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(3-Carboxy-5-sulfonatobenzoato- κ^2O^1, O^1')bis[2-(2-pyridyl)-1H-benzimidazole- κ^2N^2, N^3]zinc(II) monohydrate

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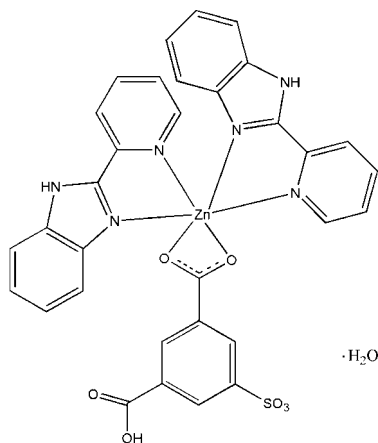
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.008$ Å; R factor = 0.064; wR factor = 0.179; data-to-parameter ratio = 16.0.

In the title compound, $[Zn(C_8H_4O_7S)(C_{12}H_9N_3)_2] \cdot H_2O$, the Zn^{II} atom has a distorted octahedral coordination geometry, defined by four N atoms from two 2-(2-pyridyl)-1H-benzimidazole ligands and two O atoms from a deprotonated carboxylate group of the 3-carboxy-5-sulfonatobenzoate ligand. In the crystal structure, the complex molecules are linked into a three-dimensional network by intermolecular $O-H \cdots O$ and $N-H \cdots O$ hydrogen bonds, and $\pi-\pi$ stacking interactions with centroid-centroid separations of 3.758 (2) and 3.597 (1) Å.

Related literature

For general background, see: Xia *et al.* (2005). For related structures, see: Kulynych & Shimizu (2002); Liu & Xu (2005); Sun *et al.* (2003); Xia *et al.* (2006).



Experimental

Crystal data

$[Zn(C_8H_4O_7S)(C_{12}H_9N_3)_2] \cdot H_2O$
 $M_r = 718.00$
 Triclinic, $P\bar{1}$
 $a = 11.086$ (4) Å
 $b = 12.695$ (5) Å
 $c = 13.347$ (4) Å
 $\alpha = 63.187$ (10)°
 $\beta = 68.376$ (13)°
 $\gamma = 87.122$ (17)°
 $V = 1543.2$ (10) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.93$ mm⁻¹
 $T = 293$ K
 $0.14 \times 0.11 \times 0.08$ mm

Data collection

Rigaku Mercury CCD diffractometer
 Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)
 $T_{min} = 0.843$, $T_{max} = 0.929$
 12166 measured reflections
 6935 independent reflections
 3857 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.179$
 $S = 0.99$
 6935 reflections
 434 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.89$ e Å⁻³
 $\Delta\rho_{min} = -0.43$ e Å⁻³

Table 1

Selected bond lengths (Å).

Zn1—N1	2.080 (4)	Zn1—N6	2.210 (4)
Zn1—N3	2.257 (4)	Zn1—O1	2.216 (3)
Zn1—N4	2.067 (4)	Zn1—O2	2.193 (3)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2B \cdots O1 ⁱ	0.86	2.15	2.884 (5)	143
N5—H5B \cdots O3 ⁱⁱ	0.86	2.05	2.833 (5)	151
O1W—H1WA \cdots O7 ⁱⁱⁱ	0.82	1.87	2.678 (5)	167
O1W—H1WB \cdots O6 ^{iv}	0.82	2.05	2.825 (5)	157
O4—H4B \cdots O1W	0.82	1.78	2.575 (4)	163

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

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2185).

References

- Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Kulynych, A. D. & Shimizu, G. K. H. (2002). *CrystEngComm*, **4**, 102–105.
 Liu, Q.-Y. & Xu, L. (2005). *Inorg. Chem. Commun.* **8**, 401–405.
 Rigaku (2002). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

Sun, D.-F., Cao, R., Sun, Y.-Q., Bi, W.-H., Yuan, D.-Q., Shi, Q. & Li, X. (2003). *Chem. Commun.* pp. 1528–1529.

Xia, C.-K., Lu, C.-Z., Yuan, D.-Q., Zhang, Q.-Z., Wu, X.-Y., Xiang, S.-C., Zhang, J.-J. & Wu, D.-M. (2006). *CrystEngComm*, **8**, 281–291.

Xia, C.-K., Lu, C.-Z., Zhang, Q.-Z., He, X., Zhang, J.-J. & Wu, D.-M. (2005). *Cryst. Growth Des.* **5**, 1569–1574.

supplementary materials

Acta Cryst. (2009). E65, m413-m414 [doi:10.1107/S1600536809009180]

(3-Carboxy-5-sulfonatobenzoato- $\kappa^2 O^1, O^1'$)bis[2-(2-pyridyl)-1*H*-benzimidazole- $\kappa^2 N^2, N^3$]zinc(II) monohydrate

L.-J. Chen, S. Lin, M.-X. Yang and X.-Y. Wu

Comment

Increasing interest has been focused on crystal engineering of supramolecular architectures organized by coordinating covalent bonds or supramolecular contacts such as hydrogen bonding and π - π interactions (Xia *et al.*, 2005). 5-Sulfoisophthalic acid (H₃sipa), which exhibits variation in possible binding modes of the two carboxylate groups and the soft sulfonate group, and a strong tendency to form large, tightly bound metal cluster, has been demonstrated as a useful bridge ligand for the construction of supramolecular structures (Kulynych & Shimizu *et al.*, 2002; Liu & Xu *et al.*, 2005; Sun *et al.*, 2003). On the other hand, 2-(2-pyridyl)-1*H*-benzimidazole (2-pbim) ligand presents multiple N-donor sites with the possibility of reversible protonation and deprotonation, and has the capacity to act as a donor or acceptor in the formation of multi-dimensional hydrogen bonded networks (Xia *et al.*, 2006). We report here the crystal structure of the title compound, which contains both Hsipa and 2-pbim ligands.

As shown in Fig. 1, the title complex consists of one Zn^{II} atom, two neutral 2-pbim ligands, one deprotonated Hsipa²⁻ ligand and one uncoordinated water molecule. The Zn^{II} atom is six-coordinated by four N atoms from two 2-pbim ligands and two O atoms from one carboxylate group of the Hsipa²⁻ ligand, forming a distorted octahedral geometry (Table 1). The chelate rings A (Zn1, N1, C7, C8, N3), B (Zn1, N4, C19, C20, N6) and C (Zn1, O1, C31, O2) are oriented at dihedral angles of A/B = 84.1 (1)°, A/C = 87.8 (1)° and B/C = 82.4 (1)°. The two 2-pbim ligands bonded to the same Zn atom are nearly perpendicular to each other.

In the crystal structure, the mononuclear Zn complex molecules are linked by intermolecular O—H...O and N—H...O hydrogen bonds involving the water molecule, the imino groups, the carboxyl groups and the sulfonate group, forming a three-dimensional network (Fig. 2 and Table 2). The structure is further stabilized by π - π stacking interactions between the benzene rings of neighboring benzimidazole moieties containing N4 and N5 atoms, and between the pyridyl ring containing N3 atom and benzimidazole moiety containing N1 and N2 atoms, with centroid-to-centroid distances of 3.758 (2) and 3.597 (1) Å, respectively.

Experimental

A mixture of Zn(NO₃)₂·6H₂O (0.092 g, 0.3 mmol), NaH₂sipa (0.053 g, 0.2 mmol), 2-pbim (0.039 g, 0.2 mmol) and H₂O (10 ml) was placed in a 18 ml Teflon-lined Parr acid digestion bomb. The pH value of the reaction mixture was adjusted to *ca* 6.0 with 10% sodium hydroxide. The mixture was then heated for 3 d at 433 K under autogeneous pressure. Slow cooling of the reaction mixture to room temperature gave colorless prism crystals (yield: *ca* 78% based on Zn)

Refinement

The water H atoms were located in a difference Fourier map and fixed in refinement with O—H = 0.82 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Other H atoms were placed geometrically and refined as riding, with C—H = 0.93, O—H = 0.82 and N—H = 0.86 Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ or $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C, N})$.

Figures

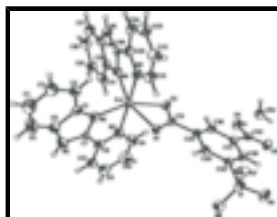


Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

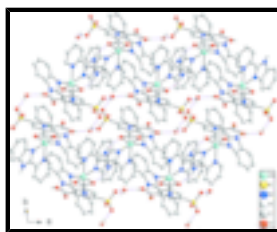


Fig. 2. A perspective view of the crystal packing down the *c* axis, showing hydrogen bonds (dashed lines). H atoms, which do not participate in hydrogen bonds, have been omitted for clarity.

(3-Carboxy-5-sulfonatobenzoato- $\kappa^2\text{O}^1, \text{O}^1$)bis[2-(2-pyridyl)-1*H*-benzimidazole- $\kappa^2\text{N}^2, \text{N}^3$]zinc(II) monohydrate

Crystal data

$[\text{Zn}(\text{C}_8\text{H}_4\text{O}_7\text{S})(\text{C}_{12}\text{H}_9\text{N}_3)_2] \cdot \text{H}_2\text{O}$

$M_r = 718.00$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 11.086(4) \text{ \AA}$

$b = 12.695(5) \text{ \AA}$

$c = 13.347(4) \text{ \AA}$

$\alpha = 63.187(10)^\circ$

$\beta = 68.376(13)^\circ$

$\gamma = 87.122(17)^\circ$

$V = 1543.2(10) \text{ \AA}^3$

$Z = 2$

$F_{000} = 736$

$D_x = 1.545 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 3438 reflections

$\theta = 2.4\text{--}27.5^\circ$

$\mu = 0.93 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism, colorless

$0.14 \times 0.11 \times 0.08 \text{ mm}$

Data collection

Rigaku Mercury CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

6935 independent reflections

3857 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

Detector resolution: 14.6306 pixels mm⁻¹
 $T = 293$ K
 ω scans
 Absorption correction: multi-scan
 (CrystalClear; Rigaku, 2002)
 $T_{\min} = 0.843$, $T_{\max} = 0.929$
 12166 measured reflections

$\theta_{\max} = 27.4^\circ$
 $\theta_{\min} = 2.4^\circ$
 $h = -13 \rightarrow 14$
 $k = -16 \rightarrow 16$
 $l = -14 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.179$
 $S = 0.99$
 6935 reflections
 434 parameters
 Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0855P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.89 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none

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	0.29944 (5)	0.17840 (5)	0.78119 (5)	0.0450 (2)
S1	0.04872 (11)	0.43789 (11)	1.21208 (10)	0.0462 (3)
N1	0.1432 (4)	0.0898 (4)	0.7857 (3)	0.0502 (10)
N2	0.0072 (4)	-0.0749 (4)	0.8695 (4)	0.0621 (11)
H2B	-0.0332	-0.1461	0.9201	0.075*
N3	0.2645 (4)	-0.0040 (4)	0.9412 (4)	0.0541 (10)
N4	0.4499 (3)	0.1749 (3)	0.6348 (3)	0.0498 (10)
N5	0.5526 (4)	0.2558 (3)	0.4336 (3)	0.0522 (10)
H5B	0.5771	0.3064	0.3577	0.063*
N6	0.3118 (4)	0.3556 (4)	0.6299 (4)	0.0507 (10)
C1	0.0720 (5)	0.1113 (5)	0.7172 (4)	0.0524 (12)
C2	0.0720 (5)	0.2091 (4)	0.6132 (4)	0.0537 (12)
H2A	0.1273	0.2798	0.5780	0.064*
C3	-0.0115 (6)	0.1981 (6)	0.5644 (6)	0.0768 (17)
H3A	-0.0120	0.2631	0.4942	0.092*
C4	-0.0948 (8)	0.0964 (7)	0.6132 (7)	0.107 (2)
H4A	-0.1491	0.0938	0.5751	0.128*
C5	-0.0999 (7)	-0.0010 (6)	0.7164 (6)	0.094 (2)
H5A	-0.1585	-0.0693	0.7506	0.113*
C6	-0.0172 (5)	0.0040 (5)	0.7683 (4)	0.0533 (12)
C7	0.1051 (4)	-0.0216 (4)	0.8756 (4)	0.0337 (9)
C8	0.1661 (4)	-0.0747 (4)	0.9639 (4)	0.0467 (11)
C9	0.3292 (5)	-0.0428 (5)	1.0183 (5)	0.0565 (13)

supplementary materials

H9A	0.3984	0.0081	1.0031	0.068*
C10	0.2964 (6)	-0.1531 (5)	1.1166 (5)	0.0701 (16)
H10A	0.3428	-0.1773	1.1670	0.084*
C11	0.1900 (6)	-0.2302 (5)	1.1404 (5)	0.0663 (15)
H11A	0.1643	-0.3067	1.2057	0.080*
C12	0.1258 (4)	-0.1844 (4)	1.0597 (4)	0.0489 (11)
H12A	0.0539	-0.2308	1.0726	0.059*
C13	0.5302 (4)	0.0978 (4)	0.6075 (5)	0.0496 (11)
C14	0.5504 (5)	-0.0146 (4)	0.6844 (4)	0.0529 (12)
H14A	0.5075	-0.0499	0.7687	0.063*
C15	0.6384 (5)	-0.0690 (4)	0.6264 (5)	0.0598 (14)
H15A	0.6554	-0.1435	0.6742	0.072*
C16	0.7031 (5)	-0.0199 (5)	0.5016 (5)	0.0694 (16)
H16A	0.7606	-0.0624	0.4684	0.083*
C17	0.6843 (5)	0.0891 (5)	0.4266 (5)	0.0623 (14)
H17A	0.7289	0.1229	0.3425	0.075*
C18	0.5970 (4)	0.1477 (4)	0.4791 (4)	0.0408 (10)
C19	0.4634 (4)	0.2702 (4)	0.5279 (3)	0.0365 (9)
C20	0.3960 (4)	0.3701 (4)	0.5214 (4)	0.0494 (11)
C21	0.2430 (4)	0.4475 (5)	0.6353 (5)	0.0545 (13)
H21A	0.1845	0.4371	0.7110	0.065*
C22	0.2562 (5)	0.5530 (5)	0.5352 (5)	0.0650 (15)
H22A	0.2092	0.6138	0.5421	0.078*
C23	0.3456 (5)	0.5667 (5)	0.4189 (5)	0.0713 (16)
H23A	0.3580	0.6363	0.3475	0.086*
C24	0.4123 (5)	0.4727 (4)	0.4171 (4)	0.0520 (12)
H24A	0.4701	0.4792	0.3427	0.062*
C25	0.3076 (4)	0.3139 (3)	0.9990 (4)	0.0342 (9)
C26	0.4187 (4)	0.3155 (4)	1.0245 (4)	0.0365 (9)
H26A	0.4935	0.2897	0.9866	0.044*
C27	0.4184 (4)	0.3552 (3)	1.1057 (3)	0.0348 (9)
C28	0.3057 (4)	0.3945 (4)	1.1619 (3)	0.0385 (10)
H28A	0.3050	0.4219	1.2160	0.046*
C29	0.1968 (4)	0.3927 (3)	1.1374 (4)	0.0374 (9)
C30	0.1967 (4)	0.3535 (3)	1.0558 (4)	0.0373 (9)
H30A	0.1223	0.3536	1.0391	0.045*
C31	0.3042 (4)	0.2663 (4)	0.9162 (4)	0.0378 (9)
C32	0.5345 (4)	0.3540 (4)	1.1378 (4)	0.0370 (9)
O1	0.1971 (3)	0.2476 (3)	0.9116 (3)	0.0423 (7)
O1W	0.8425 (3)	0.3154 (3)	1.1201 (3)	0.0623 (9)
H1WA	0.8913	0.3655	1.0516	0.093*
H1WB	0.8553	0.3320	1.1686	0.093*
O2	0.4098 (3)	0.2450 (3)	0.8526 (3)	0.0477 (8)
O3	0.5390 (3)	0.3947 (3)	1.2030 (3)	0.0506 (8)
O4	0.6277 (3)	0.3028 (3)	1.0909 (3)	0.0538 (9)
H4B	0.6863	0.2999	1.1152	0.081*
O5	0.0764 (3)	0.4722 (3)	1.2907 (3)	0.0648 (10)
O6	-0.0514 (3)	0.3350 (3)	1.2746 (3)	0.0621 (9)
O7	0.0208 (3)	0.5357 (3)	1.1155 (3)	0.0687 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0400 (3)	0.0546 (3)	0.0383 (3)	-0.0070 (2)	-0.0047 (2)	-0.0269 (3)
S1	0.0416 (6)	0.0549 (7)	0.0433 (6)	0.0136 (5)	-0.0115 (5)	-0.0285 (6)
N1	0.044 (2)	0.060 (2)	0.048 (2)	0.0038 (19)	-0.0146 (19)	-0.028 (2)
N2	0.055 (2)	0.059 (3)	0.062 (3)	-0.009 (2)	-0.020 (2)	-0.020 (2)
N3	0.045 (2)	0.064 (3)	0.062 (3)	0.011 (2)	-0.018 (2)	-0.039 (2)
N4	0.040 (2)	0.061 (2)	0.046 (2)	-0.0001 (19)	-0.0109 (18)	-0.027 (2)
N5	0.063 (2)	0.047 (2)	0.043 (2)	0.0088 (19)	-0.0158 (19)	-0.0215 (19)
N6	0.045 (2)	0.065 (3)	0.052 (2)	0.0038 (19)	-0.0195 (19)	-0.035 (2)
C1	0.047 (3)	0.077 (3)	0.041 (3)	0.015 (3)	-0.018 (2)	-0.034 (3)
C2	0.056 (3)	0.056 (3)	0.043 (3)	0.001 (2)	-0.023 (2)	-0.014 (2)
C3	0.075 (4)	0.083 (4)	0.066 (4)	-0.002 (3)	-0.038 (3)	-0.021 (3)
C4	0.118 (6)	0.119 (6)	0.085 (5)	-0.011 (5)	-0.061 (5)	-0.030 (5)
C5	0.104 (5)	0.084 (5)	0.099 (5)	-0.008 (4)	-0.064 (4)	-0.025 (4)
C6	0.056 (3)	0.059 (3)	0.043 (3)	0.004 (2)	-0.027 (2)	-0.015 (2)
C7	0.031 (2)	0.039 (2)	0.033 (2)	-0.0007 (17)	-0.0100 (17)	-0.0193 (19)
C8	0.043 (3)	0.050 (3)	0.046 (3)	0.014 (2)	-0.010 (2)	-0.028 (2)
C9	0.050 (3)	0.063 (3)	0.069 (3)	0.016 (2)	-0.040 (3)	-0.027 (3)
C10	0.068 (4)	0.071 (4)	0.072 (4)	0.027 (3)	-0.043 (3)	-0.023 (3)
C11	0.081 (4)	0.051 (3)	0.058 (3)	0.022 (3)	-0.023 (3)	-0.023 (3)
C12	0.039 (2)	0.059 (3)	0.051 (3)	0.009 (2)	-0.016 (2)	-0.029 (3)
C13	0.043 (3)	0.053 (3)	0.061 (3)	0.002 (2)	-0.019 (2)	-0.033 (3)
C14	0.062 (3)	0.041 (2)	0.046 (3)	0.005 (2)	-0.022 (2)	-0.011 (2)
C15	0.066 (3)	0.048 (3)	0.054 (3)	0.009 (3)	-0.022 (3)	-0.016 (3)
C16	0.067 (3)	0.065 (3)	0.075 (4)	0.019 (3)	-0.022 (3)	-0.036 (3)
C17	0.064 (3)	0.062 (3)	0.065 (3)	0.016 (3)	-0.017 (3)	-0.040 (3)
C18	0.042 (2)	0.044 (2)	0.040 (2)	0.007 (2)	-0.017 (2)	-0.022 (2)
C19	0.036 (2)	0.045 (2)	0.029 (2)	-0.0028 (18)	-0.0073 (17)	-0.0207 (19)
C20	0.048 (3)	0.058 (3)	0.051 (3)	0.007 (2)	-0.020 (2)	-0.031 (3)
C21	0.045 (3)	0.068 (3)	0.052 (3)	0.022 (2)	-0.015 (2)	-0.034 (3)
C22	0.049 (3)	0.068 (3)	0.069 (4)	0.011 (3)	-0.019 (3)	-0.027 (3)
C23	0.072 (4)	0.060 (3)	0.072 (4)	0.011 (3)	-0.032 (3)	-0.019 (3)
C24	0.050 (3)	0.064 (3)	0.051 (3)	0.015 (2)	-0.023 (2)	-0.032 (3)
C25	0.034 (2)	0.035 (2)	0.035 (2)	0.0031 (17)	-0.0150 (18)	-0.0161 (18)
C26	0.035 (2)	0.041 (2)	0.034 (2)	0.0098 (18)	-0.0120 (18)	-0.0193 (19)
C27	0.038 (2)	0.037 (2)	0.030 (2)	0.0065 (18)	-0.0163 (18)	-0.0146 (18)
C28	0.051 (3)	0.041 (2)	0.031 (2)	0.013 (2)	-0.0198 (19)	-0.0198 (19)
C29	0.039 (2)	0.037 (2)	0.036 (2)	0.0081 (18)	-0.0145 (19)	-0.0169 (19)
C30	0.033 (2)	0.039 (2)	0.042 (2)	0.0064 (18)	-0.0157 (19)	-0.0194 (19)
C31	0.043 (2)	0.036 (2)	0.031 (2)	0.0025 (19)	-0.0127 (19)	-0.0139 (18)
C32	0.039 (2)	0.042 (2)	0.030 (2)	0.0044 (19)	-0.0171 (19)	-0.0148 (19)
O1	0.0378 (16)	0.0528 (18)	0.0429 (17)	0.0016 (14)	-0.0164 (13)	-0.0265 (15)
O1W	0.0470 (19)	0.079 (2)	0.065 (2)	0.0038 (17)	-0.0263 (17)	-0.033 (2)
O2	0.0410 (17)	0.066 (2)	0.0487 (18)	0.0060 (15)	-0.0128 (14)	-0.0399 (17)
O3	0.061 (2)	0.063 (2)	0.0505 (19)	0.0203 (17)	-0.0378 (17)	-0.0336 (17)

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O4	0.0399 (17)	0.081 (2)	0.069 (2)	0.0196 (17)	-0.0302 (17)	-0.052 (2)
O5	0.059 (2)	0.090 (3)	0.069 (2)	0.0218 (19)	-0.0220 (18)	-0.060 (2)
O6	0.0487 (19)	0.070 (2)	0.058 (2)	-0.0001 (17)	-0.0080 (16)	-0.0316 (19)
O7	0.064 (2)	0.073 (2)	0.055 (2)	0.0364 (19)	-0.0182 (18)	-0.0244 (19)

Geometric parameters (Å, °)

Zn1—N1	2.080 (4)	C11—C12	1.401 (7)
Zn1—N3	2.257 (4)	C11—H11A	0.9300
Zn1—N4	2.067 (4)	C12—H12A	0.9300
Zn1—N6	2.210 (4)	C13—C14	1.398 (6)
Zn1—O1	2.216 (3)	C13—C18	1.421 (6)
Zn1—O2	2.193 (3)	C14—C15	1.373 (6)
S1—O5	1.431 (4)	C14—H14A	0.9300
S1—O7	1.453 (3)	C15—C16	1.381 (7)
S1—O6	1.453 (4)	C15—H15A	0.9300
S1—C29	1.798 (4)	C16—C17	1.355 (7)
N1—C7	1.332 (5)	C16—H16A	0.9300
N1—C1	1.348 (6)	C17—C18	1.371 (6)
N2—C7	1.353 (5)	C17—H17A	0.9300
N2—C6	1.387 (6)	C19—C20	1.423 (6)
N2—H2B	0.8600	C20—C24	1.368 (7)
N3—C8	1.303 (6)	C21—C22	1.364 (7)
N3—C9	1.366 (6)	C21—H21A	0.9300
N4—C19	1.351 (5)	C22—C23	1.437 (8)
N4—C13	1.371 (6)	C22—H22A	0.9300
N5—C19	1.367 (5)	C23—C24	1.376 (7)
N5—C18	1.377 (5)	C23—H23A	0.9300
N5—H5B	0.8600	C24—H24A	0.9300
N6—C20	1.335 (6)	C25—C30	1.390 (5)
N6—C21	1.377 (6)	C25—C26	1.397 (6)
C1—C2	1.384 (6)	C25—C31	1.490 (6)
C1—C6	1.449 (7)	C26—C27	1.384 (6)
C2—C3	1.356 (7)	C26—H26A	0.9300
C2—H2A	0.9300	C27—C28	1.399 (5)
C3—C4	1.364 (9)	C27—C32	1.497 (5)
C3—H3A	0.9300	C28—C29	1.367 (6)
C4—C5	1.357 (9)	C28—H28A	0.9300
C4—H4A	0.9300	C29—C30	1.386 (6)
C5—C6	1.355 (7)	C30—H30A	0.9300
C5—H5A	0.9300	C31—O1	1.251 (5)
C7—C8	1.458 (6)	C31—O2	1.267 (5)
C8—C12	1.345 (6)	C32—O3	1.211 (5)
C9—C10	1.362 (7)	C32—O4	1.306 (5)
C9—H9A	0.9300	O1W—H1WA	0.82
C10—C11	1.418 (8)	O1W—H1WB	0.82
C10—H10A	0.9300	O4—H4B	0.82
N4—Zn1—N1	100.37 (15)	C10—C11—H11A	122.0
N4—Zn1—O2	100.82 (13)	C8—C12—C11	121.3 (5)

N1—Zn1—O2	156.91 (13)	C8—C12—H12A	119.4
N4—Zn1—N6	77.61 (15)	C11—C12—H12A	119.4
N1—Zn1—N6	98.96 (15)	N4—C13—C14	130.1 (5)
O2—Zn1—N6	94.45 (13)	N4—C13—C18	109.4 (4)
N4—Zn1—O1	155.82 (14)	C14—C13—C18	120.5 (4)
N1—Zn1—O1	101.58 (13)	C15—C14—C13	115.1 (4)
O2—Zn1—O1	59.76 (10)	C15—C14—H14A	122.4
N6—Zn1—O1	89.04 (13)	C13—C14—H14A	122.4
N4—Zn1—N3	106.43 (14)	C14—C15—C16	124.1 (5)
N1—Zn1—N3	76.34 (16)	C14—C15—H15A	117.9
O2—Zn1—N3	88.94 (14)	C16—C15—H15A	117.9
N6—Zn1—N3	174.19 (13)	C17—C16—C15	121.0 (5)
O1—Zn1—N3	88.58 (13)	C17—C16—H16A	119.5
O5—S1—O7	113.4 (2)	C15—C16—H16A	119.5
O5—S1—O6	114.6 (2)	C16—C17—C18	117.6 (5)
O7—S1—O6	110.6 (2)	C16—C17—H17A	121.2
O5—S1—C29	106.1 (2)	C18—C17—H17A	121.2
O7—S1—C29	105.90 (19)	C17—C18—N5	133.7 (4)
O6—S1—C29	105.4 (2)	C17—C18—C13	121.7 (4)
C7—N1—C1	108.7 (4)	N5—C18—C13	104.6 (4)
C7—N1—Zn1	113.8 (3)	N4—C19—N5	109.7 (4)
C1—N1—Zn1	137.3 (4)	N4—C19—C20	122.6 (4)
C7—N2—C6	108.8 (4)	N5—C19—C20	127.7 (4)
C7—N2—H2B	125.6	N6—C20—C24	121.2 (4)
C6—N2—H2B	125.6	N6—C20—C19	113.3 (4)
C8—N3—C9	118.6 (4)	C24—C20—C19	125.5 (4)
C8—N3—Zn1	114.3 (3)	C22—C21—N6	123.3 (4)
C9—N3—Zn1	127.0 (4)	C22—C21—H21A	118.3
C19—N4—C13	107.0 (4)	N6—C21—H21A	118.3
C19—N4—Zn1	112.3 (3)	C21—C22—C23	117.5 (5)
C13—N4—Zn1	139.7 (3)	C21—C22—H22A	121.2
C19—N5—C18	109.3 (4)	C23—C22—H22A	121.2
C19—N5—H5B	125.3	C24—C23—C22	117.5 (5)
C18—N5—H5B	125.3	C24—C23—H23A	121.3
C20—N6—C21	118.5 (4)	C22—C23—H23A	121.3
C20—N6—Zn1	113.3 (3)	C20—C24—C23	121.9 (5)
C21—N6—Zn1	128.1 (3)	C20—C24—H24A	119.0
N1—C1—C2	133.3 (5)	C23—C24—H24A	119.0
N1—C1—C6	108.1 (4)	C30—C25—C26	119.0 (4)
C2—C1—C6	118.6 (4)	C30—C25—C31	119.7 (4)
C3—C2—C1	117.6 (5)	C26—C25—C31	121.3 (3)
C3—C2—H2A	121.2	C27—C26—C25	120.6 (4)
C1—C2—H2A	121.2	C27—C26—H26A	119.7
C2—C3—C4	123.3 (6)	C25—C26—H26A	119.7
C2—C3—H3A	118.4	C26—C27—C28	119.5 (4)
C4—C3—H3A	118.4	C26—C27—C32	121.7 (3)
C5—C4—C3	121.2 (6)	C28—C27—C32	118.8 (4)
C5—C4—H4A	119.4	C29—C28—C27	120.0 (4)
C3—C4—H4A	119.4	C29—C28—H28A	120.0

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C6—C5—C4	118.3 (6)	C27—C28—H28A	120.0
C6—C5—H5A	120.9	C28—C29—C30	120.8 (4)
C4—C5—H5A	120.9	C28—C29—S1	121.1 (3)
C5—C6—N2	134.9 (5)	C30—C29—S1	118.2 (3)
C5—C6—C1	121.1 (5)	C29—C30—C25	120.2 (4)
N2—C6—C1	104.0 (4)	C29—C30—H30A	119.9
N1—C7—N2	110.4 (4)	C25—C30—H30A	119.9
N1—C7—C8	122.6 (4)	O1—C31—O2	121.4 (4)
N2—C7—C8	127.0 (4)	O1—C31—C25	119.3 (4)
N3—C8—C12	122.8 (5)	O2—C31—C25	119.3 (4)
N3—C8—C7	112.8 (4)	O1—C31—Zn1	61.3 (2)
C12—C8—C7	124.4 (5)	O2—C31—Zn1	60.2 (2)
C10—C9—N3	122.7 (5)	C25—C31—Zn1	178.0 (3)
C10—C9—H9A	118.7	O3—C32—O4	124.1 (4)
N3—C9—H9A	118.7	O3—C32—C27	122.6 (4)
C9—C10—C11	118.6 (5)	O4—C32—C27	113.3 (4)
C9—C10—H10A	120.7	C31—O1—Zn1	89.1 (2)
C11—C10—H10A	120.7	H1WA—O1W—H1WB	106.3
C12—C11—C10	116.1 (5)	C31—O2—Zn1	89.7 (3)
C12—C11—H11A	122.0	C32—O4—H4B	109.5

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2B \cdots O1 ⁱ	0.86	2.15	2.884 (5)	143
N5—H5B \cdots O3 ⁱⁱ	0.86	2.05	2.833 (5)	151
O1W—H1WA \cdots O7 ⁱⁱⁱ	0.82	1.87	2.678 (5)	167
O1W—H1WB \cdots O6 ^{iv}	0.82	2.05	2.825 (5)	157
O4—H4B \cdots O1W	0.82	1.78	2.575 (4)	163

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

Fig. 1

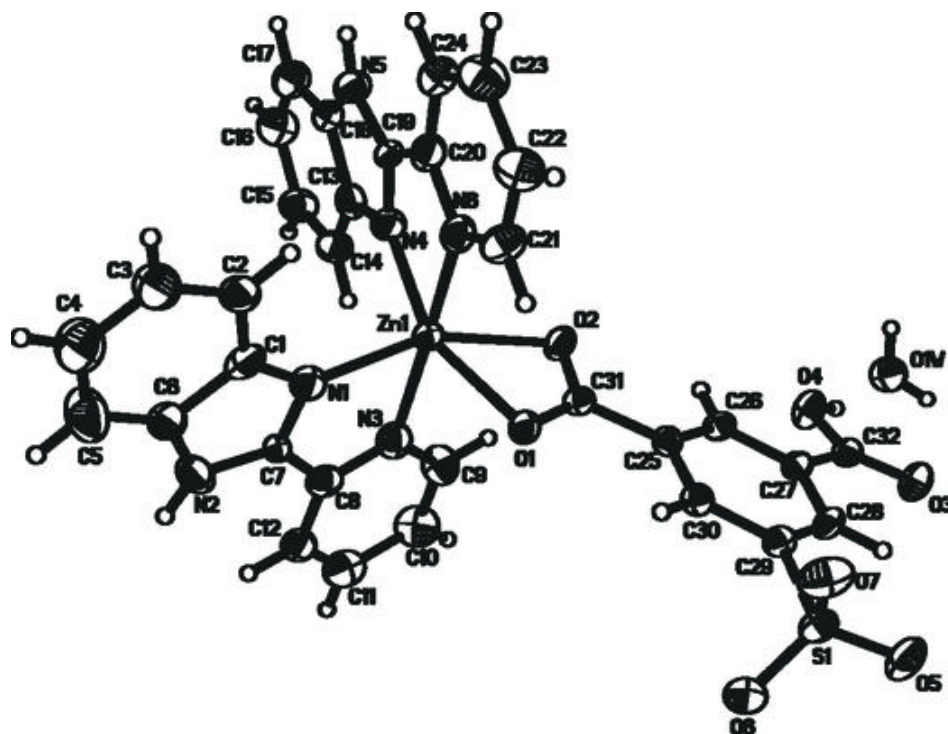


Fig. 2

