
O7—Zn2^{iv}	2.099 (3)	C20—H20	0.9300
O8—C16	1.235 (6)	C21—H21	0.9300
O8—Zn2^{iv}	2.373 (4)	C22—C23	1.376 (6)

O9—C9	1.381 (5)	C22—H22	0.9300
O9—C1	1.404 (5)	C23—C24	1.377 (6)
N1—C17	1.326 (6)	C23—H23	0.9300
N1—C21	1.331 (6)	C24—C25	1.387 (6)
N2—C22	1.330 (6)	C25—C26	1.384 (6)
N2—C26	1.334 (6)	C25—H25	0.9300
N2—Zn1^{vi}	2.045 (3)	C26—H26	0.9300
N3—C27	1.328 (8)	C27—C28	1.388 (8)
N3—C31	1.334 (8)	C27—H27	0.9300
C1—C6	1.378 (6)	C28—C29	1.375 (8)
C1—C2	1.378 (6)	C28—H28	0.9300
C2—C3	1.405 (6)	C29—C30	1.379 (7)
C2—H2B	0.9300	C29—C29^{vii}	1.491 (11)
C3—C4	1.398 (6)	C30—C31	1.377 (8)
C3—C7	1.509 (6)	C30—H30	0.9300
C4—C5	1.388 (6)	C31—H31	0.9300
C4—C8	1.513 (6)		
O5^{ii}—Zn1—O2	116.70 (13)	O9—C9—C10	115.8 (4)
O5^{ii}—Zn1—O3^{i}	109.63 (13)	C9—C10—C11	120.6 (4)
O2—Zn1—O3^{i}	113.51 (13)	C9—C10—H10	119.7
O5^{ii}—Zn1—N2^{iii}	107.27 (14)	C11—C10—H10	119.7
O2—Zn1—N2^{iii}	107.57 (14)	C10—C11—C12	119.3 (4)
O3^{i}—Zn1—N2^{iii}	100.73 (13)	C10—C11—C15	119.2 (4)
O4—Zn2—N1	95.29 (14)	C12—C11—C15	121.1 (4)
O4—Zn2—O1	87.45 (13)	C11—C12—C13	118.8 (4)
N1—Zn2—O1	90.38 (13)	C11—C12—C16	123.1 (4)
O4—Zn2—O7^{iv}	166.27 (14)	C13—C12—C16	118.0 (4)
N1—Zn2—O7^{iv}	98.40 (14)	C14—C13—C12	121.7 (4)
O1—Zn2—O7^{iv}	91.34 (13)	C14—C13—H13	119.1
O4—Zn2—O1W	90.86 (13)	C12—C13—H13	119.1
N1—Zn2—O1W	94.67 (13)	C13—C14—C9	118.7 (4)
O1—Zn2—O1W	174.81 (12)	C13—C14—H14	120.6
O7^{iv}—Zn2—O1W	89.13 (12)	C9—C14—H14	120.6
O4—Zn2—O8^{iv}	107.94 (14)	O6—C15—O5	124.5 (4)
N1—Zn2—O8^{iv}	156.04 (14)	O6—C15—C11	119.7 (4)
O1—Zn2—O8^{iv}	96.31 (13)	O5—C15—C11	115.6 (4)
O7^{iv}—Zn2—O8^{iv}	58.59 (14)	O8—C16—O7	122.3 (5)
O1W—Zn2—O8^{iv}	79.54 (13)	O8—C16—C12	120.6 (5)
O4—Zn2—C16^{iv}	136.67 (17)	O7—C16—C12	117.1 (5)
N1—Zn2—C16^{iv}	127.79 (17)	O8—C16—Zn2^{iv}	67.5 (3)
O1—Zn2—C16^{iv}	95.69 (14)	O7—C16—Zn2^{iv}	54.9 (2)
O7^{iv}—Zn2—C16^{iv}	29.90 (16)	C12—C16—Zn2^{iv}	171.5 (4)
O1W—Zn2—C16^{iv}	82.18 (13)	N1—C17—C18	122.3 (4)
O8^{iv}—Zn2—C16^{iv}	28.74 (15)	N1—C17—H17	118.9

Zn2—O1W—H1WA	109.5	C18—C17—H17	118.9
Zn2—O1W—H1WB	117.2	C17—C18—C19	120.9 (5)
H1WA—O1W—H1WB	103.2	C17—C18—H18	119.6
C7—O1—Zn2	131.5 (3)	C19—C18—H18	119.6
C7—O2—Zn1	122.5 (3)	C20—C19—C18	116.1 (4)
C8—O3—Zn1^{i}	116.1 (3)	C20—C19—C24	121.6 (4)
C8—O4—Zn2	129.6 (3)	C18—C19—C24	122.3 (4)
C15—O5—Zn1^{v}	117.9 (3)	C21—C20—C19	119.9 (4)
C16—O7—Zn2^{iv}	95.2 (3)	C21—C20—H20	120.1
C16—O8—Zn2^{iv}	83.8 (3)	C19—C20—H20	120.1
C9—O9—C1	118.8 (3)	N1—C21—C20	123.2 (4)
C17—N1—C21	117.5 (4)	N1—C21—H21	118.4
C17—N1—Zn2	122.7 (3)	C20—C21—H21	118.4
C21—N1—Zn2	119.7 (3)	N2—C22—C23	123.1 (5)
C22—N2—C26	116.7 (4)	N2—C22—H22	118.4
C22—N2—Zn1^{vi}	119.1 (3)	C23—C22—H22	118.4
C26—N2—Zn1^{vi}	124.3 (3)	C22—C23—C24	120.9 (5)
C27—N3—C31	115.1 (6)	C22—C23—H23	119.5
C6—C1—C2	121.7 (4)	C24—C23—H23	119.5
C6—C1—O9	117.4 (4)	C23—C24—C25	116.0 (4)
C2—C1—O9	120.7 (4)	C23—C24—C19	121.2 (4)
C1—C2—C3	120.0 (4)	C25—C24—C19	122.9 (4)
C1—C2—H2B	120.0	C26—C25—C24	120.0 (4)
C3—C2—H2B	120.0	C26—C25—H25	120.0
C4—C3—C2	118.6 (4)	C24—C25—H25	120.0
C4—C3—C7	124.1 (4)	N2—C26—C25	123.3 (4)
C2—C3—C7	117.1 (4)	N2—C26—H26	118.3
C5—C4—C3	119.8 (4)	C25—C26—H26	118.3
C5—C4—C8	115.4 (4)	N3—C27—C28	124.2 (7)
C3—C4—C8	124.7 (4)	N3—C27—H27	117.9
C6—C5—C4	121.4 (4)	C28—C27—H27	117.9
C6—C5—H5	119.3	C29—C28—C27	119.8 (6)
C4—C5—H5	119.3	C29—C28—H28	120.1
C1—C6—C5	118.3 (4)	C27—C28—H28	120.1
C1—C6—H6	120.8	C28—C29—C30	116.4 (5)
C5—C6—H6	120.8	C28—C29—C29^{vii}	122.0 (7)
O1—C7—O2	123.2 (4)	C30—C29—C29^{vii}	121.6 (7)
O1—C7—C3	121.1 (4)	C31—C30—C29	119.8 (6)
O2—C7—C3	115.6 (4)	C31—C30—H30	120.1
O3—C8—O4	122.7 (4)	C29—C30—H30	120.1
O3—C8—C4	116.6 (4)	N3—C31—C30	124.5 (6)
O4—C8—C4	120.6 (4)	N3—C31—H31	117.7
C14—C9—O9	123.4 (4)	C30—C31—H31	117.7
C14—C9—C10	120.8 (4)		

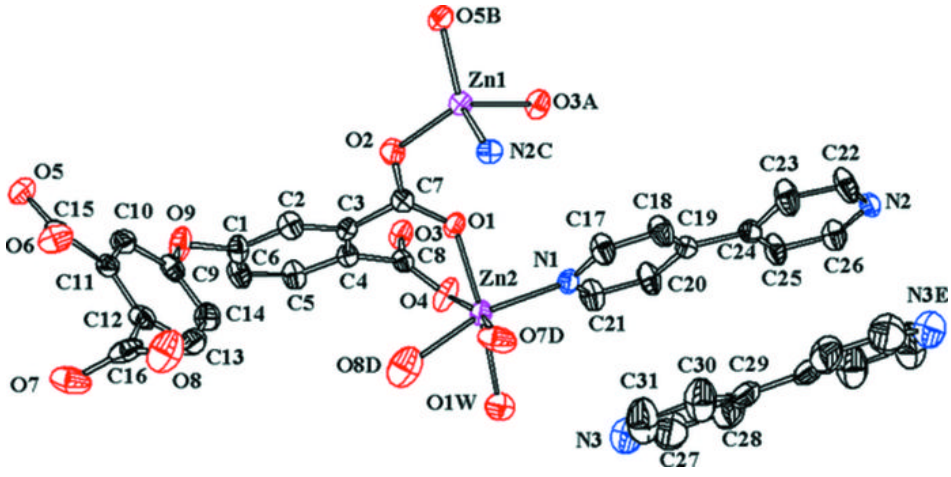
Symmetry codes: (i) −*x*, −*y*+1, −*z*; (ii) −*x*+1/2, *y*+1/2, −*z*+1/2; (iii) −*x*+1/2, *y*−1/2, −*z*−1/2; (iv) −*x*, −*y*, −*z*; (v) −*x*+1/2, *y*−1/2, −*z*+1/2; (vi) −*x*+1/2, *y*+1/2, −*z*−1/2; (vii) −*x*, −*y*+1, −*z*−1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1WA···O6^{iv}	0.82	1.95	2.770 (4)	173
O1W—H1WB···N3	0.85	2.14	2.863 (6)	143

Symmetry codes: (iv) −*x*, −*y*, −*z*.

Fig. 1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Zn1
O3A
O2
N2C
O5
C15
C10
O9
C1
C2
C3
C7
O1
C23
C22
N2
O6
C11
C9
C6
C4
C5
O3
C8
Zn2
N1
C17
C18
C19
C24
C25
C26
C12
C14
O4
C20
C21
N3E
O7
C16
O8
C13
O8D
O7D
C31
C30
C29
O1W
N3
C28
C27

Fig. 2

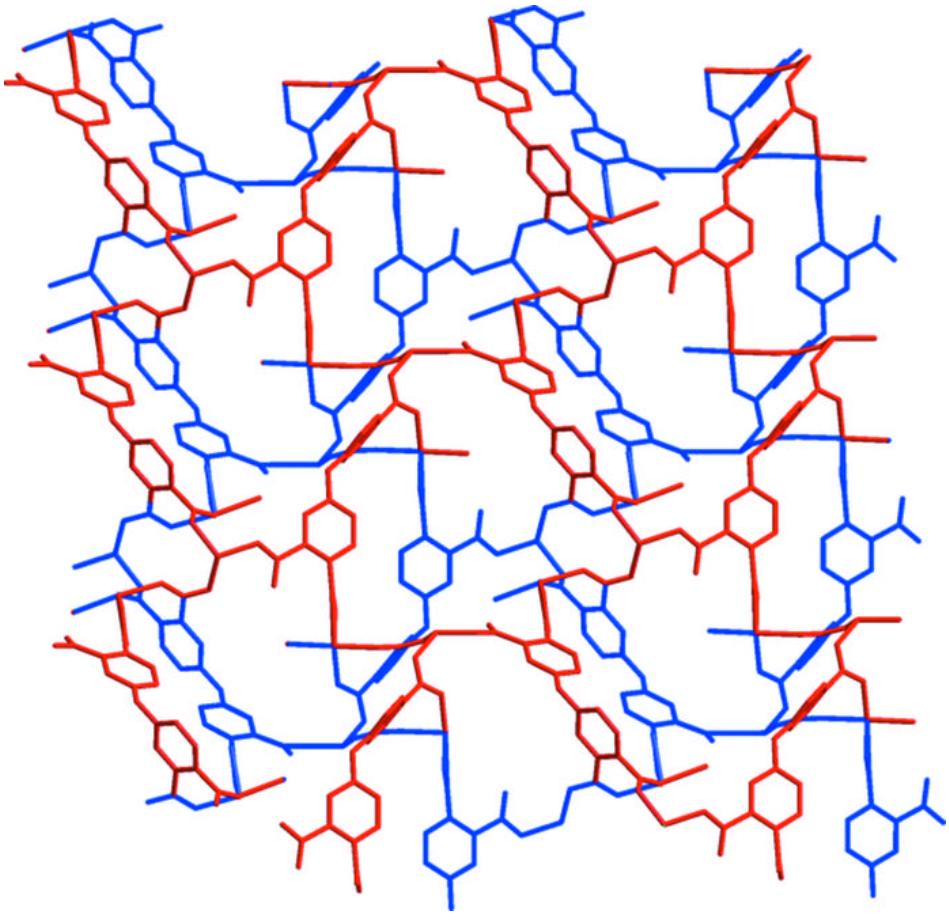

Fig. 3