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

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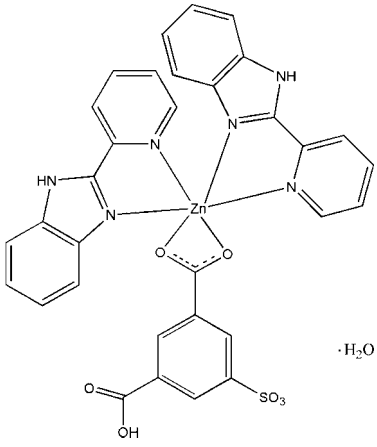
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.008 Å; $R$ factor = 0.064; $wR$ factor = 0.179; data-to-parameter ratio = 16.0.

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)-1*H*-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···O and N—H···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, $P\overline{1}$
$a$ = 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) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.93 mm$^{-1}$
$T$ = 293 K
0.14 × 0.11 × 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···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2$B$···O1$^{i}$ | 0.86 | 2.15 | 2.884 (5) | 143 |
| N5—H5$B$···O3$^{ii}$ | 0.86 | 2.05 | 2.833 (5) | 151 |
| O1$W$—H1$WA$···O7$^{iii}$ | 0.82 | 1.87 | 2.678 (5) | 167 |
| O1$W$—H1$WB$···O6$^{iv}$ | 0.82 | 2.05 | 2.825 (5) | 157 |
| O4—H4$B$···O1$W$ | 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).

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

# supporting information

*Acta Cryst.* (2009). E**65**, m413–m414 [doi:10.1107/S1600536809009180]

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

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## S1. 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 $\pi$–$\pi$ interactions (Xia *et al.*, 2005). 5-Sulfoisophthalic acid ($H_3$sipa), 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 $Hsipa^{2-}$ 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 $Hsipa^{2-}$ 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 $\pi$–$\pi$ 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.

## S2. Experimental

A mixture of $Zn(NO_3)_2.6H_2O$ (0.092 g, 0.3 mmol), $NaH_2$sipa (0.053 g, 0.2 mmol), 2-pbim (0.039 g, 0.2 mmol) and $H_2O$ (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)

## S3. Refinement

The water H atoms were located in a difference Fourier map and fixed in refinement with O—H = 0.82 Å and $U_{iso}$(H) = 1.5$U_{eq}$(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 $U_{iso}$(H) = 1.5$U_{eq}$(O) or $U_{iso}$(H) = 1.2$U_{eq}$(C, N).

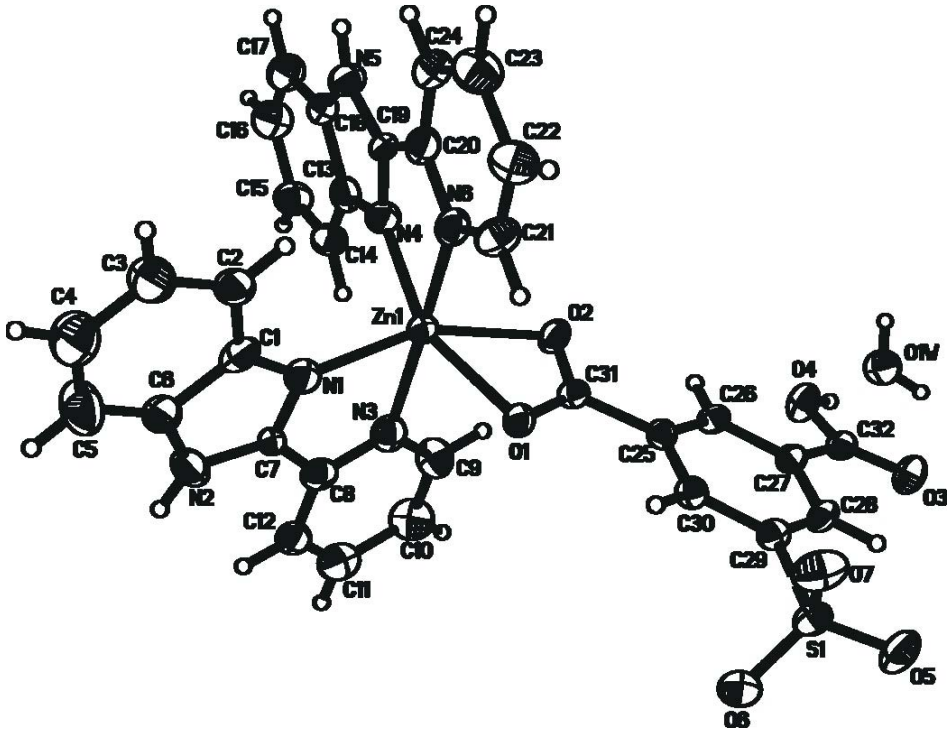


**Figure 1**

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

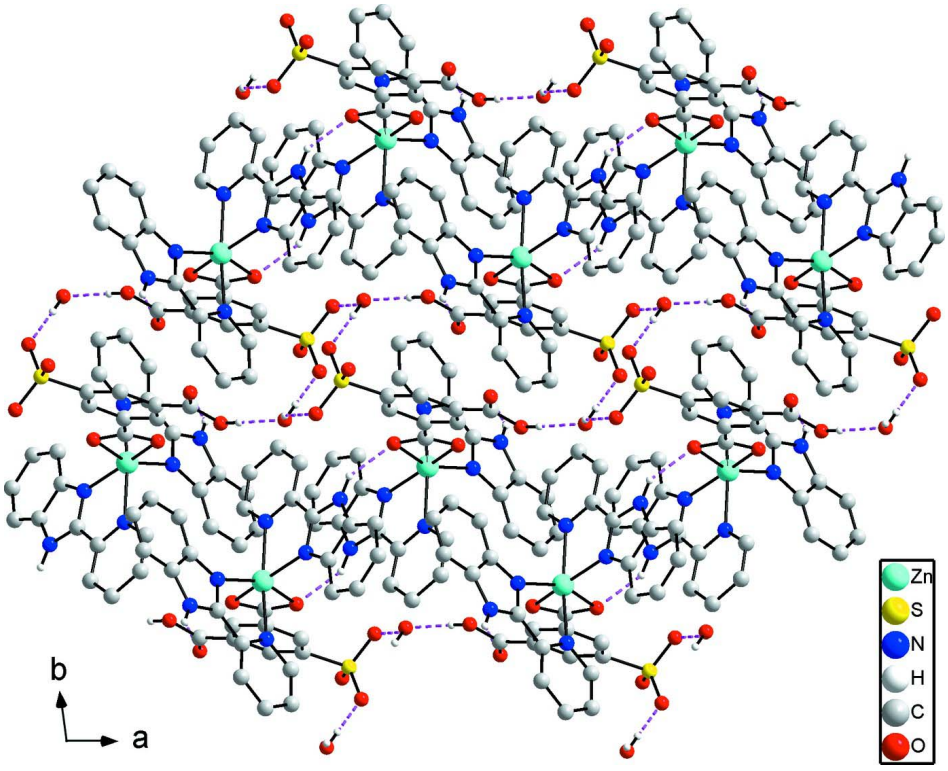


**Figure 2**

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.

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*Crystal data*

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Triclinic, $P\overline{1}$
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$a = 11.086\ (4)$ Å
$b = 12.695\ (5)$ Å
$c = 13.347\ (4)$ Å
$\alpha = 63.187\ (10)°$
$\beta = 68.376\ (13)°$
$\gamma = 87.122\ (17)°$
$V = 1543.2\ (10)$ Å$^3$
$Z = 2$
$F(000) = 736$
$D_x = 1.545$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3438 reflections
$\theta = 2.4–27.5°$
$\mu = 0.93$ mm$^{-1}$
$T = 293$ K
Prism, colorless
0.14 × 0.11 × 0.08 mm

*Data collection*

Rigaku Mercury CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 14.6306 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)
$T_{min} = 0.843$, $T_{max} = 0.929$
12166 measured reflections
6935 independent reflections
3857 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 27.4°$, $\theta_{min} = 2.4°$
$h = -13\rightarrow14$
$k = -16\rightarrow16$
$l = -14\rightarrow17$

*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
0 restraints
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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.89$ e Å$^{-3}$
$\Delta\rho_{min} = -0.43$ e Å$^{-3}$

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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) |
| 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 (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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) |
| 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, º)*

| | | | |
|---|---|---|---|
| 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 |

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|---|---|---|---|
| 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 |

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|---|---|---|---|
| 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 |

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|---|---|---|---|
| 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 |
| 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 (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2*B*···O1$^{i}$ | 0.86 | 2.15 | 2.884 (5) | 143 |
| N5—H5*B*···O3$^{ii}$ | 0.86 | 2.05 | 2.833 (5) | 151 |
| O1*W*—H1*WA*···O7$^{iii}$ | 0.82 | 1.87 | 2.678 (5) | 167 |
| O1*W*—H1*WB*···O6$^{iv}$ | 0.82 | 2.05 | 2.825 (5) | 157 |
| O4—H4*B*···O1*W* | 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*.