

## Triaqua(1,10-phenanthroline- $\kappa^2N,N'$ )-(sulfato- $\kappa O$ )zinc(II)

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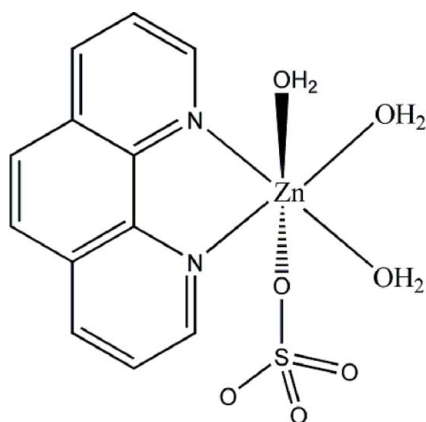
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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(C-C) = 0.004$  Å;  $R$  factor = 0.021;  $wR$  factor = 0.050; data-to-parameter ratio = 13.4.

The Zn(II) atom in the title compound,  $[Zn(SO_4)(C_{12}H_8N_2)(H_2O)_3]$ , is coordinated by one O atom from a sulfate dianion, two N atoms from a 1,10-phenanthroline molecule and three water O atoms in an octahedral geometry. An intramolecular O—H...O hydrogen bond occurs. Intermolecular O—H...O hydrogen bonds generate a layer structure parallel to (001). There are weak C—H...O interactions within the layers.

### Related literature

For related structures, see: An *et al.* (2007); Dietz *et al.* (2009); Harvey *et al.* (2000); Hu *et al.* (2009); Zheng *et al.* (2002).



### Experimental

#### Crystal data

$[Zn(SO_4)(C_{12}H_8N_2)(H_2O)_3]$

$M_r = 395.71$

Orthorhombic,  $P2_12_12_1$

$a = 8.0011$  (4) Å

$b = 9.6006$  (4) Å

$c = 19.1606$  (9) Å

$V = 1471.83$  (12) Å<sup>3</sup>

$Z = 4$

Mo  $K\alpha$  radiation

$\mu = 1.85$  mm<sup>-1</sup>

$T = 296$  K

$0.25 \times 0.16 \times 0.14$  mm

#### Data collection

Bruker APEXII diffractometer  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1996)  
 $T_{\min} = 0.710$ ,  $T_{\max} = 0.785$

7397 measured reflections  
2793 independent reflections  
2667 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$   
 $wR(F^2) = 0.050$   
 $S = 1.01$   
2793 reflections  
208 parameters  
H-atom parameters constrained

$\Delta\rho_{\max} = 0.29$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.36$  e Å<sup>-3</sup>  
Absolute structure: Flack (1983),  
1165 Friedel pairs  
Flack parameter: 0.005 (9)

**Table 1**

Selected bond lengths (Å).

|       |             |       |             |
|-------|-------------|-------|-------------|
| Zn—O7 | 2.0874 (16) | Zn—O1 | 2.1431 (15) |
| Zn—O5 | 2.1128 (15) | Zn—N2 | 2.1442 (19) |
| Zn—O6 | 2.1175 (16) | Zn—N1 | 2.1605 (19) |

**Table 2**

Hydrogen-bond geometry (Å, °).

| <i>D</i> —H... <i>A</i>    | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| O5—H51...O2 <sup>i</sup>   | 0.87        | 1.79          | 2.655 (2)             | 174                     |
| O5—H52...O4 <sup>ii</sup>  | 0.87        | 1.91          | 2.775 (2)             | 172                     |
| O6—H61...O1 <sup>ii</sup>  | 0.91        | 1.93          | 2.809 (2)             | 161                     |
| O6—H62...O3                | 0.87        | 1.86          | 2.688 (2)             | 158                     |
| O7—H71...O3 <sup>iii</sup> | 0.96        | 1.85          | 2.769 (3)             | 160                     |
| O7—H72...O4 <sup>i</sup>   | 0.83        | 1.97          | 2.797 (2)             | 173                     |
| C1—H1...O3 <sup>iii</sup>  | 0.93        | 2.51          | 3.416 (3)             | 165                     |

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

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 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: NG5108).

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**supplementary materials**

*Acta Cryst.* (2011). E67, m280-m281 [ doi:10.1107/S1600536811003138 ]

## Triaqua(1,10-phenanthroline- $\kappa^2N,N'$ )(sulfato- $\kappa O$ )zinc(II)

H. Liu, H. Qin, Y.-J. Zhang, H.-W. Yang and J. Zhang

### Comment

The design and synthesis of 1,10-phenanthroline (phen) and sulfato coordination compounds have drawn considerable attention in the last decade. For the 0D structures of phen and sulfato ligand based transition-metal complexes, see: Zheng *et al.* (2002); An *et al.* (2007); Harvey *et al.* (2000). For the chian structures, see: Dietz *et al.* (2009); Hu *et al.* (2009). Among these compounds, the zinc(II) complexes were reported by Harvey *et al.* (2000) and Hu *et al.* (2009). We herein report a new phen and sulfato coordinated zinc(II) complex, which presents similar coordiantion style for zinc atom of that reported by Harvey *et al.* (2000).

The title compound crystallizes in chiral  $P2_12_12_1$  space group with three twofold axes coexisting along  $a$ ,  $b$  and  $c$  axes respectively, which is firstly found among the known phen and sulfato ligand based transition-metal complexes. As shown in Fig. 1, the Zn atoms are each surrounded by two N atoms from one phen ligand, four O atoms from three water molecules and one sulfato group to form distorted octahedra. The distances of Zn—N are 2.1591 (19) Å and 2.1449 (19) Å, respectively. The distances of Zn—O are in the range of 2.0881 (17) Å to 2.1443 (15) Å. The complex molecule displays a strong intramolecular hydrogen bond between water O(6) and sulfato O(3) atoms with  $d(O6\cdots O3) = 2.687$  Å. The intermolecular O—H $\cdots$ O hydrogen bonds exist between water molecules and sulfato O atoms and favor the formation of two-dimensional layered supramolecular network along [0 0 1] direction (Fig. 2). There are also weak C—H $\cdots$ O interactions between phen and sulfato O atoms to consolidate the two-dimensional framework. Different to the known phen and sulfato ligand based complexes, the neighboring phen ligands in the title compound do not exist the transparent  $\pi$ — $\pi$  stacking interactions. This result indicates that solventothermal synthetic procedure may restrain the formation of  $\pi$ — $\pi$  stacking interactions between neighboring conjugated ligands.

### Experimental

A mixture of ZnSO<sub>4</sub> (0.0719 g, 0.25 mmol) and 1,10-phenanthroline (0.0496 g, 0.25 mmol) was dissolved in 8 ml 60% ( $V:V$ ) ethanol solution and stirred for about an hour. Then it was transferred and sealed in a 15 ml Teflon-lined bomb which was heated at 100 °C for 5 days and cooled to room temperature. Colorless block crystals were collected. Yield: *ca.* 25% based on Zn. Elemental analysis (%): Calcd for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O<sub>7</sub>SZn: C, 36.42; H, 3.57; N, 7.08; Zn, 16.53. Found: C, 36.04; H, 3.68; N, 7.02; Zn, 16.39.

### Refinement

The disagreeable reflections 0 4 1 and 2 0 0 have been omitted and there are 1116 Friedel pairs in the refinement. H atoms on phen ligand were added theoreticly with C—H distance of 0.93 Å. H atoms of water molecules were located from difference Fourier maps and then fixed to O atoms. All H atoms were allocated displacement parameters related to those of their parent atoms [ $U_{iso}(H) = 1.2 U_{eq}(C \text{ or } O)$ ].

## Figures

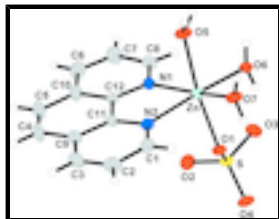


Fig. 1. The coordination feature of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

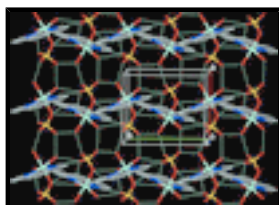


Fig. 2. A view of two-dimensional layered structures of the title compound (color codes: Zn, cyan; S, yellow; O, red; N, blue; C, grey.). H atoms are omitted for clarity.

## Triaqua(1,10-phenanthroline- $\kappa^2N,N'$ )(sulfato- $\kappa O$ )zinc(II)

### Crystal data

[Zn(SO<sub>4</sub>)(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)<sub>3</sub>]

$M_r = 395.71$

Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 8.0011$  (4) Å

$b = 9.6006$  (4) Å

$c = 19.1606$  (9) Å

$V = 1471.83$  (12) Å<sup>3</sup>

$Z = 4$

$F(000) = 808$

$D_x = 1.786$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1025 reflections

$\theta = 1.5$ – $26.5^\circ$

$\mu = 1.85$  mm<sup>-1</sup>

$T = 296$  K

Block, colourless

$0.25 \times 0.16 \times 0.14$  mm

### Data collection

Bruker APEXII  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\omega$  and  $\varphi$  scans

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

$T_{\min} = 0.710$ ,  $T_{\max} = 0.785$

7397 measured reflections

2793 independent reflections

2667 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\text{max}} = 26.0^\circ$ ,  $\theta_{\text{min}} = 2.1^\circ$

$h = -9 \rightarrow 9$

$k = -11 \rightarrow 11$

$l = -22 \rightarrow 23$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$$R[F^2 > 2\sigma(F^2)] = 0.021$$

$$wR(F^2) = 0.050$$

$$S = 1.01$$

2793 reflections

208 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0161P)^2 + 0.005P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), 1165 Friedel pairs

Flack parameter: 0.005 (9)

### 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 ( $\text{\AA}^2$ )

|     | <i>x</i>     | <i>y</i>     | <i>z</i>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|---------------|----------------------------------|
| Zn  | 0.35962 (3)  | 0.46528 (2)  | 0.682343 (13) | 0.02381 (7)                      |
| S   | 0.75438 (7)  | 0.43014 (5)  | 0.72471 (3)   | 0.02418 (13)                     |
| O1  | 0.59078 (18) | 0.36372 (14) | 0.70689 (8)   | 0.0256 (4)                       |
| O2  | 0.8188 (2)   | 0.50361 (18) | 0.66363 (10)  | 0.0400 (5)                       |
| O3  | 0.7288 (2)   | 0.52839 (19) | 0.78257 (9)   | 0.0405 (4)                       |
| O4  | 0.8701 (2)   | 0.31908 (16) | 0.74536 (10)  | 0.0368 (4)                       |
| O5  | 0.13662 (19) | 0.58142 (15) | 0.67227 (9)   | 0.0360 (4)                       |
| H51 | 0.0345       | 0.5516       | 0.6719        | 0.043*                           |
| H52 | 0.1259       | 0.6578       | 0.6961        | 0.043*                           |
| O6  | 0.3974 (2)   | 0.57293 (15) | 0.77750 (9)   | 0.0323 (4)                       |
| H61 | 0.3775       | 0.6643       | 0.7869        | 0.039*                           |
| H62 | 0.5003       | 0.5579       | 0.7908        | 0.039*                           |
| O7  | 0.2180 (2)   | 0.31186 (16) | 0.73196 (10)  | 0.0371 (4)                       |
| H71 | 0.2385       | 0.2140       | 0.7387        | 0.044*                           |
| H72 | 0.1156       | 0.3184       | 0.7392        | 0.044*                           |
| N1  | 0.4592 (2)   | 0.62126 (19) | 0.61251 (10)  | 0.0264 (4)                       |
| N2  | 0.3537 (3)   | 0.35890 (18) | 0.58398 (10)  | 0.0291 (4)                       |
| C1  | 0.3124 (3)   | 0.2282 (3)   | 0.57089 (15)  | 0.0384 (6)                       |
| H1  | 0.2798       | 0.1720       | 0.6080        | 0.046*                           |
| C2  | 0.3153 (4)   | 0.1707 (3)   | 0.50423 (16)  | 0.0489 (8)                       |
| H2  | 0.2882       | 0.0775       | 0.4975        | 0.059*                           |
| C3  | 0.3584 (4)   | 0.2526 (3)   | 0.44882 (16)  | 0.0491 (7)                       |
| H3  | 0.3586       | 0.2159       | 0.4039        | 0.059*                           |

## supplementary materials

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|     |            |            |              |            |
|-----|------------|------------|--------------|------------|
| C4  | 0.4539 (4) | 0.4834 (4) | 0.40547 (14) | 0.0534 (8) |
| H4  | 0.4550     | 0.4519     | 0.3596       | 0.064*     |
| C5  | 0.5013 (4) | 0.6158 (4) | 0.41983 (16) | 0.0560 (8) |
| H5  | 0.5333     | 0.6740     | 0.3834       | 0.067*     |
| C6  | 0.5501 (4) | 0.8055 (3) | 0.50634 (16) | 0.0513 (8) |
| H6  | 0.5799     | 0.8678     | 0.4713       | 0.062*     |
| C7  | 0.5510 (4) | 0.8461 (3) | 0.57495 (17) | 0.0478 (7) |
| H7  | 0.5808     | 0.9366     | 0.5870       | 0.057*     |
| C8  | 0.5069 (3) | 0.7504 (3) | 0.62626 (15) | 0.0356 (6) |
| H8  | 0.5112     | 0.7786     | 0.6727       | 0.043*     |
| C9  | 0.4024 (3) | 0.3920 (3) | 0.45999 (14) | 0.0385 (6) |
| C10 | 0.5032 (4) | 0.6680 (3) | 0.48954 (14) | 0.0401 (6) |
| C11 | 0.4028 (3) | 0.4397 (2) | 0.52967 (12) | 0.0270 (5) |
| C12 | 0.4559 (3) | 0.5801 (2) | 0.54475 (13) | 0.0274 (5) |

### Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$      | $U^{13}$      | $U^{23}$     |
|-----|--------------|--------------|--------------|---------------|---------------|--------------|
| Zn  | 0.02190 (13) | 0.02351 (11) | 0.02601 (13) | -0.00085 (10) | -0.00003 (11) | 0.00258 (11) |
| S   | 0.0178 (3)   | 0.0195 (2)   | 0.0353 (3)   | -0.00060 (19) | -0.0031 (2)   | -0.0023 (2)  |
| O1  | 0.0160 (7)   | 0.0222 (7)   | 0.0387 (10)  | -0.0020 (6)   | -0.0036 (7)   | -0.0028 (6)  |
| O2  | 0.0267 (9)   | 0.0472 (11)  | 0.0462 (11)  | -0.0069 (7)   | 0.0022 (7)    | 0.0116 (8)   |
| O3  | 0.0367 (9)   | 0.0395 (9)   | 0.0453 (11)  | 0.0022 (9)    | -0.0069 (8)   | -0.0196 (9)  |
| O4  | 0.0234 (8)   | 0.0299 (8)   | 0.0570 (11)  | 0.0054 (7)    | -0.0058 (9)   | 0.0058 (7)   |
| O5  | 0.0207 (8)   | 0.0286 (7)   | 0.0589 (11)  | 0.0011 (7)    | -0.0020 (9)   | 0.0013 (8)   |
| O6  | 0.0331 (9)   | 0.0277 (8)   | 0.0361 (9)   | 0.0088 (6)    | -0.0016 (7)   | -0.0025 (7)  |
| O7  | 0.0239 (9)   | 0.0271 (8)   | 0.0601 (12)  | -0.0002 (7)   | 0.0102 (8)    | 0.0125 (8)   |
| N1  | 0.0217 (10)  | 0.0288 (9)   | 0.0288 (11)  | -0.0013 (8)   | 0.0015 (8)    | 0.0004 (8)   |
| N2  | 0.0267 (10)  | 0.0287 (8)   | 0.0317 (10)  | -0.0010 (9)   | -0.0033 (10)  | -0.0012 (8)  |
| C1  | 0.0392 (16)  | 0.0324 (12)  | 0.0436 (16)  | -0.0071 (11)  | -0.0047 (12)  | 0.0014 (11)  |
| C2  | 0.0497 (18)  | 0.0393 (14)  | 0.0578 (19)  | -0.0062 (13)  | -0.0099 (14)  | -0.0176 (13) |
| C3  | 0.0487 (17)  | 0.0583 (16)  | 0.0402 (16)  | -0.0022 (15)  | -0.0058 (15)  | -0.0209 (14) |
| C4  | 0.0595 (18)  | 0.076 (2)    | 0.0244 (14)  | -0.0044 (17)  | 0.0069 (12)   | -0.0032 (14) |
| C5  | 0.068 (2)    | 0.069 (2)    | 0.0307 (16)  | -0.0089 (17)  | 0.0116 (15)   | 0.0113 (15)  |
| C6  | 0.0566 (19)  | 0.0457 (16)  | 0.0515 (19)  | -0.0135 (14)  | 0.0086 (15)   | 0.0187 (14)  |
| C7  | 0.0550 (18)  | 0.0332 (13)  | 0.0553 (19)  | -0.0153 (13)  | 0.0078 (15)   | 0.0037 (13)  |
| C8  | 0.0347 (14)  | 0.0338 (12)  | 0.0383 (15)  | -0.0065 (11)  | 0.0018 (12)   | -0.0044 (11) |
| C9  | 0.0332 (15)  | 0.0476 (14)  | 0.0347 (14)  | 0.0019 (11)   | -0.0005 (11)  | -0.0067 (12) |
| C10 | 0.0385 (15)  | 0.0482 (15)  | 0.0338 (15)  | -0.0037 (13)  | 0.0085 (12)   | 0.0071 (12)  |
| C11 | 0.0206 (11)  | 0.0342 (12)  | 0.0262 (12)  | 0.0019 (9)    | 0.0003 (9)    | -0.0021 (9)  |
| C12 | 0.0221 (12)  | 0.0324 (11)  | 0.0277 (12)  | 0.0007 (9)    | 0.0014 (10)   | 0.0009 (10)  |

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

|       |             |       |           |
|-------|-------------|-------|-----------|
| Zn—O7 | 2.0874 (16) | C1—C2 | 1.392 (4) |
| Zn—O5 | 2.1128 (15) | C1—H1 | 0.9300    |
| Zn—O6 | 2.1175 (16) | C2—C3 | 1.365 (4) |
| Zn—O1 | 2.1431 (15) | C2—H2 | 0.9300    |
| Zn—N2 | 2.1442 (19) | C3—C9 | 1.400 (4) |

|            |             |            |           |
|------------|-------------|------------|-----------|
| Zn—N1      | 2.1605 (19) | C3—H3      | 0.9300    |
| S—O2       | 1.4605 (18) | C4—C5      | 1.355 (5) |
| S—O4       | 1.4663 (16) | C4—C9      | 1.425 (4) |
| S—O3       | 1.4698 (18) | C4—H4      | 0.9300    |
| S—O1       | 1.4955 (15) | C5—C10     | 1.427 (4) |
| O5—H51     | 0.8655      | C5—H5      | 0.9300    |
| O5—H52     | 0.8678      | C6—C7      | 1.371 (4) |
| O6—H61     | 0.9094      | C6—C10     | 1.409 (4) |
| O6—H62     | 0.8738      | C6—H6      | 0.9300    |
| O7—H71     | 0.9628      | C7—C8      | 1.392 (4) |
| O7—H72     | 0.8331      | C7—H7      | 0.9300    |
| N1—C8      | 1.324 (3)   | C8—H8      | 0.9300    |
| N1—C12     | 1.357 (3)   | C9—C11     | 1.412 (3) |
| N2—C1      | 1.322 (3)   | C10—C12    | 1.405 (3) |
| N2—C11     | 1.356 (3)   | C11—C12    | 1.442 (3) |
| O7—Zn—O5   | 87.46 (6)   | N2—C1—C2   | 123.1 (3) |
| O7—Zn—O6   | 91.71 (7)   | N2—C1—H1   | 118.4     |
| O5—Zn—O6   | 86.66 (6)   | C2—C1—H1   | 118.4     |
| O7—Zn—O1   | 92.72 (6)   | C3—C2—C1   | 119.3 (2) |
| O5—Zn—O1   | 171.49 (6)  | C3—C2—H2   | 120.3     |
| O6—Zn—O1   | 84.83 (6)   | C1—C2—H2   | 120.3     |
| O7—Zn—N2   | 92.99 (7)   | C2—C3—C9   | 119.7 (3) |
| O5—Zn—N2   | 98.77 (7)   | C2—C3—H3   | 120.2     |
| O6—Zn—N2   | 172.97 (7)  | C9—C3—H3   | 120.2     |
| O1—Zn—N2   | 89.73 (7)   | C5—C4—C9   | 120.7 (3) |
| O7—Zn—N1   | 166.26 (7)  | C5—C4—H4   | 119.7     |
| O5—Zn—N1   | 83.64 (6)   | C9—C4—H4   | 119.7     |
| O6—Zn—N1   | 98.18 (7)   | C4—C5—C10  | 121.5 (3) |
| O1—Zn—N1   | 97.64 (6)   | C4—C5—H5   | 119.2     |
| N2—Zn—N1   | 78.11 (7)   | C10—C5—H5  | 119.2     |
| O2—S—O4    | 110.15 (10) | C7—C6—C10  | 119.2 (3) |
| O2—S—O3    | 110.09 (11) | C7—C6—H6   | 120.4     |
| O4—S—O3    | 110.55 (11) | C10—C6—H6  | 120.4     |
| O2—S—O1    | 109.39 (10) | C6—C7—C8   | 119.2 (3) |
| O4—S—O1    | 107.69 (9)  | C6—C7—H7   | 120.4     |
| O3—S—O1    | 108.91 (10) | C8—C7—H7   | 120.4     |
| S—O1—Zn    | 127.69 (8)  | N1—C8—C7   | 123.5 (3) |
| Zn—O5—H51  | 128.6       | N1—C8—H8   | 118.3     |
| Zn—O5—H52  | 118.8       | C7—C8—H8   | 118.3     |
| H51—O5—H52 | 101.0       | C3—C9—C11  | 117.1 (2) |
| Zn—O6—H61  | 128.0       | C3—C9—C4   | 123.3 (3) |
| Zn—O6—H62  | 107.7       | C11—C9—C4  | 119.5 (2) |
| H61—O6—H62 | 105.5       | C12—C10—C6 | 117.5 (2) |
| Zn—O7—H71  | 131.1       | C12—C10—C5 | 119.4 (3) |
| Zn—O7—H72  | 123.8       | C6—C10—C5  | 123.1 (3) |
| H71—O7—H72 | 102.6       | N2—C11—C9  | 122.6 (2) |
| C8—N1—C12  | 118.0 (2)   | N2—C11—C12 | 117.8 (2) |
| C8—N1—Zn   | 129.22 (18) | C9—C11—C12 | 119.6 (2) |
| C12—N1—Zn  | 112.53 (14) | N1—C12—C10 | 122.7 (2) |



## supplementary materials

|              |              |                |              |
|--------------|--------------|----------------|--------------|
| C1—N2—C11    | 118.0 (2)    | N1—C12—C11     | 118.0 (2)    |
| C1—N2—Zn     | 128.65 (18)  | C10—C12—C11    | 119.3 (2)    |
| C11—N2—Zn    | 113.30 (14)  |                |              |
| O2—S—O1—Zn   | -66.81 (14)  | C12—N1—C8—C7   | 1.1 (4)      |
| O4—S—O1—Zn   | 173.47 (11)  | Zn—N1—C8—C7    | -172.2 (2)   |
| O3—S—O1—Zn   | 53.56 (15)   | C6—C7—C8—N1    | -1.8 (5)     |
| O7—Zn—O1—S   | -144.44 (12) | C2—C3—C9—C11   | 1.3 (4)      |
| O6—Zn—O1—S   | -52.97 (12)  | C2—C3—C9—C4    | 178.0 (3)    |
| N2—Zn—O1—S   | 122.58 (13)  | C5—C4—C9—C3    | -177.4 (3)   |
| N1—Zn—O1—S   | 44.62 (13)   | C5—C4—C9—C11   | -0.8 (4)     |
| O7—Zn—N1—C8  | 127.7 (3)    | C7—C6—C10—C12  | 1.4 (4)      |
| O5—Zn—N1—C8  | 77.8 (2)     | C7—C6—C10—C5   | -178.9 (3)   |
| O6—Zn—N1—C8  | -7.9 (2)     | C4—C5—C10—C12  | 0.4 (5)      |
| O1—Zn—N1—C8  | -93.7 (2)    | C4—C5—C10—C6   | -179.3 (3)   |
| N2—Zn—N1—C8  | 178.2 (2)    | C1—N2—C11—C9   | 3.6 (3)      |
| O7—Zn—N1—C12 | -45.9 (4)    | Zn—N2—C11—C9   | -177.59 (18) |
| O5—Zn—N1—C12 | -95.77 (15)  | C1—N2—C11—C12  | -176.9 (2)   |
| O6—Zn—N1—C12 | 178.55 (15)  | Zn—N2—C11—C12  | 1.9 (3)      |
| O1—Zn—N1—C12 | 92.71 (15)   | C3—C9—C11—N2   | -3.9 (4)     |
| N2—Zn—N1—C12 | 4.61 (15)    | C4—C9—C11—N2   | 179.3 (2)    |
| O7—Zn—N2—C1  | -15.4 (2)    | C3—C9—C11—C12  | 176.6 (2)    |
| O5—Zn—N2—C1  | -103.3 (2)   | C4—C9—C11—C12  | -0.2 (4)     |
| O1—Zn—N2—C1  | 77.3 (2)     | C8—N1—C12—C10  | 1.0 (3)      |
| N1—Zn—N2—C1  | 175.2 (2)    | Zn—N1—C12—C10  | 175.37 (19)  |
| O7—Zn—N2—C11 | 165.96 (15)  | C8—N1—C12—C11  | -179.6 (2)   |
| O5—Zn—N2—C11 | 78.08 (16)   | Zn—N1—C12—C11  | -5.2 (2)     |
| O1—Zn—N2—C11 | -101.33 (16) | C6—C10—C12—N1  | -2.2 (4)     |
| N1—Zn—N2—C11 | -3.46 (15)   | C5—C10—C12—N1  | 178.1 (3)    |
| C11—N2—C1—C2 | -0.7 (4)     | C6—C10—C12—C11 | 178.4 (3)    |
| Zn—N2—C1—C2  | -179.3 (2)   | C5—C10—C12—C11 | -1.3 (4)     |
| N2—C1—C2—C3  | -1.8 (5)     | N2—C11—C12—N1  | 2.3 (3)      |
| C1—C2—C3—C9  | 1.4 (5)      | C9—C11—C12—N1  | -178.2 (2)   |
| C9—C4—C5—C10 | 0.7 (5)      | N2—C11—C12—C10 | -178.2 (2)   |
| C10—C6—C7—C8 | 0.4 (5)      | C9—C11—C12—C10 | 1.3 (3)      |

### Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i>    | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| O5—H51...O2 <sup>i</sup>   | 0.87        | 1.79          | 2.655 (2)             | 174                     |
| O5—H52...O4 <sup>ii</sup>  | 0.87        | 1.91          | 2.775 (2)             | 172                     |
| O6—H61...O1 <sup>ii</sup>  | 0.91        | 1.93          | 2.809 (2)             | 161                     |
| O6—H62...O3                | 0.87        | 1.86          | 2.688 (2)             | 158                     |
| O7—H71...O3 <sup>iii</sup> | 0.96        | 1.85          | 2.769 (3)             | 160                     |
| O7—H72...O4 <sup>i</sup>   | 0.83        | 1.97          | 2.797 (2)             | 173                     |
| C1—H1...O3 <sup>iii</sup>  | 0.93        | 2.51          | 3.416 (3)             | 165                     |

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

Fig. 1

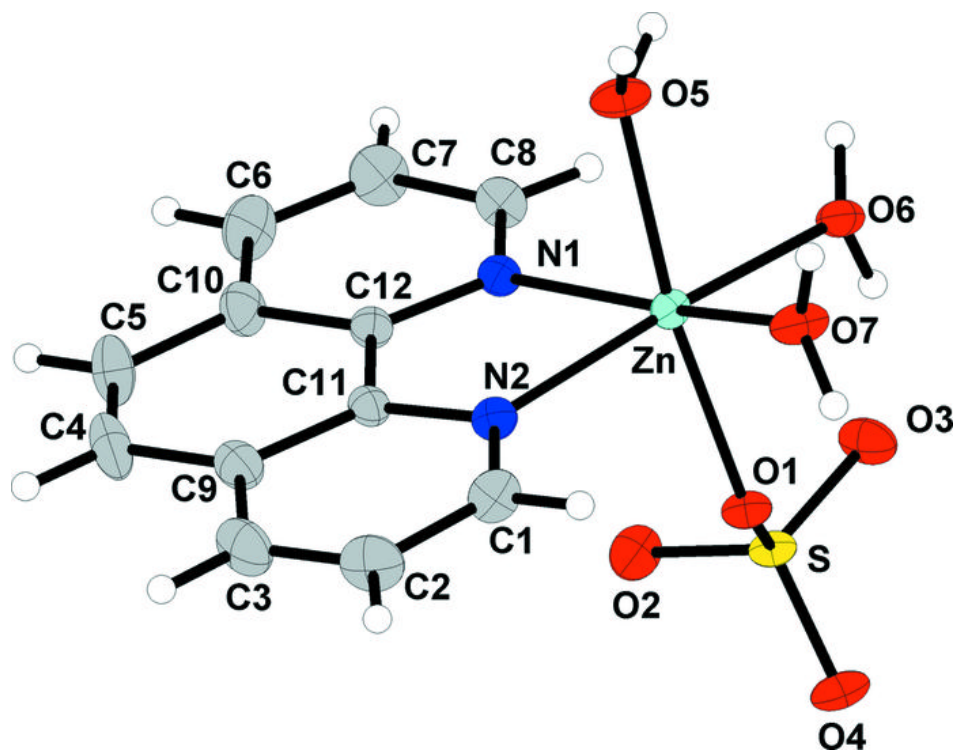


Fig. 2

