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# *catena*-Poly[piperazindiium [zincate(II)-bis($\mu$-pyridine-2,3-dicarboxylato)-$\kappa^3N,O^2:O^3;\kappa^3O^3:N,O^2$] tetrahydrate]

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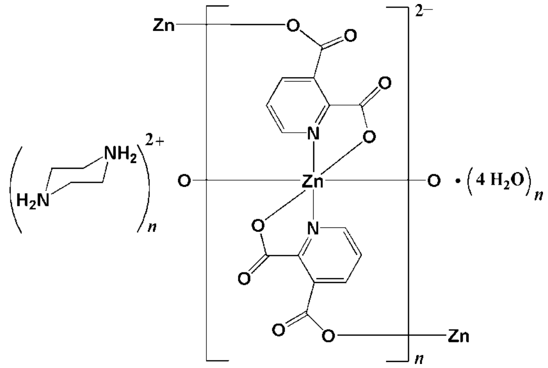
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.027; $wR$ factor = 0.071; data-to-parameter ratio = 19.4.

The centrosymmetric title compound, $\{(C_4H_{12}N_2)[Zn(C_{14}H_6N_2O_8)_2]\cdot 4H_2O\}_n$ or $\{(pipzH_2)[Zn(py\text{-}2,3\text{-}dc)_2]\cdot 4H_2O\}_n$, where py-2,3-dcH$_2$ is pyridine-2,3-dicarboxylic acid and pipz is piperazine, was obtained by the reaction of zinc(II) nitrate tetrahydrate with (pipzH$_2$)(py-2,3-dc) as a proton-transfer compound in aqueous solution. Each Zn$^{II}$ (site symmetry $\overline{1}$) is coordinated in a distorted octahedral geometry by four O atoms and two N atoms from two bidentate (py-2,3-dc)$^{2-}$ ligands, which also act as bridging ligands between Zn$^{II}$ atoms. The four donor atoms of the two coplanar (py-2,3-dc)$^{2-}$ anions form a square-planar arrangement around the Zn$^{II}$ centre. In the crystal structure, extensive O—H···O, N—H···O and C—H···O hydrogen bonds, as well as ion pairing and $\pi$–$\pi$ stacking [with a distance of 3.8693 (8) Å between two aromatic rings] between different fragments, play an important role in the stabilization of the supramolecular structure.

## Related literature

We have reported cases in which proton transfer from pyridine-2,6-dicarboxylic acid (pydcH$_2$) and benzene-1,2,4,5-tetracarboxylic acid (btcH$_4$) to piperazine (pipz) and 1,10-phenanthroline (phen) resulted in the formation of novel self-assembled (pipzH$_2$)(pydc) (Aghabozorg, Ghadermazi, Manteghi & Nakhjavan, 2006) and (phenH)$_4$(btcH$_3$)$_2$(btcH$_2$) (Aghabozorg, Ghadermazi & Attar Gharamaleki, 2006) systems, respectively. The resulting compounds, with some remaining sites as electron donors, can coordinate to metallic ions (Aghabozorg, Ghasemikhah, Ghadermazi *et al.*, 2006; Aghabozorg, Ghasemikhah, Soleimannejad *et al.*, 2006; Aghabozorg, Sadr-khanlou *et al.*, 2007; Aghabozorg, Zabihi *et al.*, 2006; Aghabozorg, Bahrami *et al.*, 2007).



## Experimental

### *Crystal data*

$(C_4H_{12}N_2)[Zn(C_{14}H_6N_2O_8)_2]\cdot 4H_2O$
$M_r$ = 555.80
Triclinic, $P\overline{1}$
$a$ = 6.6535 (6) Å
$b$ = 8.4170 (8) Å
$c$ = 10.3399 (9) Å
$\alpha$ = 78.493 (2)°
$\beta$ = 79.524 (2)°
$\gamma$ = 71.284 (2)°
$V$ = 533.07 (8) Å$^3$
$Z$ = 1
Mo $K\alpha$ radiation
$\mu$ = 1.23 mm$^{-1}$
$T$ = 100 (2) K
0.35 × 0.31 × 0.20 mm

### *Data collection*

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)
$T_{min}$ = 0.673, $T_{max}$ = 0.791
6813 measured reflections
3105 independent reflections
2876 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.020

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.071
$S$ = 1.00
3105 reflections
160 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.45 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.46 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Zn1—N1 | 2.0543 (10) | Zn1—O3$^{i}$ | 2.2985 (9) |
| Zn1—O1 | 2.0605 (9) | | |
| N1$^{ii}$—Zn1—O1 | 99.34 (4) | N1—Zn1—O3$^{i}$ | 88.21 (4) |
| N1—Zn1—O1 | 80.66 (4) | O1—Zn1—O3$^{i}$ | 85.62 (3) |
| N1$^{ii}$—Zn1—O3$^{i}$ | 91.79 (4) | O1$^{ii}$—Zn1—O3$^{i}$ | 94.38 (3) |
| C2—C1—C6—O2 | 4.81 (17) | C1—C2—C7—O3 | 96.11 (14) |
| C2—C1—C6—O1 | −175.42 (11) | C1—C2—C7—O4 | −88.75 (14) |

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

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1$S$—H2$S$···O1$W^{iii}$ | 0.89 | 1.87 | 2.753 (2) | 174 |
| N1$S$—H1$S$···O3$^{iv}$ | 0.89 | 2.15 | 3.012 (1) | 164 |
| N1$S$—H1$S$···O4$^{iv}$ | 0.89 | 2.35 | 3.054 (1) | 137 |
| O1$W$—H1$W$1···O4$^{v}$ | 0.85 | 2.01 | 2.842 (2) | 168 |
| O1$W$—H2$W$1···O2$W^{vi}$ | 0.85 | 1.93 | 2.746 (2) | 159 |
| O2$W$—H1$W$2···O4$^{v}$ | 0.85 | 1.92 | 2.763 (1) | 172 |
| O2$W$—H2$W$2···O1 | 0.85 | 2.06 | 2.868 (1) | 159 |
| C2$S$—H2$SA$···O2$^{iv}$ | 0.97 | 2.43 | 3.298 (2) | 148 |
| C2$S$—H2$SA$···O4$^{iv}$ | 0.97 | 2.58 | 3.264 (2) | 128 |

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| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C2$S$—H2$SB$···O1 | 0.97 | 2.46 | 3.307 (2) | 145 |
| C2$S$—H2$SB$···O2 | 0.97 | 2.54 | 3.420 (2) | 151 |
| C4—H4$A$···O1$W^{\mathrm{vii}}$ | 0.93 | 2.43 | 3.264 (2) | 150 |

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2156).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, m2468-m2469    [ **doi:10.1107/S1600536807042651** ]

# *catena*-Poly[piperazindiium [zincate(II)-bis($\mu$-pyridine-2,3-dicarboxylato)-$\kappa^3N,O^2:O^3;\kappa^3O^3:N,O^2$] tetrahydrate]

**H. Aghabozorg, S. Daneshvar, E. Motyeian, M. Ghadermazi and J. Attar Gharamaleki**

## Comment

Here we report a new polymeric compound obtained from reaction of zinc(II) nitrate tetrahydrate with ($pipzH_2$)(py-2,3-dc) as proton-transfer compound. The crystal structure of the title polymeric compound is shown in Fig. 1.Some selected bond distances and bond angles are listed in Table 1. The intermolecular hydrogen bond distances are listed in Table 2.

This compound crystallizes in the triclinic system, space group $P\overline{1}$, with one formula in the unit cell. In anionic complex, $[Zn(py\text{-}2,3\text{-}dc)_2]^{2-}$, the $Zn^{II}$ (site symmetry $\overline{1}$) is hexacoordinated by two nitrogen atoms N1, and N1c (c: $-x, -y, -z$) and four oxygen atoms O1, O1c, O3a and O3d of carboxylate groups (a: $x - 1, y, z$; d: $-x + 1, -y, -z$) of two $(py\text{-}2,3\text{-}dc)^{2-}$ fragments which also act as bridging ligands between $Zn^{II}$. O3a and O3d atoms from two neighbor $(py\text{-}2,3\text{-}dc)^{2-}$ fragments occupy the axial positions, while O1, O1c, N1, N1c from two $(py\text{-}2,3\text{-}dc)^{2-}$ fragments as bidentate ligands, form the equatorial plane. The N—Zn—N and O—Zn—O bond angles are linear. The four donor atoms of the two coplanar $(py\text{-}2,3\text{-}dc)^{2-}$ anions form a square-planar arrangement around the $Zn^{II}$ center.

The equatorial Zn—N and Zn—O bond lengths for Zn1 are 2.0543 (10) and 2.0605 (9) Å, respectively. The axial Zn—O bond length [2.2985 (9) Å] is significantly longer than equatorial bond lengths which is consistent with the corresponding data reported in literature (Aghabozorg, Sadr-khanlou *et al.*, 2007). According to bond lengths, bond and torsion angles, arrangement of the six donor atoms around $Zn^{II}$ is a distorted octahedral. The angle between plane passing from pyridine ring (N1/C1—C5) and the plane passing carboxylate group (OCO) is 88.15 (3)°, indicating that these bridging carboxylate groups are almost perpendicular to the aromatic ring.

A considerable feature of the compound (I) is the presence of π–π stacking with distance of 3.8693 (8) Å ($1 - x, -1 - y, -z$) between two centroids of aromatic rings (Aghabozorg, Zabihi, *et al.*, 2006) (Fig. 2).

In the crystal structure, the spaces between two layers of $[Zn(py\text{-}2,3\text{-}dc)_2]^{2-}$ fragments are filled with layers of $(pipzH_2)^{2+}$ cations and uncoordinated water molecules (Fig. 3). The most important features of the crystal structure of **(I)** is the presence of a large number of O—H···O, N—H···O and C—H···O hydrogen bonds between $(pipzH_2)^{2+}$ and $[Zn(py\text{-}2,3\text{-}dc)_2]^{2-}$ fragments and uncoordinated water molecules with D···A distances ranging from 2.746 (2) Å to 3.420 (2) Å (Table 2). Ion pairing and π–π stacking are also effective in the stabilization of the crystal structure. These interactions result in the formation of a supramolecular structure (Fig. 4).

## Experimental

The proton-transfer ion pair was prepared by a reaction between piperazine and pyridine-2,3-dicarboxylic acid. Starting with a 1:1 molar ratio of the reactants in THF, a puffy white precipitate was obtained. By recrystallization in an aqueous solution, pale-yellow crystals were obtained. A solution of $Zn(NO_3)_2·4H_2O$ (130 mg, 0.5 mmol) in water (20 ml) was added to an aqueous solution of $(pipzH_2)$(py-2,3-dc)(253 mg, 1.0 mmol) in water (20 ml) in a 1:2 molar ratio. Colorless crystals of (I) suitable for X-ray characterization were obtained after a few days at room temperature.

### Refinement

The hydrogen atoms of NH2 group and H2O were found in difference Fourier synthesis. The H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model with the $U_{iso}$(H) parameters equal to 1.2 $U_{eq}$(Ci) where $U_{eq}$(Ci) are the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded.

### Figures

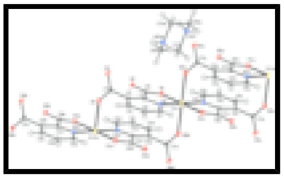


Fig. 1. The structure of (I), showing the atom-numbering scheme and displacement. Ellipsoids are at the 50% probability level. Water molecules are omitted for clarity·Atoms marked with a, c, d and e suffixes are related by the symmetry codes: (a: $x - 1, y, z$; b: $x + 1, y, z;$ c: $-x, -y, -z$; d: $-x + 1, -y, -z;$ e: $-x, -y, -z+1$).

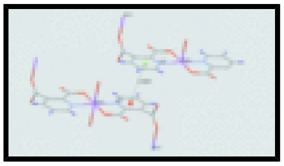


Fig. 2. π-π Stacking interactions between two aromatic rings of (I), The average distance between the planes is 3.8693 (8) Å ($1 - x, -1 - y, -z$).

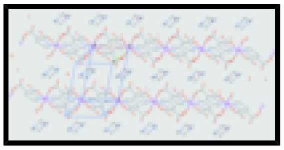


Fig. 3. A layered packing diagram of (I). The space between the two layers of $[Zn(py\text{-}2,3\text{-}dc)_2]^{2-}$ fragments is filled with a layer of $(pipzH_2)^{2+}$ cations and water molecules.

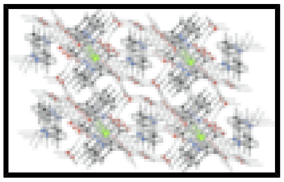


Fig. 4. The crystal packing of (I), hydrogen bonds are shown as dashed lines.

### *catena*-Poly[piperazindiium [zincate(II)-bis(μ-pyridine-2,3-dicarboxylato)- κ$^3$*N*,*O*$^2$:*O*$^3$;κ$^3$*O*$^3$:*N*,*O*$^2$] tetrahydrate]

*Crystal data*

| | |
|---|---|
| $(C_4H_{12}N_2)[Zn(C_{14}H_6N_2O_8)_2]·4H_2O$ | $Z = 1$ |
| $M_r = 555.80$ | $F_{000} = 288$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.731$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo *K*α radiation<br>λ = 0.71073 Å |
| $a = 6.6535$ (6) Å | Cell parameters from 3747 reflections |
| $b = 8.4170$ (8) Å | θ = 2.6–30.1° |
| $c = 10.3399$ (9) Å | μ = 1.23 mm$^{-1}$ |

| | |
|---|---|
| $\alpha$ = 78.493 (2)° | $T$ = 100 (2) K |
| $\beta$ = 79.524 (2)° | Plate, colourless |
| $\gamma$ = 71.284 (2)° | 0.35 × 0.31 × 0.20 mm |
| $V$ = 533.07 (8) Å$^3$ | |

### *Data collection*

| | |
|---|---|
| Bruker APEXII CCD area-detector diffractometer | 3105 independent reflections |
| Radiation source: fine-focus sealed tube | 2876 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\rm int}$ = 0.020 |
| $T$ = 100(2) K | $\theta_{\rm max}$ = 30.1° |
| $\varphi$ and $\omega$ scans | $\theta_{\rm min}$ = 2.0° |
| Absorption correction: multi-scan (APEX2; Bruker, 2005) | $h = -9 \rightarrow 9$ |
| $T_{\rm min}$ = 0.673, $T_{\rm max}$ = 0.791 | $k = -11 \rightarrow 11$ |
| 6813 measured reflections | $l = -14 \rightarrow 14$ |

### *Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: mixed |
| $R[F^2 > 2\sigma(F^2)]$ = 0.027 | H-atom parameters constrained |
| $wR(F^2)$ = 0.071 | $w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.2057P]$<br>where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 1.01 | $(\Delta/\sigma)_{\rm max}$ < 0.001 |
| 3105 reflections | $\Delta\rho_{\rm max}$ = 0.45 e Å$^{-3}$ |
| 160 parameters | $\Delta\rho_{\rm min}$ = −0.46 e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | 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$^2$)*

| | $x$ | $y$ | $z$ | $U_{\rm iso}$*/$U_{\rm eq}$ |
|---|---|---|---|---|
| Zn1 | 0.0000 | 0.0000 | 0.0000 | 0.01300 (7) |
| O1 | 0.19351 (14) | 0.09480 (11) | −0.15435 (9) | 0.01152 (17) |

| | | | | |
|---|---|---|---|---|
| O2 | 0.52743 (14) | 0.02875 (12) | −0.25947 (9) | 0.01283 (18) |
| O3 | 0.96403 (14) | −0.15685 (12) | −0.14797 (9) | 0.01339 (18) |
| O4 | 0.87264 (15) | −0.31878 (12) | −0.25892 (9) | 0.01359 (18) |
| N1 | 0.28879 (16) | −0.17768 (13) | 0.03105 (10) | 0.00907 (18) |
| C1 | 0.45027 (19) | −0.15066 (15) | −0.06130 (11) | 0.0087 (2) |
| C2 | 0.65942 (19) | −0.25589 (15) | −0.05727 (12) | 0.0084 (2) |
| C3 | 0.6983 (2) | −0.38953 (16) | 0.04854 (12) | 0.0124 (2) |
| H3A | 0.8366 | −0.4613 | 0.0549 | 0.015* |
| C4 | 0.5320 (2) | −0.41542 (16) | 0.14380 (12) | 0.0128 (2) |
| H4A | 0.5570 | −0.5034 | 0.2149 | 0.015* |
| C5 | 0.32724 (19) | −0.30735 (16) | 0.13094 (12) | 0.0105 (2) |
| H5A | 0.2139 | −0.3254 | 0.1933 | 0.013* |
| C6 | 0.38876 (19) | 0.00268 (15) | −0.16781 (12) | 0.0089 (2) |
| C7 | 0.84343 (19) | −0.23815 (15) | −0.16344 (12) | 0.0099 (2) |
| N1S | −0.16806 (17) | 0.12631 (13) | −0.56677 (10) | 0.0114 (2) |
| H2S | −0.3041 | 0.1894 | −0.5687 | 0.014* |
| H1S | −0.1003 | 0.1518 | −0.6465 | 0.014* |
| C1S | −0.0706 (2) | 0.16761 (16) | −0.46338 (13) | 0.0136 (2) |
| H1SA | −0.1517 | 0.1488 | −0.3768 | 0.016* |
| H1SB | −0.0750 | 0.2862 | −0.4828 | 0.016* |
| C2S | 0.1594 (2) | 0.05685 (16) | −0.46129 (13) | 0.0124 (2) |
| H2SA | 0.2420 | 0.0797 | −0.5466 | 0.015* |
| H2SB | 0.2215 | 0.0831 | −0.3933 | 0.015* |
| O1W | −0.42260 (15) | 0.66016 (12) | −0.41719 (10) | 0.01514 (18) |
| H1W1 | −0.3478 | 0.6809 | −0.3678 | 0.018* |
| H2W1 | −0.3500 | 0.6226 | −0.4871 | 0.018* |
| O2W | 0.14990 (16) | 0.39242 (12) | −0.35148 (9) | 0.01651 (19) |
| H1W2 | 0.0730 | 0.4798 | −0.3174 | 0.020* |
| H2W2 | 0.1794 | 0.3169 | −0.2840 | 0.020* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Zn1 | 0.00588 (10) | 0.01412 (11) | 0.01298 (11) | 0.00031 (7) | 0.00178 (7) | 0.00357 (7) |
| O1 | 0.0074 (4) | 0.0114 (4) | 0.0122 (4) | −0.0002 (3) | 0.0000 (3) | 0.0010 (3) |
| O2 | 0.0097 (4) | 0.0146 (4) | 0.0111 (4) | −0.0027 (3) | 0.0012 (3) | 0.0012 (3) |
| O3 | 0.0091 (4) | 0.0167 (4) | 0.0141 (4) | −0.0053 (3) | 0.0007 (3) | −0.0013 (3) |
| O4 | 0.0125 (4) | 0.0149 (4) | 0.0104 (4) | −0.0006 (3) | 0.0010 (3) | −0.0032 (3) |
| N1 | 0.0072 (4) | 0.0103 (4) | 0.0093 (4) | −0.0026 (4) | 0.0000 (3) | −0.0015 (3) |
| C1 | 0.0082 (5) | 0.0088 (5) | 0.0085 (5) | −0.0020 (4) | −0.0004 (4) | −0.0018 (4) |
| C2 | 0.0076 (5) | 0.0091 (5) | 0.0085 (5) | −0.0025 (4) | −0.0001 (4) | −0.0017 (4) |
| C3 | 0.0093 (5) | 0.0124 (5) | 0.0125 (5) | −0.0010 (4) | −0.0013 (4) | 0.0014 (4) |
| C4 | 0.0127 (5) | 0.0126 (5) | 0.0110 (5) | −0.0030 (4) | −0.0012 (4) | 0.0018 (4) |
| C5 | 0.0099 (5) | 0.0119 (5) | 0.0093 (5) | −0.0043 (4) | 0.0009 (4) | −0.0006 (4) |
| C6 | 0.0091 (5) | 0.0086 (5) | 0.0092 (5) | −0.0027 (4) | −0.0017 (4) | −0.0013 (4) |
| C7 | 0.0064 (5) | 0.0101 (5) | 0.0090 (5) | 0.0010 (4) | −0.0004 (4) | 0.0017 (4) |
| N1S | 0.0100 (5) | 0.0129 (5) | 0.0099 (4) | −0.0031 (4) | −0.0012 (4) | 0.0011 (4) |
| C1S | 0.0132 (6) | 0.0128 (5) | 0.0160 (6) | −0.0044 (4) | −0.0015 (4) | −0.0044 (4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2S | 0.0123 (5) | 0.0131 (5) | 0.0131 (5) | −0.0052 (4) | −0.0025 (4) | −0.0017 (4) |
| O1W | 0.0122 (4) | 0.0181 (5) | 0.0138 (4) | −0.0042 (4) | −0.0004 (3) | −0.0009 (3) |
| O2W | 0.0215 (5) | 0.0121 (4) | 0.0123 (4) | −0.0005 (4) | −0.0012 (4) | −0.0017 (3) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Zn1—N1$^{i}$ | 2.0543 (10) | C3—H3A | 0.9300 |
| Zn1—N1 | 2.0543 (10) | C4—C5 | 1.3869 (17) |
| Zn1—O1 | 2.0605 (9) | C4—H4A | 0.9300 |
| Zn1—O1$^{i}$ | 2.0605 (9) | C5—H5A | 0.9300 |
| Zn1—O3$^{ii}$ | 2.2984 (9) | N1S—C1S | 1.4931 (16) |
| Zn1—O3$^{iii}$ | 2.2985 (9) | N1S—C2S$^{v}$ | 1.4948 (16) |
| O1—C6 | 1.2803 (14) | N1S—H2S | 0.8919 |
| O2—C6 | 1.2355 (15) | N1S—H1S | 0.8863 |
| O3—C7 | 1.2572 (15) | C1S—C2S | 1.5160 (18) |
| O3—Zn1$^{iv}$ | 2.2985 (9) | C1S—H1SA | 0.9700 |
| O4—C7 | 1.2594 (15) | C1S—H1SB | 0.9700 |
| N1—C5 | 1.3381 (16) | C2S—N1S$^{v}$ | 1.4948 (16) |
| N1—C1 | 1.3472 (15) | C2S—H2SA | 0.9700 |
| C1—C2 | 1.3921 (16) | C2S—H2SB | 0.9700 |
| C1—C6 | 1.5179 (16) | O1W—H1W1 | 0.8500 |
| C2—C3 | 1.3980 (16) | O1W—H2W1 | 0.8500 |
| C2—C7 | 1.5131 (16) | O2W—H1W2 | 0.8501 |
| C3—C4 | 1.3839 (17) | O2W—H2W2 | 0.8500 |
| N1$^{i}$—Zn1—N1 | 180.00 (10) | C5—C4—H4A | 120.7 |
| N1$^{i}$—Zn1—O1 | 99.34 (4) | N1—C5—C4 | 121.61 (11) |
| N1—Zn1—O1 | 80.66 (4) | N1—C5—H5A | 119.2 |
| N1$^{i}$—Zn1—O1$^{i}$ | 80.66 (4) | C4—C5—H5A | 119.2 |
| N1—Zn1—O1$^{i}$ | 99.34 (4) | O2—C6—O1 | 125.37 (11) |
| O1—Zn1—O1$^{i}$ | 180.00 (7) | O2—C6—C1 | 118.55 (11) |
| N1$^{i}$—Zn1—O3$^{ii}$ | 88.21 (4) | O1—C6—C1 | 116.08 (10) |
| N1—Zn1—O3$^{ii}$ | 91.79 (4) | O3—C7—O4 | 124.35 (11) |
| O1—Zn1—O3$^{ii}$ | 94.38 (3) | O3—C7—C2 | 119.85 (11) |
| O1$^{i}$—Zn1—O3$^{ii}$ | 85.62 (3) | O4—C7—C2 | 115.61 (11) |
| N1$^{i}$—Zn1—O3$^{iii}$ | 91.79 (4) | C1S—N1S—C2S$^{v}$ | 110.07 (10) |
| N1—Zn1—O3$^{iii}$ | 88.21 (4) | C1S—N1S—H2S | 111.2 |
| O1—Zn1—O3$^{iii}$ | 85.62 (3) | C2S$^{v}$—N1S—H2S | 108.8 |
| O1$^{i}$—Zn1—O3$^{iii}$ | 94.38 (3) | C1S—N1S—H1S | 109.5 |
| O3$^{ii}$—Zn1—O3$^{iii}$ | 180.00 (3) | C2S$^{v}$—N1S—H1S | 111.3 |
| C6—O1—Zn1 | 114.73 (8) | H2S—N1S—H1S | 105.9 |
| C7—O3—Zn1$^{iv}$ | 140.01 (8) | N1S—C1S—C2S | 109.90 (10) |
| C5—N1—C1 | 120.13 (11) | N1S—C1S—H1SA | 109.7 |
| C5—N1—Zn1 | 127.08 (8) | C2S—C1S—H1SA | 109.7 |
| C1—N1—Zn1 | 112.76 (8) | N1S—C1S—H1SB | 109.7 |
| N1—C1—C2 | 121.76 (11) | C2S—C1S—H1SB | 109.7 |

| | | | |
|---|---|---|---|
| N1—C1—C6 | 115.51 (10) | H1SA—C1S—H1SB | 108.2 |
| C2—C1—C6 | 122.72 (10) | N1S$^{v}$—C2S—C1S | 110.09 (10) |
| C1—C2—C3 | 117.62 (11) | N1S$^{v}$—C2S—H2SA | 109.6 |
| C1—C2—C7 | 123.78 (11) | C1S—C2S—H2SA | 109.6 |
| C3—C2—C7 | 118.54 (10) | N1S$^{v}$—C2S—H2SB | 109.6 |
| C4—C3—C2 | 120.27 (11) | C1S—C2S—H2SB | 109.6 |
| C4—C3—H3A | 119.9 | H2SA—C2S—H2SB | 108.2 |
| C2—C3—H3A | 119.9 | H1W1—O1W—H2W1 | 113.2 |
| C3—C4—C5 | 118.57 (11) | H1W2—O2W—H2W2 | 103.3 |
| C3—C4—H4A | 120.7 | | |

| | | | |
|---|---|---|---|
| N1$^{i}$—Zn1—O1—C6 | −175.52 (8) | C1—C2—C3—C4 | 0.88 (18) |
| N1—Zn1—O1—C6 | 4.48 (8) | C7—C2—C3—C4 | −176.55 (11) |
| O3$^{ii}$—Zn1—O1—C6 | 95.58 (8) | C2—C3—C4—C5 | 0.63 (19) |
| O3$^{iii}$—Zn1—O1—C6 | −84.42 (8) | C1—N1—C5—C4 | 0.91 (18) |
| O1—Zn1—N1—C5 | 176.22 (11) | Zn1—N1—C5—C4 | −177.46 (9) |
| O1$^{i}$—Zn1—N1—C5 | −3.78 (11) | C3—C4—C5—N1 | −1.56 (19) |
| O3$^{ii}$—Zn1—N1—C5 | 82.07 (10) | Zn1—O1—C6—O2 | 174.12 (10) |
| O3$^{iii}$—Zn1—N1—C5 | −97.93 (10) | Zn1—O1—C6—C1 | −5.63 (13) |
| O1—Zn1—N1—C1 | −2.26 (8) | N1—C1—C6—O2 | −176.02 (10) |
| O1$^{i}$—Zn1—N1—C1 | 177.74 (8) | C2—C1—C6—O2 | 4.81 (17) |
| O3$^{ii}$—Zn1—N1—C1 | −96.40 (8) | N1—C1—C6—O1 | 3.75 (15) |
| O3$^{iii}$—Zn1—N1—C1 | 83.60 (8) | C2—C1—C6—O1 | −175.42 (11) |
| C5—N1—C1—C2 | 0.71 (17) | Zn1$^{iv}$—O3—C7—O4 | −177.67 (8) |
| Zn1—N1—C1—C2 | 179.30 (9) | Zn1$^{iv}$—O3—C7—C2 | −2.98 (19) |
| C5—N1—C1—C6 | −178.48 (10) | C1—C2—C7—O3 | 96.11 (14) |
| Zn1—N1—C1—C6 | 0.12 (12) | C3—C2—C7—O3 | −86.63 (15) |
| N1—C1—C2—C3 | −1.58 (18) | C1—C2—C7—O4 | −88.75 (14) |
| C6—C1—C2—C3 | 177.55 (11) | C3—C2—C7—O4 | 88.51 (14) |
| N1—C1—C2—C7 | 175.70 (11) | C2S$^{v}$—N1S—C1S—C2S | 58.59 (14) |
| C6—C1—C2—C7 | −5.17 (18) | N1S—C1S—C2S—N1S$^{v}$ | −58.60 (14) |

Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) −*x*+1, −*y*, −*z*; (iii) *x*−1, *y*, *z*; (iv) *x*+1, *y*, *z*; (v) −*x*, −*y*, −*z*−1.

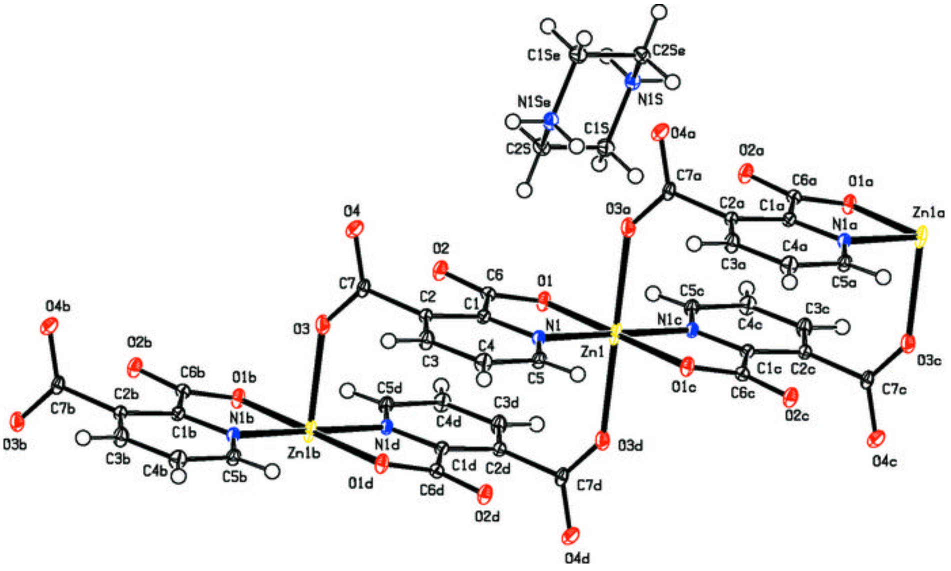
*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1S—H2S···O1W$^{vi}$ | 0.89 | 1.87 | 2.753 (2) | 174 |
| N1S—H1S···O3$^{vii}$ | 0.89 | 2.15 | 3.012 (1) | 164 |
| N1S—H1S···O4$^{vii}$ | 0.89 | 2.35 | 3.054 (1) | 137 |
| O1W—H1W1···O4$^{viii}$ | 0.85 | 2.01 | 2.842 (2) | 168 |
| O1W—H2W1···O2W$^{ix}$ | 0.85 | 1.93 | 2.746 (2) | 159 |
| O2W—H1W2···O4$^{viii}$ | 0.85 | 1.92 | 2.763 (1) | 172 |
| O2W—H2W2···O1 | 0.85 | 2.06 | 2.868 (1) | 159 |
| C2S—H2SA···O2$^{vii}$ | 0.97 | 2.43 | 3.298 (2) | 148 |
| C2S—H2SA···O4$^{vii}$ | 0.97 | 2.58 | 3.264 (2) | 128 |

| | | | | |
|---|---|---|---|---|
| C2S—H2SB···O1 | 0.97 | 2.46 | 3.307 (2) | 145 |
| C2S—H2SB···O2 | 0.97 | 2.54 | 3.420 (2) | 151 |
| C4—H4A···O1W$^{x}$ | 0.93 | 2.43 | 3.264 (2) | 150 |

Symmetry codes: (vi) $-x-1$, $-y+1$, $-z-1$; (vii) $-x+1$, $-y$, $-z-1$; (viii) $x-1$, $y+1$, $z$; (ix) $-x$, $-y+1$, $-z-1$; (x) $-x$, $-y$, $-z$.

**Fig. 1**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C2Se
N1Se
N1S
C1S
C2S
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O2a
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C1a
N1a
Zn1a
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C5a
O4
O2
C6
O1
C7
C2
C1
N1
C5c
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C3c
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O3
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O1b
C3
C4
C5
C1c
C2c
C7b
C2b
N1b
C5d
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C6c
C4d
C3d
O2c
C7c
C1b
Zn1b
N1d
O3d
O3b
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C6d
C7d
O4c
O2d
O4d

Fig. 2

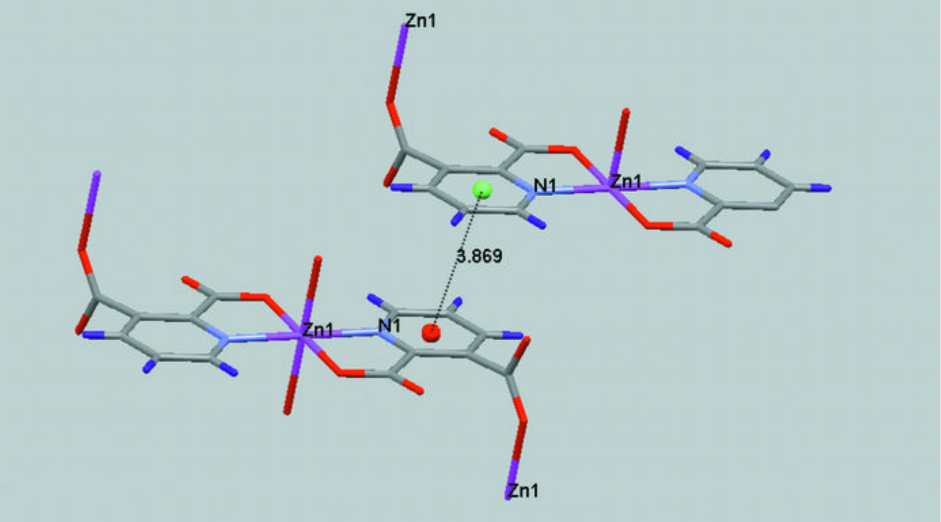

**Fig. 3**

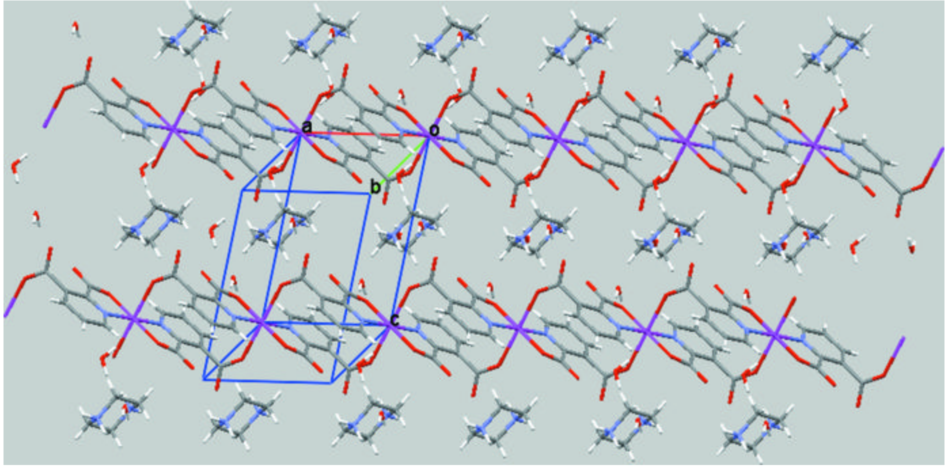

Fig. 4