

catena-Poly[[[aquabis(4,4'-bipyridine- κ N)zinc]- μ -L-tyrosinato- κ^3 N,O¹:O^{1'}] nitrate dihydrate]

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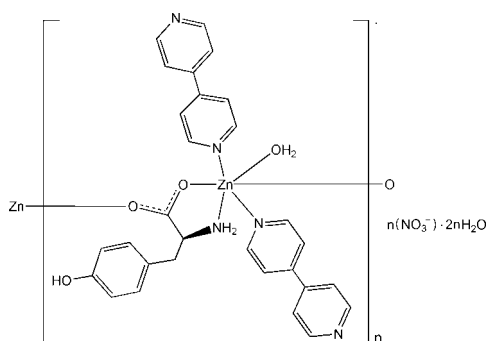
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.010$ Å; R factor = 0.056; wR factor = 0.091; data-to-parameter ratio = 12.8.

In the title compound, $[[\text{Zn}(\text{C}_9\text{H}_{10}\text{NO}_3)(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})-\text{NO}_3 \cdot 2\text{H}_2\text{O}]_n$, the Zn^{II} atom is six-coordinated in a distorted octahedral geometry by two carboxylate O atoms and one amino N atom from two L-tyrosinate ligands, two N atoms from two 4,4'-bipyridine ligands, and one water molecule. Adjacent Zn atoms are bridged by the bidentate carboxylate groups into a cationic chain extending along [010]. $\text{N}-\text{H} \cdots \text{N}$, $\text{O}-\text{H} \cdots \text{N}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds link the cationic chains, nitrate anions and uncoordinated water molecules into a supramolecular network. $\pi-\pi$ interactions between the pyridine rings and between the pyridine and benzene rings [centroid-centroid distances = 3.615 (4) and 3.636 (4) Å] are present.

Related literature

For general background to the structures and properties of chiral coordination polymers, see: Dai *et al.* (2005); Kesanli & Lin (2003); Vaidhyanathan *et al.* (2006); Zaworotko (2001). For related structures, see: Lou & Hong (2008); Lou *et al.* (2005, 2007); Zhang & Hu (2009).



Experimental

Crystal data

$[\text{Zn}(\text{C}_9\text{H}_{10}\text{NO}_3)(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})-\text{NO}_3 \cdot 2\text{H}_2\text{O}]_n$
 $M_r = 673.98$
 Monoclinic, $P2_1$
 $a = 12.737$ (3) Å
 $b = 10.351$ (2) Å
 $c = 12.921$ (3) Å
 $\beta = 117.897$ (5)°
 $V = 1505.5$ (6) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.88$ mm⁻¹
 $T = 293$ K
 $0.22 \times 0.09 \times 0.02$ mm

Data collection

Bruker APEX CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.830$, $T_{\text{max}} = 0.983$
 7908 measured reflections
 5199 independent reflections
 3621 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.091$
 $S = 0.97$
 5199 reflections
 406 parameters
 1 restraint
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.47$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.42$ e Å⁻³
 Absolute structure: Flack (1983), 2352 Friedel pairs
 Flack parameter: 0.045 (14)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1A} \cdots \text{N3}^{\text{i}}$	0.90	2.49	3.336 (6)	156
$\text{O3}-\text{H3} \cdots \text{O4}$	0.86	1.94	2.748 (7)	155
$\text{O1W}-\text{H1C} \cdots \text{O2W}$	0.82	1.79	2.611 (6)	173
$\text{O1W}-\text{H1D} \cdots \text{N3}^{\text{ii}}$	0.82	2.33	3.133 (6)	167
$\text{O2W}-\text{H2A} \cdots \text{O4}^{\text{iii}}$	0.82	2.10	2.889 (7)	160
$\text{O2W}-\text{H2B} \cdots \text{O3W}$	0.82	1.97	2.774 (7)	168
$\text{O3W}-\text{H3C} \cdots \text{O6}^{\text{iv}}$	0.83	2.20	2.962 (7)	153
$\text{O3W}-\text{H3D} \cdots \text{N5}^{\text{v}}$	0.82	2.09	2.851 (6)	154

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

Data collection: SMART (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and Mercury (Macrae *et al.*, 2006); 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: HG5047).

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supplementary materials

Acta Cryst. (2011). E67, m884-m885 [doi:10.1107/S1600536811021088]

***catena*-Poly[[[aquabis(4,4'-bipyridine- κ N)zinc]- μ -L-tyrosinato- κ^3 N, O^1 : O^1'] nitrate dihydrate]**

S.-Q. Li and N.-H. Hu

Comment

There has been considerable interest in chiral coordination polymers, which exhibit potential applications in asymmetric catalysis and chiral separation (Kesanli & Lin, 2003). Self-assembly based on a mixed-ligand system containing both chiral and achiral ligands is an effective approach to the construction of chiral complexes (Dai *et al.*, 2005; Vaidhyanathan *et al.*, 2006; Zaworotko, 2001). Amino acids can be used as chiral building blocks, with their amino and carboxylate groups binding to metal ions in flexible modes (Lou *et al.*, 2005, 2007; Lou & Hong, 2008). We previously reported a chiral two-dimensional coordination polymer, [Cu₂(L-tyr)₂(4,4-bipy)(NO₃)₂(H₂O)₂]_n, (II), which contains Cu^{II} ions, L-tyrosinate (L-tyr) and 4,4'-bipyridine (4,4-bipy) ligands in a 2:2:1 ratio (Zhang & Hu, 2009). Herein, we present the title compound, (I), a one-dimensional Zn(II) complex with a 1:1:2 ratio of the metal ion and organic ligands.

In (I), the Zn^{II} atom is six-coordinated by two O atoms and one N atom from two L-tyr ligands, two N atoms from two 4,4'-bipy ligands and one water molecule in a distorted octahedral geometry (Fig. 1). The L-tyr ligand bridges adjacent Zn atoms through the carboxylate group, forming a cationic chiral [Zn(L-tyr)(4,4-bipy)₂(H₂O)]_n chain extending along [0 1 0]. The separation between the Zn atoms in the chain is 5.441 (1) Å. The hydroxyl O atom of the phenol group is uncoordinated. The L-tyr ligand binds to the Zn atoms in a μ -(κ^3 N, O : O') mode, the same as that observed in (II). However, the 4,4'-bipy ligand adopts a monodentate terminal mode, different from the bridging mode in (II), which leads to a one-dimensional comb-like structure (Fig. 2) rather than a layer structure as shown in (II). Therefore, in the mixed-ligand system, the L-tyr ligand provides a chiral source, while the binding mode of the 4,4'-bipy ligand is an important factor affecting structural architectures. N—H \cdots N, O—H \cdots N and O—H \cdots O hydrogen bonds (Table 1) link the cationic chains, nitrate anions and uncoordinated water molecules into a supramolecular network. Intrachain π – π interactions between the pyridine rings, Cg1 \cdots Cg2ⁱ = 3.615 (4) Å, and interchain π – π interactions between the pyridine and benzene rings, Cg2 \cdots Cg3ⁱⁱ = 3.636 (4) Å, stabilize the structure [Cg1, Cg2 and Cg3 are the centroids of the N3/C15–C19, N5/C25–C29 and C4–C9 rings. Symmetry codes: (i) 2 - x, -1/2 + y, -z; (ii) 1 + x, y, 1 + z].

Experimental

Zn(NO₃)₂·6H₂O (0.119 g, 0.4 mmol) and L-tyrosine (0.072 g, 0.4 mmol) were dissolved in hot water (25 ml) under stirring. To this solution 4,4'-bipyridine (0.062 g, 0.4 mmol) in methanol (10 ml) was added. The resulting solution was allowed to stand at room temperature and yellow crystals suitable for X-ray diffraction analysis were obtained after two weeks.

Refinement

H atoms bonded to O atoms were located in a difference Fourier map and refined as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Other H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 (aromatic), 0.97 (CH₂) and 0.98 (CH) Å and N—H = 0.90 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Figures

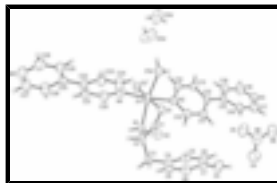


Fig. 1. The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $2 - x, -1/2 + y, -z$.]

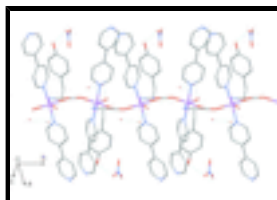


Fig. 2. A view of the chain structure in the title compound. H atoms have been omitted for clarity. Dashed lines denote hydrogen bonds.

catena-Poly[[aquabis(4,4'-bipyridine- κ N)zinc - μ -L-tyrosinato- κ^3 N, O^1 : O^1 '] nitrate dihydrate]

Crystal data

$[\text{Zn}(\text{C}_9\text{H}_{10}\text{NO}_3)(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$

$M_r = 673.98$

Monoclinic, $P2_1$

Hall symbol: $P\ 2_1yb$

$a = 12.737\ (3)\ \text{\AA}$

$b = 10.351\ (2)\ \text{\AA}$

$c = 12.921\ (3)\ \text{\AA}$

$\beta = 117.897\ (5)^\circ$

$V = 1505.5\ (6)\ \text{\AA}^3$

$Z = 2$

$F(000) = 700$

$D_x = 1.487\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 5180 reflections

$\theta = 2.0\text{--}25.1^\circ$

$\mu = 0.88\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Column, yellow

$0.22 \times 0.09 \times 0.02\ \text{mm}$

Data collection

Bruker APEX CCD
diffractometer

Radiation source: sealed tube
graphite

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.830, T_{\max} = 0.983$

7908 measured reflections

5199 independent reflections

3621 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

$\theta_{\max} = 25.1^\circ, \theta_{\min} = 1.8^\circ$

$h = -11 \rightarrow 15$

$k = -12 \rightarrow 12$

$l = -15 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.056$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$wR(F^2) = 0.091$	$w = 1/[\sigma^2(F_o^2) + (0.0098P)^2]$
$S = 0.97$	where $P = (F_o^2 + 2F_c^2)/3$
5199 reflections	$(\Delta/\sigma)_{\max} < 0.001$
406 parameters	$\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$
1 restraint	$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 2352 Friedel pairs Flack parameter: 0.045 (14)

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.98663 (5)	0.52948 (6)	0.05781 (6)	0.03552 (18)
O1	0.9437 (3)	0.7189 (3)	-0.0165 (4)	0.0392 (10)
O2	0.9765 (3)	0.8500 (3)	-0.1340 (4)	0.0357 (11)
O3	0.4363 (3)	0.5483 (5)	-0.4711 (4)	0.0674 (14)
H3	0.3776	0.6001	-0.4868	0.101*
O4	0.2786 (5)	0.7124 (6)	-0.4484 (5)	0.0832 (19)
O5	0.4065 (4)	0.7555 (4)	-0.2707 (4)	0.0655 (14)
O6	0.2188 (4)	0.7763 (6)	-0.3267 (5)	0.0892 (19)
O1W	0.9788 (3)	0.6216 (4)	0.2010 (4)	0.0521 (12)
H1C	1.0047	0.6030	0.2708	0.078*
H1D	0.9433	0.6905	0.1879	0.078*
O2W	1.0732 (4)	0.5515 (5)	0.4204 (4)	0.0979 (18)
H2A	1.1231	0.6008	0.4678	0.147*
H2B	1.0447	0.5075	0.4538	0.147*
O3W	0.9978 (4)	0.3726 (5)	0.5315 (4)	0.0868 (18)
H3C	0.9287	0.3486	0.4905	0.130*
H3D	1.0422	0.3110	0.5413	0.130*
N1	0.9777 (3)	0.5024 (4)	-0.1113 (4)	0.0343 (13)
H1A	1.0334	0.4451	-0.1055	0.041*
H1B	0.9060	0.4704	-0.1617	0.041*
N2	0.7974 (4)	0.4738 (4)	-0.0048 (5)	0.0357 (13)
N3	0.1952 (4)	0.3563 (6)	-0.1416 (5)	0.0517 (15)
N4	1.1758 (4)	0.5685 (4)	0.1397 (5)	0.0419 (15)
N5	1.7923 (4)	0.7197 (6)	0.3878 (5)	0.0560 (17)
N6	0.3008 (6)	0.7476 (6)	-0.3472 (6)	0.0569 (18)
C1	0.9696 (4)	0.7405 (5)	-0.0963 (5)	0.0303 (14)
C2	0.9972 (4)	0.6270 (5)	-0.1564 (5)	0.0323 (15)
H2	1.0823	0.6317	-0.1328	0.039*
C3	0.9319 (4)	0.6385 (6)	-0.2899 (5)	0.0385 (15)
H3A	0.9466	0.7234	-0.3121	0.046*
H3B	0.9636	0.5750	-0.3230	0.046*
C4	0.7991 (5)	0.6185 (6)	-0.3409 (5)	0.0398 (16)
C5	0.7253 (5)	0.7113 (6)	-0.3317 (5)	0.0419 (16)
H5	0.7578	0.7901	-0.2967	0.050*
C6	0.6048 (5)	0.6907 (6)	-0.3729 (5)	0.0453 (17)
H6	0.5583	0.7541	-0.3633	0.054*

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C7	0.5535 (6)	0.5759 (6)	-0.4284 (6)	0.0501 (19)
C8	0.6243 (6)	0.4824 (6)	-0.4417 (6)	0.0502 (19)
H8	0.5902	0.4062	-0.4814	0.060*
C9	0.7457 (5)	0.5019 (6)	-0.3962 (5)	0.0447 (18)
H9	0.7926	0.4366	-0.4024	0.054*
C10	0.7067 (4)	0.5145 (7)	-0.1040 (5)	0.0410 (15)
H10	0.7238	0.5597	-0.1564	0.049*
C11	0.5883 (5)	0.4938 (5)	-0.1342 (5)	0.0410 (18)
H11	0.5285	0.5253	-0.2046	0.049*
C12	0.5601 (5)	0.4255 (5)	-0.0580 (5)	0.0331 (15)
C13	0.6544 (5)	0.3816 (5)	0.0445 (5)	0.0402 (16)
H13	0.6397	0.3333	0.0970	0.048*
C14	0.7698 (5)	0.4086 (5)	0.0695 (6)	0.0426 (17)
H14	0.8311	0.3807	0.1406	0.051*
C15	0.4342 (5)	0.4008 (5)	-0.0871 (5)	0.0371 (16)
C16	0.3420 (5)	0.4794 (6)	-0.1647 (6)	0.051 (2)
H16	0.3583	0.5509	-0.1985	0.062*
C17	0.2266 (6)	0.4506 (7)	-0.1911 (6)	0.061 (2)
H17	0.1665	0.5008	-0.2475	0.073*
C18	0.2840 (5)	0.2878 (6)	-0.0652 (6)	0.055 (2)
H18	0.2659	0.2222	-0.0269	0.066*
C19	0.4017 (5)	0.3041 (5)	-0.0364 (6)	0.0474 (18)
H19	0.4589	0.2492	0.0175	0.057*
C20	1.2537 (5)	0.4846 (6)	0.1388 (6)	0.0489 (19)
H20	1.2252	0.4049	0.1035	0.059*
C21	1.3747 (5)	0.5066 (6)	0.1865 (5)	0.0451 (18)
H21	1.4246	0.4441	0.1815	0.054*
C22	1.4206 (5)	0.6245 (6)	0.2425 (5)	0.0365 (15)
C23	1.3409 (5)	0.7119 (6)	0.2452 (6)	0.0525 (19)
H23	1.3669	0.7916	0.2816	0.063*
C24	1.2206 (5)	0.6801 (6)	0.1929 (6)	0.0532 (19)
H24	1.1682	0.7410	0.1955	0.064*
C25	1.5496 (5)	0.6566 (5)	0.2940 (5)	0.0361 (15)
C26	1.6280 (5)	0.5827 (6)	0.2715 (6)	0.054 (2)
H26	1.6011	0.5100	0.2240	0.065*
C27	1.7453 (6)	0.6179 (7)	0.3199 (7)	0.063 (2)
H27	1.7956	0.5663	0.3036	0.076*
C28	1.7173 (6)	0.7898 (7)	0.4097 (6)	0.056 (2)
H28	1.7472	0.8616	0.4580	0.068*
C29	1.5978 (5)	0.7626 (6)	0.3650 (5)	0.0449 (17)
H29	1.5498	0.8160	0.3829	0.054*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0329 (3)	0.0303 (3)	0.0443 (4)	0.0015 (4)	0.0188 (3)	0.0008 (5)
O1	0.042 (2)	0.037 (2)	0.044 (3)	0.0051 (18)	0.025 (2)	-0.001 (2)
O2	0.032 (2)	0.027 (2)	0.049 (3)	-0.0040 (18)	0.019 (2)	0.000 (2)

O3	0.036 (2)	0.078 (4)	0.073 (3)	-0.007 (3)	0.013 (2)	0.006 (3)
O4	0.071 (4)	0.107 (5)	0.063 (4)	-0.003 (3)	0.024 (3)	-0.014 (4)
O5	0.041 (3)	0.070 (3)	0.070 (4)	-0.004 (2)	0.012 (3)	-0.005 (3)
O6	0.049 (3)	0.129 (5)	0.085 (5)	0.014 (3)	0.027 (3)	-0.001 (4)
O1W	0.055 (3)	0.056 (3)	0.045 (3)	0.019 (2)	0.023 (2)	0.004 (2)
O2W	0.099 (3)	0.102 (5)	0.057 (4)	-0.033 (4)	0.007 (3)	0.006 (4)
O3W	0.048 (3)	0.079 (3)	0.113 (5)	0.006 (3)	0.021 (3)	0.002 (4)
N1	0.029 (2)	0.026 (3)	0.045 (3)	-0.001 (2)	0.014 (2)	-0.004 (2)
N2	0.037 (3)	0.033 (3)	0.039 (4)	0.004 (2)	0.019 (3)	0.004 (2)
N3	0.033 (3)	0.073 (4)	0.051 (4)	-0.001 (3)	0.020 (3)	-0.004 (3)
N4	0.038 (3)	0.028 (3)	0.057 (4)	0.000 (2)	0.020 (3)	0.004 (2)
N5	0.037 (3)	0.064 (4)	0.061 (5)	-0.006 (3)	0.018 (3)	0.004 (4)
N6	0.053 (4)	0.050 (4)	0.067 (6)	-0.005 (3)	0.027 (4)	0.000 (4)
C1	0.018 (3)	0.034 (4)	0.039 (4)	0.002 (2)	0.013 (3)	-0.002 (3)
C2	0.028 (3)	0.025 (3)	0.049 (4)	0.003 (3)	0.022 (3)	0.002 (3)
C3	0.037 (4)	0.049 (4)	0.038 (4)	0.002 (3)	0.024 (3)	0.003 (3)
C4	0.045 (4)	0.041 (4)	0.030 (4)	-0.002 (3)	0.015 (3)	0.003 (3)
C5	0.045 (4)	0.039 (4)	0.039 (4)	-0.008 (3)	0.017 (3)	-0.004 (3)
C6	0.047 (4)	0.049 (4)	0.037 (4)	0.007 (3)	0.017 (3)	0.008 (3)
C7	0.043 (4)	0.065 (5)	0.037 (4)	-0.006 (4)	0.014 (3)	0.008 (3)
C8	0.056 (5)	0.044 (4)	0.049 (5)	-0.013 (3)	0.023 (4)	-0.009 (3)
C9	0.051 (4)	0.042 (5)	0.046 (4)	0.006 (3)	0.027 (3)	0.001 (3)
C10	0.038 (3)	0.039 (4)	0.053 (4)	0.001 (4)	0.027 (3)	0.016 (4)
C11	0.032 (3)	0.048 (5)	0.044 (4)	0.002 (3)	0.018 (3)	0.006 (3)
C12	0.032 (3)	0.027 (3)	0.047 (5)	0.000 (3)	0.023 (3)	-0.008 (3)
C13	0.040 (4)	0.042 (4)	0.040 (4)	0.006 (3)	0.020 (3)	0.008 (3)
C14	0.037 (4)	0.044 (4)	0.040 (5)	0.011 (3)	0.012 (3)	0.007 (3)
C15	0.033 (4)	0.038 (4)	0.051 (5)	-0.005 (3)	0.028 (3)	-0.008 (3)
C16	0.033 (4)	0.067 (5)	0.061 (5)	0.003 (3)	0.028 (3)	0.014 (4)
C17	0.054 (5)	0.079 (5)	0.060 (6)	0.011 (4)	0.036 (4)	0.022 (4)
C18	0.044 (4)	0.049 (4)	0.079 (6)	-0.009 (4)	0.035 (4)	0.002 (4)
C19	0.038 (4)	0.040 (4)	0.062 (5)	-0.010 (3)	0.022 (4)	0.001 (3)
C20	0.043 (4)	0.045 (4)	0.058 (5)	-0.008 (3)	0.022 (4)	-0.014 (3)
C21	0.038 (3)	0.042 (5)	0.057 (4)	-0.001 (3)	0.023 (3)	-0.003 (4)
C22	0.033 (4)	0.036 (3)	0.036 (4)	0.001 (3)	0.013 (3)	0.004 (3)
C23	0.034 (4)	0.036 (4)	0.079 (6)	-0.004 (3)	0.018 (4)	-0.014 (4)
C24	0.042 (4)	0.034 (4)	0.078 (6)	0.005 (3)	0.023 (4)	-0.005 (4)
C25	0.033 (3)	0.040 (4)	0.036 (4)	-0.001 (3)	0.016 (3)	0.009 (3)
C26	0.037 (4)	0.053 (5)	0.071 (6)	-0.010 (3)	0.025 (4)	-0.007 (4)
C27	0.043 (4)	0.073 (5)	0.078 (6)	0.002 (4)	0.033 (4)	-0.008 (5)
C28	0.049 (5)	0.062 (5)	0.053 (6)	-0.005 (4)	0.020 (5)	0.004 (4)
C29	0.039 (4)	0.052 (4)	0.045 (5)	-0.005 (3)	0.021 (3)	-0.003 (4)

Geometric parameters (Å, °)

Zn1—O1	2.139 (4)	C6—C7	1.383 (7)
Zn1—O2 ⁱ	2.052 (4)	C6—H6	0.9300
Zn1—O1W	2.125 (4)	C7—C8	1.389 (8)
Zn1—N1	2.153 (4)	C8—C9	1.388 (7)

supplementary materials

Zn1—N2	2.229 (4)	C8—H8	0.9300
Zn1—N4	2.169 (5)	C9—H9	0.9300
O1—C1	1.240 (6)	C10—C11	1.386 (6)
O2—C1	1.252 (6)	C10—H10	0.9300
O3—C7	1.357 (6)	C11—C12	1.388 (7)
O3—H3	0.8600	C11—H11	0.9300
O4—N6	1.256 (7)	C12—C13	1.383 (7)
O5—N6	1.245 (6)	C12—C15	1.488 (7)
O6—N6	1.229 (6)	C13—C14	1.377 (7)
O1W—H1C	0.8248	C13—H13	0.9300
O1W—H1D	0.8190	C14—H14	0.9300
O2W—H2A	0.8222	C15—C19	1.363 (8)
O2W—H2B	0.8196	C15—C16	1.395 (8)
O3W—H3C	0.8253	C16—C17	1.377 (8)
O3W—H3D	0.8211	C16—H16	0.9300
N1—C2	1.483 (6)	C17—H17	0.9300
N1—H1A	0.9000	C18—C19	1.376 (7)
N1—H1B	0.9000	C18—H18	0.9300
N2—C10	1.330 (6)	C19—H19	0.9300
N2—C14	1.349 (7)	C20—C21	1.384 (7)
N3—C18	1.309 (7)	C20—H20	0.9300
N3—C17	1.327 (7)	C21—C22	1.399 (8)
N4—C20	1.323 (6)	C21—H21	0.9300
N4—C24	1.328 (6)	C22—C23	1.373 (7)
N5—C27	1.321 (8)	C22—C25	1.494 (7)
N5—C28	1.331 (8)	C23—C24	1.395 (7)
C1—C2	1.537 (7)	C23—H23	0.9300
C2—C3	1.529 (7)	C24—H24	0.9300
C2—H2	0.9800	C25—C29	1.377 (7)
C3—C4	1.514 (7)	C25—C26	1.392 (7)
C3—H3A	0.9700	C26—C27	1.372 (8)
C3—H3B	0.9700	C26—H26	0.9300
C4—C5	1.388 (7)	C27—H27	0.9300
C4—C9	1.405 (8)	C28—C29	1.381 (7)
C5—C6	1.386 (7)	C28—H28	0.9300
C5—H5	0.9300	C29—H29	0.9300
O2 ⁱ —Zn1—O1W	94.70 (16)	C9—C8—C7	120.4 (6)
O2 ⁱ —Zn1—O1	177.13 (17)	C9—C8—H8	119.8
O1W—Zn1—O1	82.75 (16)	C7—C8—H8	119.8
O2 ⁱ —Zn1—N1	105.10 (16)	C8—C9—C4	121.2 (6)
O1W—Zn1—N1	160.17 (15)	C8—C9—H9	119.4
O1—Zn1—N1	77.43 (16)	C4—C9—H9	119.4
O2 ⁱ —Zn1—N4	88.95 (15)	N2—C10—C11	124.3 (5)
O1W—Zn1—N4	89.17 (18)	N2—C10—H10	117.9
O1—Zn1—N4	92.32 (15)	C11—C10—H10	117.9
N1—Zn1—N4	92.21 (18)	C10—C11—C12	119.1 (6)
O2 ⁱ —Zn1—N2	84.61 (15)	C10—C11—H11	120.5
O1W—Zn1—N2	87.08 (16)	C12—C11—H11	120.5

O1—Zn1—N2	93.93 (15)	C13—C12—C11	116.7 (5)
N1—Zn1—N2	93.61 (17)	C13—C12—C15	122.4 (6)
N4—Zn1—N2	172.26 (19)	C11—C12—C15	120.9 (5)
C1—O1—Zn1	115.3 (4)	C14—C13—C12	120.7 (6)
C1—O2—Zn1 ⁱⁱ	132.4 (4)	C14—C13—H13	119.6
C7—O3—H3	129.2	C12—C13—H13	119.6
Zn1—O1W—H1C	133.6	N2—C14—C13	122.6 (6)
Zn1—O1W—H1D	117.2	N2—C14—H14	118.7
H1C—O1W—H1D	109.1	C13—C14—H14	118.7
H2A—O2W—H2B	109.4	C19—C15—C16	115.5 (5)
H3C—O3W—H3D	108.4	C19—C15—C12	122.6 (6)
C2—N1—Zn1	110.2 (3)	C16—C15—C12	121.8 (5)
C2—N1—H1A	109.6	C17—C16—C15	119.6 (6)
Zn1—N1—H1A	109.6	C17—C16—H16	120.2
C2—N1—H1B	109.6	C15—C16—H16	120.2
Zn1—N1—H1B	109.6	N3—C17—C16	124.6 (6)
H1A—N1—H1B	108.1	N3—C17—H17	117.7
C10—N2—C14	116.5 (5)	C16—C17—H17	117.7
C10—N2—Zn1	124.9 (4)	N3—C18—C19	125.7 (6)
C14—N2—Zn1	118.0 (4)	N3—C18—H18	117.1
C18—N3—C17	114.5 (6)	C19—C18—H18	117.1
C20—N4—C24	115.7 (5)	C15—C19—C18	119.9 (6)
C20—N4—Zn1	122.7 (4)	C15—C19—H19	120.0
C24—N4—Zn1	121.6 (4)	C18—C19—H19	120.0
C27—N5—C28	115.4 (6)	N4—C20—C21	124.8 (6)
O6—N6—O5	121.6 (7)	N4—C20—H20	117.6
O6—N6—O4	119.7 (7)	C21—C20—H20	117.6
O5—N6—O4	118.7 (7)	C20—C21—C22	118.9 (6)
O1—C1—O2	125.5 (5)	C20—C21—H21	120.6
O1—C1—C2	119.6 (5)	C22—C21—H21	120.6
O2—C1—C2	114.9 (5)	C23—C22—C21	116.9 (5)
N1—C2—C3	114.0 (5)	C23—C22—C25	121.0 (5)
N1—C2—C1	110.3 (4)	C21—C22—C25	122.1 (5)
C3—C2—C1	112.2 (5)	C22—C23—C24	119.4 (6)
N1—C2—H2	106.6	C22—C23—H23	120.3
C3—C2—H2	106.6	C24—C23—H23	120.3
C1—C2—H2	106.6	N4—C24—C23	124.3 (6)
C4—C3—C2	112.9 (4)	N4—C24—H24	117.8
C4—C3—H3A	109.0	C23—C24—H24	117.8
C2—C3—H3A	109.0	C29—C25—C26	115.9 (5)
C4—C3—H3B	109.0	C29—C25—C22	121.9 (5)
C2—C3—H3B	109.0	C26—C25—C22	122.1 (6)
H3A—C3—H3B	107.8	C27—C26—C25	119.6 (6)
C5—C4—C9	116.9 (5)	C27—C26—H26	120.2
C5—C4—C3	122.1 (5)	C25—C26—H26	120.2
C9—C4—C3	121.0 (5)	N5—C27—C26	124.9 (6)
C6—C5—C4	122.2 (6)	N5—C27—H27	117.5
C6—C5—H5	118.9	C26—C27—H27	117.5
C4—C5—H5	118.9	N5—C28—C29	124.1 (7)

supplementary materials

C7—C6—C5	120.1 (6)	N5—C28—H28	118.0
C7—C6—H6	120.0	C29—C28—H28	118.0
C5—C6—H6	120.0	C25—C29—C28	120.1 (6)
O3—C7—C6	123.7 (6)	C25—C29—H29	120.0
O3—C7—C8	117.2 (6)	C28—C29—H29	120.0
C6—C7—C8	119.1 (6)		
O1W—Zn1—O1—C1	158.7 (4)	C5—C4—C9—C8	1.5 (9)
N1—Zn1—O1—C1	-21.9 (4)	C3—C4—C9—C8	179.1 (6)
N4—Zn1—O1—C1	69.8 (4)	C14—N2—C10—C11	-0.1 (9)
N2—Zn1—O1—C1	-114.8 (4)	Zn1—N2—C10—C11	-170.7 (5)
O2 ⁱ —Zn1—N1—C2	-158.5 (3)	N2—C10—C11—C12	-0.6 (10)
O1W—Zn1—N1—C2	24.7 (6)	C10—C11—C12—C13	-0.3 (8)
O1—Zn1—N1—C2	22.9 (3)	C10—C11—C12—C15	-179.9 (5)
N4—Zn1—N1—C2	-69.0 (3)	C11—C12—C13—C14	1.8 (8)
N2—Zn1—N1—C2	116.1 (3)	C15—C12—C13—C14	-178.7 (5)
O2 ⁱ —Zn1—N2—C10	-149.5 (5)	C10—N2—C14—C13	1.7 (8)
O1W—Zn1—N2—C10	115.5 (5)	Zn1—N2—C14—C13	172.9 (4)
O1—Zn1—N2—C10	32.9 (5)	C12—C13—C14—N2	-2.6 (9)
N1—Zn1—N2—C10	-44.7 (5)	C13—C12—C15—C19	-20.4 (8)
O2 ⁱ —Zn1—N2—C14	40.0 (4)	C11—C12—C15—C19	159.2 (6)
O1W—Zn1—N2—C14	-55.0 (4)	C13—C12—C15—C16	156.8 (6)
O1—Zn1—N2—C14	-137.5 (4)	C11—C12—C15—C16	-23.7 (8)
N1—Zn1—N2—C14	144.9 (4)	C19—C15—C16—C17	-4.3 (9)
O2 ⁱ —Zn1—N4—C20	46.0 (5)	C12—C15—C16—C17	178.3 (6)
O1W—Zn1—N4—C20	140.7 (5)	C18—N3—C17—C16	-1.6 (10)
O1—Zn1—N4—C20	-136.6 (5)	C15—C16—C17—N3	4.7 (11)
N1—Zn1—N4—C20	-59.1 (5)	C17—N3—C18—C19	-1.8 (10)
O2 ⁱ —Zn1—N4—C24	-135.0 (5)	C16—C15—C19—C18	1.4 (9)
O1W—Zn1—N4—C24	-40.3 (5)	C12—C15—C19—C18	178.7 (5)
O1—Zn1—N4—C24	42.4 (5)	N3—C18—C19—C15	1.8 (10)
N1—Zn1—N4—C24	119.9 (5)	C24—N4—C20—C21	-1.2 (10)
Zn1—O1—C1—O2	-163.6 (4)	Zn1—N4—C20—C21	177.9 (5)
Zn1—O1—C1—C2	15.9 (6)	N4—C20—C21—C22	1.4 (10)
Zn1 ⁱⁱ —O2—C1—O1	26.8 (8)	C20—C21—C22—C23	-0.6 (9)
Zn1 ⁱⁱ —O2—C1—C2	-152.8 (4)	C20—C21—C22—C25	-178.7 (6)
Zn1—N1—C2—C3	-149.2 (3)	C21—C22—C23—C24	-0.2 (10)
Zn1—N1—C2—C1	-21.9 (5)	C25—C22—C23—C24	178.0 (6)
O1—C1—C2—N1	4.6 (7)	C20—N4—C24—C23	0.3 (10)
O2—C1—C2—N1	-175.8 (4)	Zn1—N4—C24—C23	-178.8 (5)
O1—C1—C2—C3	133.0 (5)	C22—C23—C24—N4	0.4 (11)
O2—C1—C2—C3	-47.4 (6)	C23—C22—C25—C29	12.6 (9)
N1—C2—C3—C4	56.5 (6)	C21—C22—C25—C29	-169.3 (6)
C1—C2—C3—C4	-69.8 (6)	C23—C22—C25—C26	-166.2 (6)
C2—C3—C4—C5	73.9 (7)	C21—C22—C25—C26	11.9 (9)
C2—C3—C4—C9	-103.5 (6)	C29—C25—C26—C27	0.2 (9)
C9—C4—C5—C6	1.0 (9)	C22—C25—C26—C27	179.0 (6)
C3—C4—C5—C6	-176.5 (5)	C28—N5—C27—C26	0.7 (11)

C4—C5—C6—C7	-1.8 (9)	C25—C26—C27—N5	-0.4 (11)
C5—C6—C7—O3	180.0 (5)	C27—N5—C28—C29	-0.9 (11)
C5—C6—C7—C8	0.1 (9)	C26—C25—C29—C28	-0.3 (9)
O3—C7—C8—C9	-177.5 (5)	C22—C25—C29—C28	-179.2 (6)
C6—C7—C8—C9	2.4 (10)	N5—C28—C29—C25	0.7 (11)
C7—C8—C9—C4	-3.2 (9)		

Symmetry codes: (i) $-x+2, y-1/2, -z$; (ii) $-x+2, y+1/2, -z$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1A...N3 ⁱⁱⁱ	0.90	2.49	3.336 (6)	156
O3—H3...O4	0.86	1.94	2.748 (7)	155
O1W—H1C...O2W	0.82	1.79	2.611 (6)	173
O1W—H1D...N3 ^{iv}	0.82	2.33	3.133 (6)	167
O2W—H2A...O4 ^v	0.82	2.10	2.889 (7)	160
O2W—H2B...O3W	0.82	1.97	2.774 (7)	168
O3W—H3C...O6 ^{vi}	0.83	2.20	2.962 (7)	153
O3W—H3D...N5 ^{vii}	0.82	2.09	2.851 (6)	154

Symmetry codes: (iii) $x+1, y, z$; (iv) $-x+1, y+1/2, -z$; (v) $x+1, y, z+1$; (vi) $-x+1, y-1/2, -z$; (vii) $-x+3, y-1/2, -z+1$.

Fig. 1

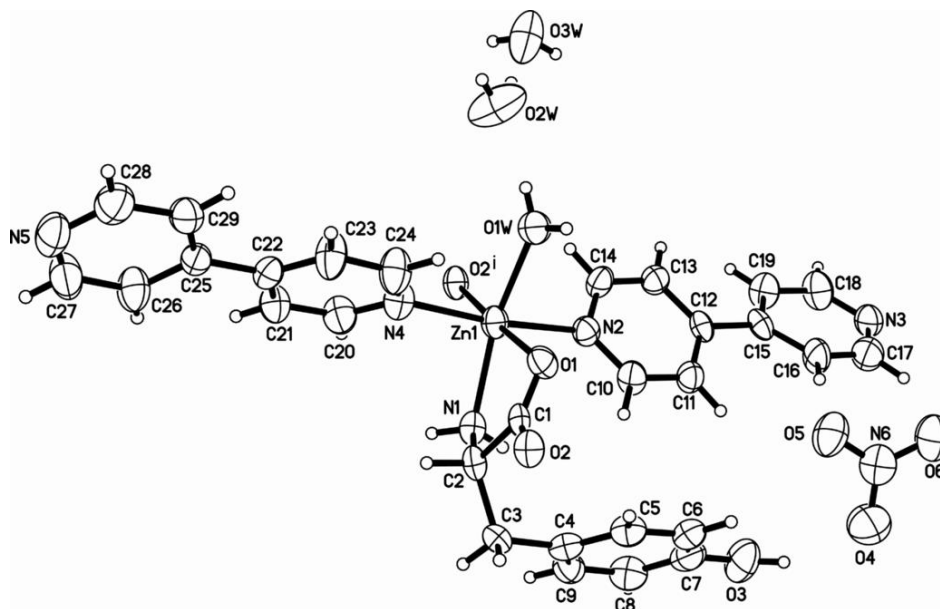


Fig. 2

