Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Aqua(2-hydroxy-5-sulfonatobenzoato-κO^1)bis(2-phenyl-1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthrene-κ^2N^7,N^8)-zinc(II)

Qiang Han,[a] Xiang-Cheng Wang,[b] Xiu-Ying Li,[b] Guan-Xin Yao[a] and Yong-Sheng Yan[b]*

[a]School of Material Science and Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China, and [b]School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China
Correspondence e-mail: yys@ujs.edu.cn

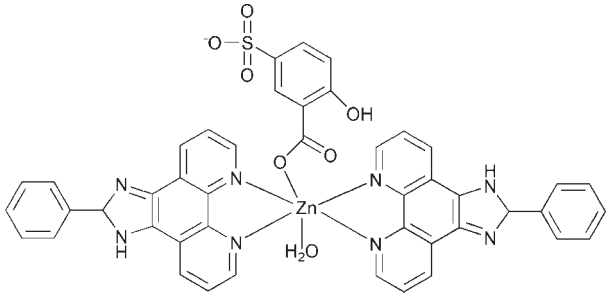
Received 25 September 2009; accepted 26 September 2009

Key indicators: single-crystal X-ray study; T = 292 K; mean σ(C–C) = 0.005 Å; R factor = 0.049; wR factor = 0.132; data-to-parameter ratio = 11.8.

In the title compound, $[Zn(C_7H_4O_6S)(C_{19}H_{12}N_4)_2(H_2O)]$, the Zn^{II} ion is coordinated by two *N*,*N*′-bidentate 2-phenyl-1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthrene ligands, one *O*-monodentate 5-sulfosalicylate dianion and a water molecule. This results in a distorted *cis*-ZnO_2N_4 octahedral coordination geometry for the metal ion. In the crystal, molecules are expanded into a three-dimensional supramolecular motif *via* O—H···O, O—H···N and N—H···(O,S) hydrogen bonds. In addition, π–π stacking interactions between the aromatic rings of the polycyclic ligands consolidate the sturcture [shortest centroid–centroid distance = 3.501 (2) Å].

Related literature

For related structures, see: Che *et al.* (2008); Li *et al.* (2009); Liu *et al.* (2009). For the synthesis of the ligand, see: Steck & Day (1943).



Experimental

Crystal data

$[Zn(C_7H_4O_6S)(C_{19}H_{12}N_4)_2(H_2O)]$
M_r = 892.20
Monoclinic, $P2_1/n$
a = 8.3257 (8) Å
b = 25.926 (2) Å
c = 18.3271 (13) Å
β = 101.259 (8)°
V = 3879.8 (6) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 1.94 mm^{-1}
T = 292 K
0.27 × 0.26 × 0.23 mm

Data collection

Oxford Diffraction Gemini R Ultra diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.621, T_{max} = 0.640
15767 measured reflections
6808 independent reflections
4337 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.132
S = 0.97
6808 reflections
575 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—O1	2.080 (3)	Zn—N2	2.184 (3)
Zn—O*W*1	2.196 (3)	Zn—N5	2.141 (3)
Zn—N1	2.177 (3)	Zn—N6	2.120 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*C*···O2	0.82	1.82	2.547 (4)	147
O*W*1—H1*WA*···O2	0.86 (2)	1.90 (3)	2.712 (4)	157 (5)
O*W*1—H1*WB*···N7^{i}	0.840 (19)	2.05 (2)	2.877 (4)	170 (4)
N4—H4*B*···O6^{ii}	0.86 (4)	2.05 (4)	2.883 (4)	162 (4)
N4—H4*B*···S1^{ii}	0.86 (4)	3.02 (4)	3.854 (4)	163 (3)
N8—H8*B*···O4^{iii}	0.96 (5)	1.85 (5)	2.794 (5)	167 (5)
N8—H8*B*···S1^{iii}	0.96 (5)	2.94 (5)	3.793 (4)	148 (4)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

The authors thank Jiangsu University for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5120).

References

Che, G.-B., Liu, C.-B., Liu, B., Wang, Q.-W. & Xu, Z.-L. (2008). *CrystEngComm*, **10**, 184–191.
Li, C.-X., Li, X.-Y., Liu, C.-B., Yan, Y.-S. & Che, G.-B. (2009). *Acta Cryst.* E**65**, m53.
Liu, D.-M., Li, X.-Y., Wang, X.-C., Li, C.-X. & Liu, C.-B. (2009). *Acta Cryst.* E**65**, o1308.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction, Abingdon, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Steck, E. A. & Day, A. R. (1943). *J. Am. Chem. Soc.* **65**, 452–456.

supplementary materials

Acta Cryst. (2009). E**65**, m1282-m1283 [**doi:10.1107/S1600536809039154**]

Aqua(2-hydroxy-5-sulfonatobenzoato-κO^1)bis(2-phenyl-1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthrene-κ^2N^7,N^8)zinc(II)

Q. Han, X.-C. Wang, X.-Y. Li, G.-X. Yao and Y.-S. Yan

Comment

1,10-phenanthroline (phen) and its derivatives has been widely used to build supramolecular architectures owing to their excellent coordinating ability and large conjugated system (Che *et al.*, 2008; Li *et al.*, 2009). Whenas, building blocks derived from the appropriate modification of phen, such as 2-phenyl-1*H*-1,3,7,8-tetra-azacyclopenta[*l*]phenanthrene (*L*) have received considerably less attention (Liu *et al.*, 2009). Hereby, we have prepared the title compound, namely, $[Zn(C_{19}H_{12}N_4)_2(C_7H_4O_6S)H_2O]$ or $[Zn(L)_2(HSSA)H_2O]$ (I), based on *L* and 5-sulfosalicylic acid (H_3SSA) ligands.

In the compound (I), each Zn atom is six-coordinated by four N atoms from two *L* ligands, one O atom from a HSSA ligand and one water molecule (Fig. 1). The Zn—O distances range from 2.080 (3) Å to 2.196 (3) Å and the Zn—N lengths from 2.120 (3) to 2.184 (3) Å (Table 1). The N1, N5, N6, O1W atoms comprise the basal plane, while the O1 and N2 atoms occupy the axial position. In (I), $–CO_2H$ and $–SO_3H$ groups are deprotonated, but –OH groups are neutral. The carboxylate group of a HSSA ligand displays monodentate bridging coordination mode, whenas –OH and $–SO_3^-$ groups are uncoordinated.

The neighboring mononuclear Zn^{II} units interact by various hydrogen bonds, leading to a three-dimensional supramolecular structure (Fig. 2): (*a*) N—H···O or N—H···S hydrogen bonds between imidazole rings donors and the sulfonic groups of the HSSA ligands [N4···O6^{i}: 2.883 (4) Å; N4···S1^{i}: 3.854 (4) Å; N8···O4^{ii}: 2.794 (5) Å; N8···S1^{ii}: 3.793 (4) Å, symmetry code: (i) -*x* + 3/2, *y* - 1/2, -*z* + 3/2, (ii) -*x* + 1, -*y* + 1, -*z* + 1]. (*b*) O—H···O or O—H···N hydrogen bonds involving the coordinated water molecule OW1 and the O2, N7^{ii} atoms [O1W···O2: 2.712 (4) Å; O1W···N7^{iii}: 2.877 (4) Å, symmetry code: (iii) *x* + 1/2, -*y* + 1/2, *z* + 1/2]. (*c*) Intramolecular O—H···O hydrogen bonds involving hydroxy oxygen atom of HSSA anion and carboxylate O2 atom [O3···O2: 2.547 (4) Å] (Table 2). In addition, π-π stacking interactions between *L* ligands further intensify the current architectures with a shortest stacking distance of 3.501 (2) Å.

Experimental

The *L* ligand was synthesized according to the literature method (Steck & Day, 1943). A mixture of *L*, H_3SSA, $Zn(NO_3)_2$ and water in the mole ratio 1:1:1:4000 was placed in a 25 ml Teflon-lined autoclave and heated for 4 d at 433 K under autogenous pressure. Upon cooling and opening the bomb, yellow blocks of (I) were obtained, which were washed with H_2O and dried in air (62% yield based on Zn).

Refinement

All H atoms on C atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding, with U_{iso}(H)= 1.2U_{eq}(C). The hydrogen atoms of water molecules were located from difference Fourier maps and their positions and U_{iso} values were refined freely.

Figures

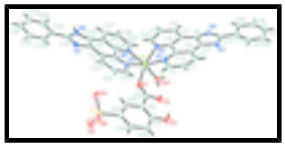


Fig. 1. View of the local coordination of compound (I) with displacement ellipsoids drawn at the 30% probability level. (arbitrary spheres for the H atoms).

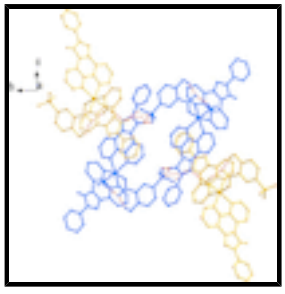


Fig. 2. View of three-dimensional superamolecular structure of (I) built up *via* hydrogen bonds and π-π interactions. Most H atoms have been omitted.

Aqua(2-hydroxy-5-sulfonatobenzoato-κ*O*^{1})bis(2-phenyl-1*H*-1,3,7,8-tetraazacyclopenta[*l*]phenanthrene-κ^2*N*^{7},*N*^{8})zinc(II)

Crystal data

$[Zn(C_7H_4O_6S)(C_{19}H_{12}N_4)_2(H_2O)]$	F_{000} = 1832
	D_x = 1.527 Mg m^{-3}
M_r = 892.20	D_m = 1.527 Mg m^{-3}
	D_m measured by not measured
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, λ = 1.5418 Å
Hall symbol: -P 2yn	Cell parameters from 3619 reflections
a = 8.3257 (8) Å	θ = 4.9–67.0º
b = 25.926 (2) Å	μ = 1.94 mm^{-1}
c = 18.3271 (13) Å	T = 292 K
β = 101.259 (8)º	Block, yellow
V = 3879.8 (6) Å^3	0.27 × 0.26 × 0.23 mm
Z = 4	

Data collection

Oxford Diffraction Gemini R Ultra diffractometer	6808 independent reflections
Radiation source: fine-focus sealed tube	4337 reflections with $I > 2\sigma(I)$
Monochromator: mirror	R_{int} = 0.055

Detector resolution: 10.2375 pixels mm^{-1}

T = 292 K

ω scans

Absorption correction: multi-scan
(Crys Alis RED; Oxford Diffraction, 2006)

T_{min} = 0.621, T_{max} = 0.640

15767 measured reflections

θ_{max} = 67.1º

θ_{min} = 4.9º

h = −9→9

k = −30→30

l = −21→19

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.049

$wR(F^2)$ = 0.132

S = 0.97

6808 reflections

575 parameters

2 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.41 e $Å^{-3}$

$\Delta\rho_{min}$ = −0.28 e $Å^{-3}$

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}
C1	0.8928 (5)	0.36143 (15)	0.8278 (2)	0.0515 (10)
H1	0.8158	0.3878	0.8189	0.062*
C2	1.0106 (6)	0.36325 (16)	0.8925 (2)	0.0577 (11)
H2	1.0148	0.3908	0.9252	0.069*
C3	1.1200 (5)	0.32385 (16)	0.9071 (2)	0.0542 (11)
H3	1.1966	0.3235	0.9515	0.065*
C4	1.1179 (5)	0.28381 (14)	0.85566 (19)	0.0413 (8)
C5	1.2235 (5)	0.24000 (14)	0.86501 (19)	0.0440 (9)
C6	1.2180 (5)	0.20368 (14)	0.80857 (19)	0.0419 (8)

C7	1.1048 (4)	0.20682 (14)	0.73901 (18)	0.0399 (8)
C8	1.0964 (5)	0.17231 (15)	0.6789 (2)	0.0465 (9)
H8	1.1703	0.1451	0.6817	0.056*
C9	0.9786 (5)	0.17933 (16)	0.6169 (2)	0.0517 (10)
H9	0.9734	0.1577	0.5761	0.062*
C10	0.8664 (5)	0.21915 (15)	0.6151 (2)	0.0496 (10)
H10	0.7850	0.2230	0.5728	0.059*
C11	0.9915 (5)	0.24714 (13)	0.73182 (18)	0.0399 (8)
C12	0.9970 (5)	0.28631 (14)	0.79011 (18)	0.0408 (8)
C13	1.3962 (5)	0.18131 (14)	0.90865 (19)	0.0433 (9)
C14	1.5168 (5)	0.15014 (14)	0.9583 (2)	0.0446 (9)
C15	1.5650 (5)	0.16544 (16)	1.0328 (2)	0.0517 (10)
H15	1.5198	0.1949	1.0496	0.062*
C16	1.6782 (5)	0.13724 (17)	1.0811 (2)	0.0580 (11)
H16	1.7114	0.1482	1.1301	0.070*
C17	1.7434 (6)	0.09257 (17)	1.0573 (2)	0.0600 (11)
H17	1.8186	0.0731	1.0904	0.072*
C18	1.6960 (5)	0.07698 (16)	0.9839 (2)	0.0585 (11)
H18	1.7404	0.0472	0.9676	0.070*
C19	1.5831 (5)	0.10548 (15)	0.9349 (2)	0.0499 (10)
H19	1.5513	0.0946	0.8858	0.060*
C20	0.4122 (5)	0.23843 (15)	0.5864 (2)	0.0499 (10)
H20	0.4109	0.2184	0.6283	0.060*
C21	0.3110 (5)	0.22443 (15)	0.5196 (2)	0.0515 (10)
H21	0.2462	0.1950	0.5168	0.062*
C22	0.3083 (5)	0.25462 (14)	0.4581 (2)	0.0474 (9)
H22	0.2404	0.2461	0.4132	0.057*
C23	0.4081 (4)	0.29835 (13)	0.46294 (17)	0.0377 (8)
C24	0.4131 (5)	0.33440 (14)	0.40410 (18)	0.0402 (8)
C25	0.5154 (5)	0.37647 (14)	0.41540 (18)	0.0409 (8)
C26	0.6232 (5)	0.38829 (13)	0.48406 (18)	0.0397 (8)
C27	0.7254 (5)	0.43149 (14)	0.4979 (2)	0.0455 (9)
H27	0.7312	0.4551	0.4604	0.055*
C28	0.8174 (5)	0.43826 (15)	0.5685 (2)	0.0521 (10)
H28	0.8873	0.4664	0.5792	0.063*
C29	0.8042 (5)	0.40256 (14)	0.6231 (2)	0.0469 (9)
H29	0.8662	0.4078	0.6705	0.056*
C30	0.6169 (4)	0.35370 (13)	0.54261 (18)	0.0388 (8)
C31	0.5108 (4)	0.30925 (13)	0.53248 (18)	0.0374 (8)
C32	0.3580 (5)	0.37973 (15)	0.30428 (19)	0.0446 (9)
C33	0.2823 (5)	0.40102 (16)	0.23082 (19)	0.0482 (9)
C34	0.1441 (6)	0.37953 (18)	0.1892 (2)	0.0624 (12)
H34	0.0982	0.3507	0.2072	0.075*
C35	0.0714 (7)	0.3997 (2)	0.1212 (3)	0.0758 (15)
H35	−0.0223	0.3843	0.0938	0.091*
C36	0.1369 (7)	0.4422 (2)	0.0939 (3)	0.0833 (16)
H36	0.0882	0.4559	0.0481	0.100*
C37	0.2733 (8)	0.4642 (3)	0.1343 (3)	0.101 (2)
H37	0.3186	0.4931	0.1161	0.122*

C38	0.3453 (7)	0.4437 (2)	0.2027 (3)	0.0862 (18)
H38	0.4385	0.4593	0.2301	0.103*
C39	0.4948 (5)	0.35307 (16)	0.8007 (2)	0.0493 (10)
C40	0.4200 (5)	0.40138 (15)	0.82448 (19)	0.0451 (9)
C41	0.4235 (6)	0.41146 (17)	0.8999 (2)	0.0554 (11)
C42	0.3566 (6)	0.45676 (17)	0.9206 (2)	0.0618 (12)
H42	0.3606	0.4638	0.9706	0.074*
C43	0.2841 (6)	0.49147 (17)	0.8672 (2)	0.0591 (11)
H43	0.2375	0.5216	0.8813	0.071*
C44	0.2805 (5)	0.48158 (14)	0.7923 (2)	0.0462 (9)
C45	0.3491 (5)	0.43707 (14)	0.77218 (19)	0.0456 (9)
H45	0.3479	0.4308	0.7221	0.055*
O1	0.5147 (4)	0.35041 (11)	0.73431 (14)	0.0549 (7)
O2	0.5356 (4)	0.31814 (11)	0.84891 (15)	0.0637 (8)
O3	0.4895 (5)	0.37738 (13)	0.95378 (15)	0.0761 (10)
H3C	0.5247	0.3523	0.9347	0.114*
O4	0.2865 (4)	0.52048 (11)	0.66450 (15)	0.0647 (8)
O5	0.0217 (4)	0.50440 (12)	0.69531 (18)	0.0720 (9)
O6	0.1886 (4)	0.57477 (10)	0.75266 (16)	0.0630 (8)
OW1	0.6019 (4)	0.24205 (11)	0.75763 (15)	0.0530 (7)
S1	0.18387 (13)	0.52366 (4)	0.72053 (5)	0.0505 (3)
N1	0.8838 (4)	0.32410 (12)	0.77783 (16)	0.0455 (8)
N2	0.8700 (4)	0.25209 (11)	0.67122 (15)	0.0430 (7)
N3	1.3373 (4)	0.22601 (12)	0.92645 (16)	0.0470 (8)
N4	1.3291 (4)	0.16684 (13)	0.83680 (17)	0.0434 (7)
N5	0.5096 (4)	0.27879 (11)	0.59281 (15)	0.0414 (7)
N6	0.7089 (4)	0.36156 (12)	0.61175 (15)	0.0417 (7)
N7	0.3145 (4)	0.33662 (12)	0.33373 (15)	0.0423 (7)
N8	0.4802 (4)	0.40487 (12)	0.35073 (15)	0.0447 (8)
Zn	0.67652 (6)	0.304312 (19)	0.69016 (2)	0.04405 (16)
H1WA	0.560 (6)	0.2603 (18)	0.788 (2)	0.085 (18)*
H1WB	0.671 (4)	0.2195 (13)	0.776 (2)	0.058 (13)*
H4B	1.342 (5)	0.1371 (16)	0.818 (2)	0.043 (11)*
H8B	0.547 (6)	0.434 (2)	0.344 (3)	0.085 (17)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.064 (3)	0.042 (2)	0.044 (2)	0.0063 (19)	−0.0015 (19)	−0.0042 (17)
C2	0.079 (3)	0.048 (2)	0.041 (2)	−0.002 (2)	−0.002 (2)	−0.0106 (17)
C3	0.064 (3)	0.051 (2)	0.038 (2)	−0.003 (2)	−0.0128 (18)	−0.0074 (18)
C4	0.050 (2)	0.0380 (18)	0.0314 (17)	−0.0051 (17)	−0.0021 (15)	0.0011 (15)
C5	0.048 (2)	0.047 (2)	0.0324 (18)	−0.0059 (17)	−0.0038 (16)	0.0048 (16)
C6	0.045 (2)	0.044 (2)	0.0322 (17)	−0.0035 (17)	−0.0024 (15)	0.0022 (15)
C7	0.047 (2)	0.044 (2)	0.0267 (16)	−0.0041 (17)	0.0017 (15)	0.0040 (14)
C8	0.056 (2)	0.048 (2)	0.0356 (19)	0.0032 (18)	0.0089 (17)	0.0000 (16)
C9	0.066 (3)	0.056 (2)	0.0306 (18)	0.000 (2)	0.0017 (18)	−0.0087 (17)
C10	0.058 (2)	0.055 (2)	0.0294 (18)	0.001 (2)	−0.0065 (17)	−0.0026 (17)

C11	0.047 (2)	0.0413 (19)	0.0286 (17)	−0.0035 (17)	−0.0001 (15)	0.0037 (15)
C12	0.049 (2)	0.0410 (19)	0.0287 (17)	−0.0045 (17)	−0.0016 (15)	0.0019 (14)
C13	0.049 (2)	0.044 (2)	0.0316 (18)	−0.0045 (17)	−0.0055 (16)	0.0034 (15)
C14	0.045 (2)	0.045 (2)	0.040 (2)	−0.0043 (17)	0.0002 (16)	0.0065 (16)
C15	0.061 (3)	0.051 (2)	0.038 (2)	−0.0033 (19)	−0.0032 (18)	0.0024 (17)
C16	0.064 (3)	0.066 (3)	0.038 (2)	−0.004 (2)	−0.0071 (19)	0.0076 (19)
C17	0.059 (3)	0.062 (3)	0.051 (2)	0.003 (2)	−0.007 (2)	0.017 (2)
C18	0.062 (3)	0.047 (2)	0.063 (3)	0.001 (2)	0.003 (2)	0.009 (2)
C19	0.053 (2)	0.046 (2)	0.047 (2)	−0.0073 (18)	−0.0001 (18)	0.0042 (18)
C20	0.058 (2)	0.049 (2)	0.039 (2)	−0.0043 (19)	−0.0012 (18)	0.0097 (17)
C21	0.063 (3)	0.046 (2)	0.041 (2)	−0.0081 (19)	−0.0027 (18)	0.0044 (17)
C22	0.056 (2)	0.045 (2)	0.0347 (19)	−0.0025 (18)	−0.0071 (17)	0.0005 (16)
C23	0.044 (2)	0.0413 (19)	0.0252 (16)	0.0053 (16)	0.0013 (14)	−0.0024 (14)
C24	0.050 (2)	0.044 (2)	0.0238 (16)	0.0019 (17)	0.0010 (15)	−0.0011 (14)
C25	0.050 (2)	0.043 (2)	0.0270 (17)	0.0046 (17)	0.0020 (15)	0.0029 (15)
C26	0.048 (2)	0.0403 (19)	0.0274 (17)	0.0037 (16)	−0.0017 (15)	−0.0009 (14)
C27	0.058 (2)	0.041 (2)	0.0337 (19)	−0.0006 (18)	0.0008 (17)	0.0044 (15)
C28	0.061 (3)	0.045 (2)	0.045 (2)	−0.0053 (19)	−0.0036 (18)	−0.0003 (17)
C29	0.056 (2)	0.045 (2)	0.0335 (19)	−0.0041 (18)	−0.0068 (17)	−0.0026 (16)
C30	0.048 (2)	0.0364 (18)	0.0296 (17)	0.0071 (16)	0.0015 (15)	−0.0014 (14)
C31	0.043 (2)	0.0379 (18)	0.0291 (16)	0.0048 (16)	0.0020 (14)	−0.0001 (14)
C32	0.053 (2)	0.047 (2)	0.0319 (18)	0.0041 (18)	0.0035 (17)	0.0003 (16)
C33	0.059 (2)	0.056 (2)	0.0275 (17)	0.005 (2)	0.0025 (17)	0.0031 (16)
C34	0.075 (3)	0.064 (3)	0.040 (2)	−0.004 (2)	−0.010 (2)	0.006 (2)
C35	0.083 (3)	0.080 (3)	0.050 (3)	−0.006 (3)	−0.021 (2)	0.013 (2)
C36	0.092 (4)	0.102 (4)	0.046 (3)	0.009 (3)	−0.013 (3)	0.025 (3)
C37	0.112 (5)	0.120 (5)	0.061 (3)	−0.026 (4)	−0.012 (3)	0.047 (3)
C38	0.091 (4)	0.097 (4)	0.056 (3)	−0.029 (3)	−0.021 (3)	0.031 (3)
C39	0.055 (2)	0.055 (2)	0.035 (2)	0.0003 (19)	0.0029 (17)	0.0078 (18)
C40	0.053 (2)	0.050 (2)	0.0326 (19)	−0.0002 (18)	0.0077 (16)	0.0055 (16)
C41	0.068 (3)	0.064 (3)	0.032 (2)	0.000 (2)	0.0034 (18)	0.0131 (18)
C42	0.093 (3)	0.065 (3)	0.0281 (19)	0.008 (3)	0.013 (2)	0.0021 (19)
C43	0.082 (3)	0.056 (2)	0.040 (2)	0.001 (2)	0.015 (2)	−0.0049 (19)
C44	0.058 (2)	0.041 (2)	0.0368 (19)	−0.0056 (18)	0.0042 (17)	0.0010 (16)
C45	0.063 (2)	0.046 (2)	0.0279 (18)	−0.0028 (18)	0.0090 (17)	0.0049 (16)
O1	0.0694 (19)	0.0610 (17)	0.0317 (14)	0.0165 (14)	0.0037 (12)	0.0042 (12)
O2	0.088 (2)	0.0598 (17)	0.0427 (15)	0.0196 (16)	0.0106 (15)	0.0163 (13)
O3	0.115 (3)	0.079 (2)	0.0325 (14)	0.024 (2)	0.0107 (16)	0.0190 (14)
O4	0.102 (2)	0.0548 (17)	0.0377 (15)	−0.0002 (16)	0.0142 (15)	0.0096 (12)
O5	0.069 (2)	0.0657 (19)	0.070 (2)	−0.0097 (16)	−0.0132 (16)	0.0058 (16)
O6	0.090 (2)	0.0400 (15)	0.0534 (16)	0.0009 (15)	0.0012 (15)	−0.0008 (13)
OW1	0.070 (2)	0.0505 (17)	0.0360 (14)	0.0062 (15)	0.0031 (14)	0.0059 (13)
S1	0.0690 (7)	0.0400 (5)	0.0379 (5)	−0.0021 (5)	−0.0012 (5)	0.0026 (4)
N1	0.0531 (19)	0.0443 (17)	0.0342 (16)	0.0029 (15)	−0.0038 (14)	−0.0004 (13)
N2	0.0509 (18)	0.0456 (17)	0.0283 (15)	0.0036 (14)	−0.0026 (13)	0.0015 (13)
N3	0.0510 (19)	0.0470 (18)	0.0363 (16)	−0.0050 (15)	−0.0077 (14)	0.0020 (13)
N4	0.0508 (19)	0.0391 (18)	0.0361 (16)	0.0011 (15)	−0.0022 (14)	0.0026 (14)
N5	0.0493 (18)	0.0415 (16)	0.0288 (14)	−0.0026 (14)	−0.0035 (13)	0.0059 (12)
N6	0.0513 (18)	0.0471 (17)	0.0231 (14)	0.0014 (15)	−0.0014 (13)	−0.0002 (12)

N7	0.0512 (19)	0.0480 (18)	0.0246 (14)	0.0032 (14)	−0.0007 (13)	−0.0028 (13)
N8	0.059 (2)	0.0480 (18)	0.0236 (14)	0.0009 (16)	−0.0001 (14)	0.0014 (13)
Zn	0.0535 (3)	0.0465 (3)	0.0276 (2)	0.0027 (2)	−0.00348 (19)	0.0027 (2)

Geometric parameters (Å, °)

C1—N1	1.324 (5)	C26—C30	1.407 (5)
C1—C2	1.384 (6)	C27—C28	1.380 (5)
C1—H1	0.9300	C27—H27	0.9300
C2—C3	1.360 (6)	C28—C29	1.382 (6)
C2—H2	0.9300	C28—H28	0.9300
C3—C4	1.400 (5)	C29—N6	1.318 (5)
C3—H3	0.9300	C29—H29	0.9300
C4—C12	1.410 (5)	C30—N6	1.362 (4)
C4—C5	1.426 (5)	C30—C31	1.442 (5)
C5—N3	1.371 (5)	C31—N5	1.360 (4)
C5—C6	1.393 (5)	C32—N7	1.322 (5)
C6—N4	1.359 (5)	C32—N8	1.359 (5)
C6—C7	1.432 (5)	C32—C33	1.478 (5)
C7—C11	1.397 (5)	C33—C38	1.368 (7)
C7—C8	1.410 (5)	C33—C34	1.369 (6)
C8—C9	1.361 (5)	C34—C35	1.377 (6)
C8—H8	0.9300	C34—H34	0.9300
C9—C10	1.389 (6)	C35—C36	1.367 (8)
C9—H9	0.9300	C35—H35	0.9300
C10—N2	1.332 (5)	C36—C37	1.354 (8)
C10—H10	0.9300	C36—H36	0.9300
C11—N2	1.354 (4)	C37—C38	1.386 (6)
C11—C12	1.468 (5)	C37—H37	0.9300
C12—N1	1.348 (5)	C38—H38	0.9300
C13—N3	1.324 (5)	C39—O1	1.261 (5)
C13—N4	1.378 (5)	C39—O2	1.265 (5)
C13—C14	1.460 (5)	C39—C40	1.501 (6)
C14—C19	1.386 (6)	C40—C45	1.379 (5)
C14—C15	1.404 (5)	C40—C41	1.401 (5)
C15—C16	1.371 (6)	C41—O3	1.359 (5)
C15—H15	0.9300	C41—C42	1.384 (6)
C16—C17	1.385 (7)	C42—C43	1.378 (6)
C16—H16	0.9300	C42—H42	0.9300
C17—C18	1.386 (6)	C43—C44	1.392 (5)
C17—H17	0.9300	C43—H43	0.9300
C18—C19	1.381 (6)	C44—C45	1.369 (6)
C18—H18	0.9300	C44—S1	1.776 (4)
C19—H19	0.9300	C45—H45	0.9300
C20—N5	1.315 (5)	O3—H3C	0.8200
C20—C21	1.392 (5)	O4—S1	1.461 (3)
C20—H20	0.9300	O5—S1	1.429 (3)
C21—C22	1.369 (5)	O6—S1	1.448 (3)
C21—H21	0.9300	OW1—H1WA	0.86 (2)

C22—C23	1.398 (5)	OW1—H1WB	0.840 (19)
C22—H22	0.9300	N4—H4B	0.86 (4)
C23—C31	1.417 (4)	N8—H8B	0.96 (5)
C23—C24	1.434 (5)	Zn—O1	2.080 (3)
C24—C25	1.374 (5)	Zn—OW1	2.196 (3)
C24—N7	1.388 (4)	Zn—N1	2.177 (3)
C25—N8	1.377 (4)	Zn—N2	2.184 (3)
C25—C26	1.429 (5)	Zn—N5	2.141 (3)
C26—C27	1.400 (5)	Zn—N6	2.120 (3)
N1—C1—C2	123.5 (4)	N5—C31—C30	117.4 (3)
N1—C1—H1	118.2	C23—C31—C30	121.5 (3)
C2—C1—H1	118.2	N7—C32—N8	112.4 (3)
C3—C2—C1	118.6 (4)	N7—C32—C33	125.8 (3)
C3—C2—H2	120.7	N8—C32—C33	121.7 (3)
C1—C2—H2	120.7	C38—C33—C34	117.5 (4)
C2—C3—C4	120.2 (3)	C38—C33—C32	121.2 (4)
C2—C3—H3	119.9	C34—C33—C32	121.3 (4)
C4—C3—H3	119.9	C33—C34—C35	121.6 (4)
C3—C4—C12	116.9 (3)	C33—C34—H34	119.2
C3—C4—C5	125.6 (3)	C35—C34—H34	119.2
C12—C4—C5	117.4 (3)	C36—C35—C34	120.0 (5)
N3—C5—C6	110.4 (3)	C36—C35—H35	120.0
N3—C5—C4	128.3 (3)	C34—C35—H35	120.0
C6—C5—C4	121.3 (3)	C37—C36—C35	119.5 (4)
N4—C6—C5	105.7 (3)	C37—C36—H36	120.3
N4—C6—C7	131.2 (3)	C35—C36—H36	120.3
C5—C6—C7	122.9 (3)	C36—C37—C38	120.1 (5)
C11—C7—C8	118.1 (3)	C36—C37—H37	119.9
C11—C7—C6	116.2 (3)	C38—C37—H37	119.9
C8—C7—C6	125.6 (4)	C33—C38—C37	121.3 (5)
C9—C8—C7	119.0 (4)	C33—C38—H38	119.3
C9—C8—H8	120.5	C37—C38—H38	119.3
C7—C8—H8	120.5	O1—C39—O2	124.6 (4)
C8—C9—C10	119.4 (4)	O1—C39—C40	117.8 (3)
C8—C9—H9	120.3	O2—C39—C40	117.6 (3)
C10—C9—H9	120.3	C45—C40—C41	118.9 (4)
N2—C10—C9	123.0 (3)	C45—C40—C39	120.2 (3)
N2—C10—H10	118.5	C41—C40—C39	120.8 (3)
C9—C10—H10	118.5	O3—C41—C42	118.6 (4)
N2—C11—C7	122.0 (3)	O3—C41—C40	121.6 (4)
N2—C11—C12	116.3 (3)	C42—C41—C40	119.8 (4)
C7—C11—C12	121.6 (3)	C43—C42—C41	120.2 (4)
N1—C12—C4	122.4 (3)	C43—C42—H42	119.9
N1—C12—C11	117.4 (3)	C41—C42—H42	119.9
C4—C12—C11	120.3 (3)	C42—C43—C44	120.1 (4)
N3—C13—N4	111.9 (3)	C42—C43—H43	119.9
N3—C13—C14	125.0 (3)	C44—C43—H43	119.9
N4—C13—C14	123.1 (3)	C45—C44—C43	119.4 (4)
C19—C14—C15	118.8 (3)	C45—C44—S1	118.1 (3)

C19—C14—C13	122.5 (3)	C43—C44—S1	122.5 (3)
C15—C14—C13	118.7 (4)	C44—C45—C40	121.5 (3)
C16—C15—C14	120.5 (4)	C44—C45—H45	119.2
C16—C15—H15	119.8	C40—C45—H45	119.2
C14—C15—H15	119.8	C39—O1—Zn	128.6 (3)
C15—C16—C17	120.3 (4)	C41—O3—H3C	109.5
C15—C16—H16	119.8	Zn—OW1—H1WA	99 (4)
C17—C16—H16	119.8	Zn—OW1—H1WB	119 (3)
C16—C17—C18	119.6 (4)	H1WA—OW1—H1WB	118 (5)
C16—C17—H17	120.2	O5—S1—O6	113.6 (2)
C18—C17—H17	120.2	O5—S1—O4	113.49 (19)
C19—C18—C17	120.3 (4)	O6—S1—O4	111.35 (19)
C19—C18—H18	119.9	O5—S1—C44	106.73 (18)
C17—C18—H18	119.9	O6—S1—C44	106.79 (17)
C18—C19—C14	120.5 (4)	O4—S1—C44	104.06 (19)
C18—C19—H19	119.7	C1—N1—C12	118.2 (3)
C14—C19—H19	119.7	C1—N1—Zn	127.7 (3)
N5—C20—C21	122.9 (4)	C12—N1—Zn	112.3 (2)
N5—C20—H20	118.5	C10—N2—C11	118.2 (3)
C21—C20—H20	118.5	C10—N2—Zn	127.9 (3)
C22—C21—C20	119.0 (4)	C11—N2—Zn	112.6 (2)
C22—C21—H21	120.5	C13—N3—C5	105.0 (3)
C20—C21—H21	120.5	C6—N4—C13	106.9 (3)
C21—C22—C23	119.8 (3)	C6—N4—H4B	127 (3)
C21—C22—H22	120.1	C13—N4—H4B	125 (3)
C23—C22—H22	120.1	C20—N5—C31	119.4 (3)
C22—C23—C31	117.8 (3)	C20—N5—Zn	127.5 (2)
C22—C23—C24	125.8 (3)	C31—N5—Zn	113.1 (2)
C31—C23—C24	116.4 (3)	C29—N6—C30	118.6 (3)
C25—C24—N7	110.1 (3)	C29—N6—Zn	127.6 (2)
C25—C24—C23	120.8 (3)	C30—N6—Zn	113.8 (2)
N7—C24—C23	128.9 (3)	C32—N7—C24	104.8 (3)
C24—C25—N8	105.9 (3)	C32—N8—C25	106.9 (3)
C24—C25—C26	124.5 (3)	C32—N8—H8B	133 (3)
N8—C25—C26	129.4 (3)	C25—N8—H8B	120 (3)
C27—C26—C30	118.9 (3)	O1—Zn—N6	92.25 (12)
C27—C26—C25	125.9 (3)	O1—Zn—N5	97.90 (12)
C30—C26—C25	115.1 (3)	N1—Zn—N2	76.13 (11)
C28—C27—C26	118.6 (3)	N6—Zn—N5	78.42 (11)
C28—C27—H27	120.7	O1—Zn—N1	93.32 (12)
C26—C27—H27	120.7	N6—Zn—N1	98.51 (12)
C27—C28—C29	119.0 (4)	N5—Zn—N1	168.46 (12)
C27—C28—H28	120.5	O1—Zn—N2	166.53 (10)
C29—C28—H28	120.5	N6—Zn—N2	97.52 (12)
N6—C29—C28	123.8 (3)	N5—Zn—N2	93.14 (11)
N6—C29—H29	118.1	O1—Zn—OW1	85.83 (12)
C28—C29—H29	118.1	N6—Zn—OW1	169.79 (11)
N6—C30—C26	121.1 (3)	N5—Zn—OW1	91.90 (11)
N6—C30—C31	117.3 (3)	N1—Zn—OW1	91.62 (11)

C26—C30—C31	121.6 (3)	N2—Zn—OW1	86.12 (12)
N5—C31—C23	121.1 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3C···O2	0.82	1.82	2.547 (4)	147
OW1—H1WA···O2	0.86 (2)	1.90 (3)	2.712 (4)	157 (5)
OW1—H1WB···N7^{i}	0.840 (19)	2.05 (2)	2.877 (4)	170 (4)
N4—H4B···O6^{ii}	0.86 (4)	2.05 (4)	2.883 (4)	162 (4)
N4—H4B···S1^{ii}	0.86 (4)	3.02 (4)	3.854 (4)	163 (3)
N8—H8B···O4^{iii}	0.96 (5)	1.85 (5)	2.794 (5)	167 (5)
N8—H8B···S1^{iii}	0.96 (5)	2.94 (5)	3.793 (4)	148 (4)

Symmetry codes: (i) *x*+1/2, −*y*+1/2, *z*+1/2; (ii) −*x*+3/2, *y*−1/2, −*z*+3/2; (iii) −*x*+1, −*y*+1, −*z*+1.

Fig. 1

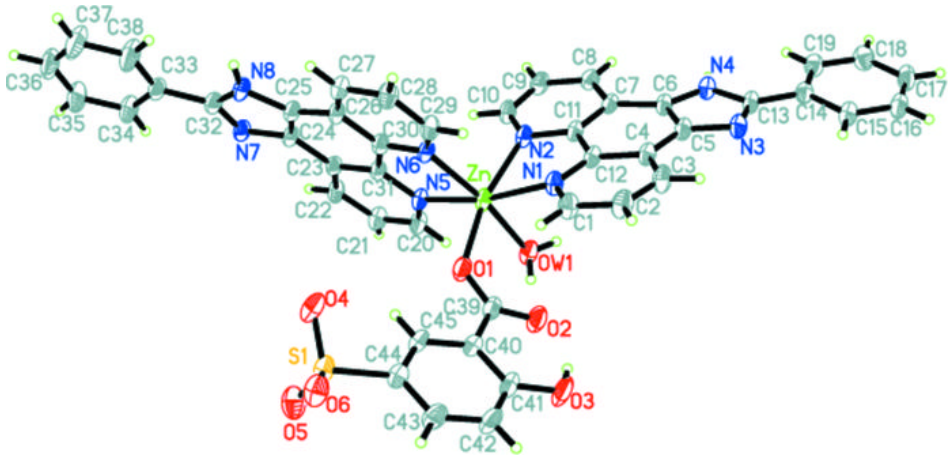

C37
C38
C36
C33
N8
C27
C25
C28
C26
C29
C10
C9
C8
C7
C6
N4
C19
C18
C17
C35
C34
C32
N7
C24
C30
N6
N5
Zn
N2
N1
C11
C4
C5
N3
C13
C14
C15
C16
C23
C31
C12
C3
C22
C21
C20
C1
C2
O1
OW1
O4
C39
C45
O2
S1
C44
C40
O6
C41
O3
O5
C43
C42

Fig. 2