Crystal structure of poly[[aqua(μ-2,3-dihydro-thieno[3,4-b][1,4]dioxine-5,7-dicarboxylato-κ^2O^5:O^7)[μ-di(pyridin-4-yl)sulfane-κ^2N:N']zinc] 0.26-hydrate]

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The crystal structure of the title polymer, {[Zn(C$_8$H$_4$O$_6$S)(C$_{10}$H$_8$N$_2$S)(H$_2$O)]·0.26H$_2$O}$_n$, is characterized by a layered arrangement parallel to the ab plane. The zinc cation is five-coordinated in a slightly distorted trigonal–bipyramidal coordination environment defined by two pyridine ligands, two carboxylate groups of two thiophene dicarboxylate ligands, and by one water molecule. The ethylene bridge in the dioxine ligand is disordered over two sets of sites [occupancy ratio 0.624 (9):0.376 (9)]. Several hydrogen-bonding interactions of the types O—H···O, C—H···O, C—H···S and C—H···N ensure the cohesion within the crystal structure.

1. Chemical context

Complexes constructed by metal ions and organic ligands are of continuous interest due to the vast diversity and feasible tailorability of their structures and functions compared with purely inorganic compounds (Zhang *et al.*, 2015).
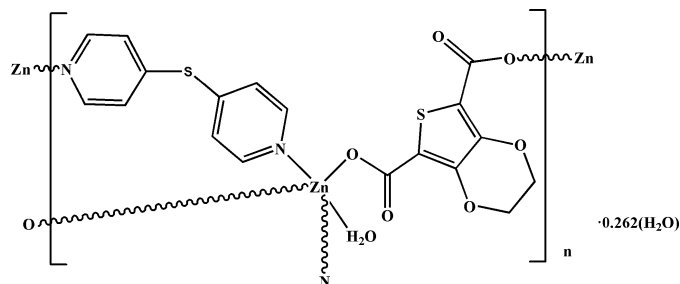
The incorporation of both carboxylic and pyridine ligands can lead to a variety of structures (Schoedel *et al.*, 2016). Complexes based on thiophene derivatives with carboxylic acid functionalities are of some interest as anticancer agents (Chen *et al.*, 1998, 1999; Guo *et al.*, 2009). In this context, we report here on synthesis and crystal structure of the title compound, [Zn(C$_8$H$_4$O$_6$S)(C$_{10}$H$_8$N$_2$S)(H$_2$O)]·0.26H$_2$O, (1).

2. Structural commentary

In the crystal structure of (1), the zinc ion is coordinated by four organic ligands and one water molecule, giving rise to a slightly distorted trigonal–bipyramidal coordination environment. Two nitrogen atoms are delivered by two symmetry-related pyridine ligands, two oxygen atoms of two carboxyl groups stem from two symmetry-related thiophene carboxyl-
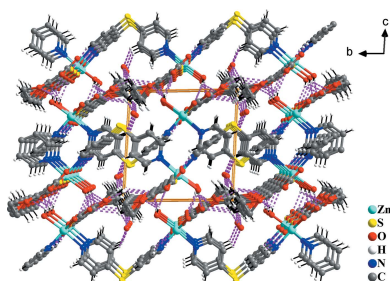
Table 1
Selected geometric parameters (Å, °).

Zn1—O5	1.9835 (15)	Zn1—O7	2.1375 (17)
Zn1—O4^i	2.0285 (15)	Zn1—N2^{ii}	2.2107 (18)
Zn1—N1	2.1131 (18)		
O5—Zn1—O4^i	117.56 (6)	N1—Zn1—O7	85.43 (7)
O5—Zn1—N1	95.66 (7)	O5—Zn1—N2^{ii}	95.24 (7)
O4^i—Zn1—N1	146.78 (7)	O4^i—Zn1—N2^{ii}	85.85 (7)
O5—Zn1—O7	93.06 (6)	N1—Zn1—N2^{ii}	91.17 (7)
O4^i—Zn1—O7	92.61 (6)	O7—Zn1—N2^{ii}	171.31 (6)

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

ate ligands, and one O atom from the aqua ligand (Fig. 1). In the trigonal bipyramid, the axial angle O7—Zn1—N2 is 171.31 (6)°. The Zn^{II} ion is co-planar with the O5—N1—O4 equatorial plane, with the deviation of the Zn atom from this plane being 0.0034 (3) Å. The equatorial Zn1—N1 bond length is 2.1131 (18) Å, while the axial Zn1—N2 bond is longer, 2.2107 (18) Å. Similarly, the two equatorial Zn1—O (O4, O5) bond lengths, ranging from 1.9835 (15) to 2.0285 (15) Å, are shorter than the axial Zn1—O7 bond of 2.1375 (17) Å. These are typical values, numerical details of which are given in Table 1.

3. Supramolecular features

The bridging coordinating mode of the organic ligands leads to the formation of polymeric layers parallel to the *ab* plane (Fig. 2).

There are several types of hydrogen bonds in the structure. One intramolecular hydrogen bond is present and extends from a (pyridine)C—H group (C10—H10*A*) to the coordinating O5 atom of the carboxyl group. Another (pyridine)C—H group (C18—H18*A*) is hydrogen-bonded to the disordered O8 atom of the lattice water molecule. Three O—H⋯O interactions are present between the coordinating water molecule to either the carboxyl group oxygen atoms or the dioxine oxygen atom in the thiophene derivative with *D*⋯*A* distances ranging between 2.733 (2) and 3.123 (2) Å and corresponding O—H⋯O angles of 135 (2) and 159 (2)°. Numerous other C—H⋯O interactions are present between the disordered dioxine C—H groups and a carboxyl O atom

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O7—H7A⋯O2^{iii}	0.83 (1)	2.48 (2)	3.123 (2)	135 (2)
O7—H7A⋯O4^{iii}	0.83 (1)	2.04 (2)	2.746 (2)	143 (2)
O7—H7B⋯O6^{iv}	0.83 (1)	1.94 (1)	2.733 (2)	159 (2)
C3—H3A⋯O6^v	0.97	2.66	3.275 (9)	122
C4—H4A⋯O8^{iii}	0.97	2.27	3.015 (17)	133
C3A—H3D⋯O6^v	0.97	2.60	3.473 (19)	150
C4A—H4C⋯O8^{vi}	0.97	1.93	2.566 (16)	121
C10—H10A⋯O5	0.93	2.50	3.079 (3)	121
C14—H14A⋯O3^i	0.93	2.51	3.213 (3)	133
C15—H15A⋯S1^{vii}	0.93	3.01	3.768 (2)	140
C15—H15A⋯O3^{vii}	0.93	2.57	3.096 (3)	116
C15—H15A⋯N1^{viii}	0.93	2.67	3.227 (3)	119
C18—H18A⋯O8	0.93	2.58	3.190 (13)	123

Symmetry codes: (i) $x + 1, y, z$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x + 2, -y + 1, -z$; (v) $-x + 1, -y + 2, -z$; (vi) $x - 1, y + 1, z$; (vii) $-x + 1, -y, -z + 1$; (viii) $x, y - 1, z$.

(O6) or the lattice water atom O8. Other C—H⋯O interactions involve pyridyl C—H groups and the carboxyl O3 atom. In addition, one C—H⋯S interaction and one C—H⋯N interaction are found between pyridyl C—H groups and the sulfane S1 atom or the pyridyl N1 atom (Fig. 3). It is expected that other extensive hydrogen bonds are formed with the lattice water molecules as the donor group and the coordinating water molecules or carbonyl O atoms from the layers as acceptors (O8⋯O distances in the range 2.87–3.13 Å). However, since the H atoms of the disordered O8 atom were not modelled, a definite statement cannot be made. Numerical details of the hydrogen bonding are given in Table 2.

4. Database survey

Some complexes based on tddc^{2-} (H$_2$ttdc is 2,3-dihydro-thieno[3,4-*b*][1,4]dioxine-5,7-dicarboxylic acid) (Guo *et al.*, 2009) or di(pyridin-4-yl)sulfane (Liu *et al.*, 2015; Han *et al.*,
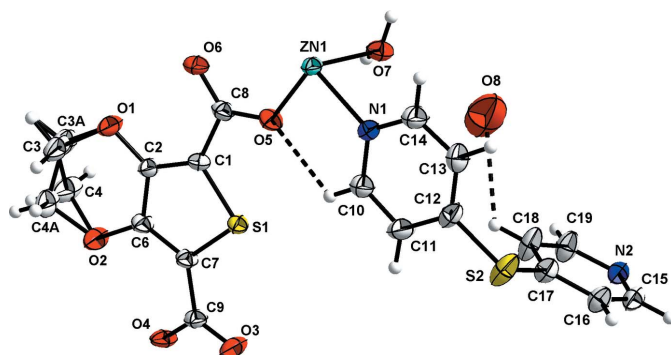
Figure 1
The asymmetric unit of (1), with displacement ellipsoids drawn at the 50% probability level. Hydrogen bonding is indicated by dashed lines.
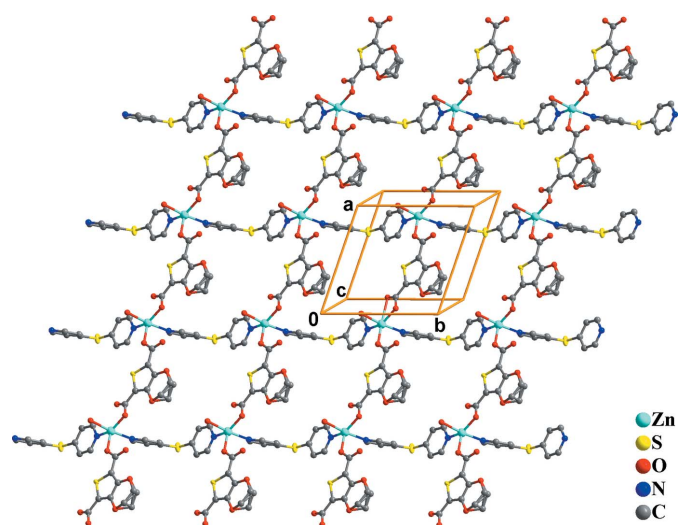
Figure 2
The polymeric layer in the crystal structure of (1), extending along the *ab* plane (H atoms have been omitted for clarity).

Table 3
Experimental details.

Crystal data	
Chemical formula	[Zn($C_8H_4O_6S$)($C_{10}H_8N_2S$)(H_2O)]·0.26H_2O
M_r	504.57
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	295
a, b, c (Å)	10.0052 (6), 10.2173 (5), 10.6694 (5)
α, β, γ (°)	87.515 (4), 68.625 (5), 73.988 (5)
V (Å^3)	974.27 (10)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.52
Crystal size (mm)	$0.32 \times 0.25 \times 0.20$
Data collection	
Diffractometer	Rigaku SuperNova, single source at offset, EosS2
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.784, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10924, 3925, 3549
R_{int}	0.021
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.659
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.069, 1.01
No. of reflections	3925
No. of parameters	306
No. of restraints	47
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.58, −0.39

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2004) and *publCIF* (Westrip, 2010).

2015) have been reported, but a complex incorporating both ligands was not found.

5. Synthesis and crystallization

2,3-Dihydrothieno[3,4-*b*][1,4]dioxine-5,7-dicarboxylic acid (H$_2$ttdc) was prepared as reported (Zhang *et al.*, 2011), and di(pyridin-4-yl)sulfane was formed *in situ* from the reactant 4,4′-dithiodipyridine in the synthesis. A mixture of zinc nitrate (0.06 g, 0.21 mmol), H$_2$ttdc (0.02 g, 0.10 mmol), 4,4′-dithiodipyridine (0.02 g, 0.10 mmol), 5 ml dimethylformamide and 3 ml water was mixed and heated at 353 K for 3 days. After cooling, 0.17 g light-yellow crystals were collected in a yield of 32%.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms attached to carbon were positioned geometrically and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C). The H atoms of the coordinating water molecule were located in a difference map and restrained to have comparable bond lengths using DFIX
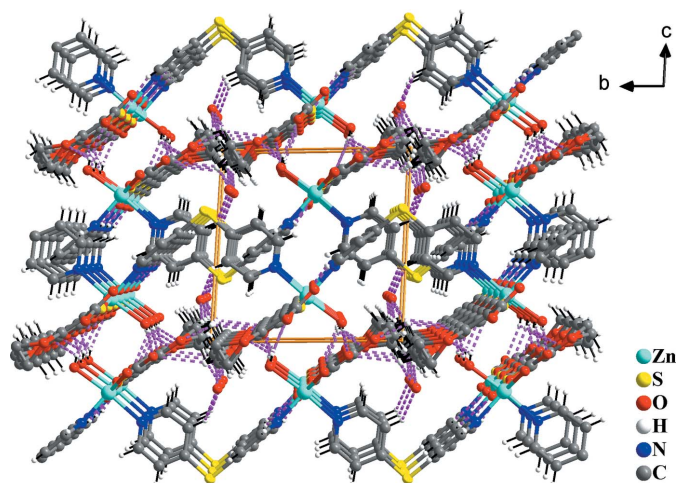

Figure 3
Part of the crystal structure of (1), showing the network formed by intermolecular C—H···O, O—H···O, C—H···S and C—H···N hydrogen bonds (shown as dashed lines).

and DANG commands to keep their geometries reasonable; U_{iso}(H) values were set to 1.5U_{eq}(O). The hydrogen atoms of the disordered lattice water molecule [occupancy 0.262 (10)] could not be retrieved from difference maps and thus were not part of the model. Two carbon atoms of the dioxine moiety are disordered over two sets of sites and were refined in two parts (C3–C4/C3*A*–C4*A*) with a refined occupancy ratio of 0.624 (9)/0.376 (9). Soft restraints (DFIX, SIMU, SADI) were applied on the disordered atoms to keep their geometries and atomic displacement parameters reasonable.

Funding information

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supporting information

Crystal structure of poly[[aqua(*μ*-2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5,7-dicarboxylato-*κ²O⁵:O⁷*)[*μ*-di(pyridin-4-yl)sulfane-*κ²N:N′*]zinc] 0.26-hydrate]

Wen-Liang Wu and Bing Hu

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2004); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Poly[[aqua(*μ*-2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5,7-dicarboxylato-*κ²O⁵:O⁷*)[*μ*-di(pyridin-4-yl)sulfane-*κ²N:N′*]zinc] 0.26-hydrate]

Crystal data

[Zn($C_8H_4O_6S$)($C_{10}H_8N_2S$)(H_2O)]·0.26H_2O	$Z = 2$
$M_r = 504.57$	$F(000) = 512.7$
Triclinic, $P\bar{1}$	$D_x = 1.718$ Mg m^{-3}
$a = 10.0052$ (6) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 10.2173$ (5) Å	Cell parameters from 6096 reflections
$c = 10.6694$ (5) Å	$\theta = 4.1–27.2°$
$\alpha = 87.515$ (4)°	$\mu = 1.52$ mm^{-1}
$\beta = 68.625$ (5)°	$T = 295$ K
$\gamma = 73.988$ (5)°	Block, yellow
$V = 974.27$ (10) Å^3	$0.32 \times 0.25 \times 0.20$ mm

Data collection

Rigaku SuperNova, single source at offset, EosS2 diffractometer	10924 measured reflections
	3925 independent reflections
	3549 reflections with $I > 2\sigma(I)$
Radiation source: micro-focus sealed X-ray tube	$R_{int} = 0.021$
Detector resolution: 8.0584 pixels mm^{-1}	$\theta_{max} = 27.9°$, $\theta_{min} = 3.5°$
ω scans	$h = -12 \rightarrow 12$
Absorption correction: multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)	$k = -13 \rightarrow 13$
	$l = -14 \rightarrow 13$
$T_{min} = 0.784$, $T_{max} = 1.000$	

Refinement

Refinement on F^2	306 parameters
Least-squares matrix: full	47 restraints
$R[F^2 > 2\sigma(F^2)] = 0.030$	Hydrogen site location: mixed
$wR(F^2) = 0.069$	H atoms treated by a mixture of independent
$S = 1.01$	and constrained refinement
3925 reflections	

$w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 0.8P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.39$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Zn1	0.87280 (3)	0.50627 (3)	0.23783 (3)	0.02570 (9)	
S1	0.40744 (6)	0.53672 (5)	0.19475 (5)	0.02461 (13)	
S2	0.66583 (9)	0.04878 (7)	0.67347 (6)	0.04739 (19)	
O1	0.46527 (18)	0.85023 (18)	−0.01437 (18)	0.0414 (4)	
O2	0.17934 (19)	0.80589 (19)	0.0274 (2)	0.0467 (5)	
O3	0.11429 (19)	0.47305 (18)	0.27948 (18)	0.0425 (4)	
O4	0.03227 (16)	0.59934 (17)	0.13592 (15)	0.0315 (4)	
O5	0.69482 (17)	0.54177 (17)	0.18673 (16)	0.0341 (4)	
O6	0.72194 (17)	0.71896 (18)	0.05940 (18)	0.0417 (4)	
O7	0.98637 (17)	0.32423 (18)	0.10848 (16)	0.0331 (4)	
H7A	0.949 (2)	0.331 (3)	0.0497 (19)	0.050*	
H7B	1.0774 (12)	0.315 (3)	0.075 (2)	0.050*	
N1	0.8030 (2)	0.37482 (18)	0.39130 (18)	0.0271 (4)	
N2	0.7799 (2)	−0.31732 (19)	0.38683 (18)	0.0293 (4)	
C1	0.5018 (2)	0.6525 (2)	0.1156 (2)	0.0234 (4)	
C2	0.4201 (2)	0.7464 (2)	0.0563 (2)	0.0260 (5)	
C3	0.3432 (9)	0.9506 (9)	−0.0350 (10)	0.050 (2)	0.624 (9)
H3A	0.3823	1.0115	−0.1018	0.060*	0.624 (9)
H3B	0.2798	1.0046	0.0487	0.060*	0.624 (9)
C4	0.2518 (6)	0.8826 (6)	−0.0820 (6)	0.0520 (16)	0.624 (9)
H4A	0.1773	0.9509	−0.1056	0.062*	0.624 (9)
H4B	0.3160	0.8218	−0.1611	0.062*	0.624 (9)
C3A	0.3637 (11)	0.9273 (19)	−0.0762 (13)	0.049 (4)	0.376 (9)
H3C	0.3861	0.8817	−0.1623	0.059*	0.376 (9)
H3D	0.3792	1.0171	−0.0932	0.059*	0.376 (9)
C4A	0.2024 (9)	0.9430 (7)	0.0105 (12)	0.055 (3)	0.376 (9)
H4C	0.1787	0.9870	0.0977	0.066*	0.376 (9)
H4D	0.1377	0.9989	−0.0322	0.066*	0.376 (9)
C6	0.2801 (2)	0.7233 (2)	0.0760 (2)	0.0275 (5)	
C7	0.2570 (2)	0.6134 (2)	0.1493 (2)	0.0246 (4)	
C8	0.6522 (2)	0.6389 (2)	0.1185 (2)	0.0270 (5)	
C9	0.1274 (2)	0.5569 (2)	0.1920 (2)	0.0271 (5)	
C10	0.6685 (3)	0.3545 (3)	0.4234 (3)	0.0364 (5)	
H10A	0.6029	0.4076	0.3856	0.044*	
C11	0.6230 (3)	0.2585 (3)	0.5098 (3)	0.0419 (6)	
H11A	0.5276	0.2488	0.5314	0.050*	

C12	0.7185 (3)	0.1776 (2)	0.5640 (2)	0.0333 (5)	
C13	0.8558 (3)	0.1991 (3)	0.5352 (3)	0.0445 (6)	
H13A	0.9224	0.1476	0.5728	0.053*	
C14	0.8924 (3)	0.2991 (3)	0.4487 (3)	0.0452 (7)	
H14A	0.9852	0.3141	0.4299	0.054*	
C15	0.7464 (3)	−0.3252 (2)	0.5191 (2)	0.0332 (5)	
H15A	0.7490	−0.4104	0.5540	0.040*	
C16	0.7082 (3)	−0.2146 (2)	0.6076 (2)	0.0347 (5)	
H16A	0.6836	−0.2252	0.6995	0.042*	
C17	0.7074 (3)	−0.0877 (2)	0.5566 (2)	0.0331 (5)	
C18	0.7401 (3)	−0.0775 (3)	0.4195 (3)	0.0446 (7)	
H18A	0.7383	0.0065	0.3820	0.054*	
C19	0.7751 (3)	−0.1935 (2)	0.3391 (2)	0.0404 (6)	
H19A	0.7966	−0.1852	0.2472	0.049*	
O8	0.9744 (16)	0.0639 (13)	0.2164 (12)	0.126 (7)	0.262 (10)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02134 (13)	0.02812 (15)	0.03265 (15)	−0.01234 (10)	−0.01248 (10)	0.00955 (10)
S1	0.0224 (3)	0.0256 (3)	0.0299 (3)	−0.0091 (2)	−0.0128 (2)	0.0050 (2)
S2	0.0788 (5)	0.0330 (3)	0.0288 (3)	−0.0272 (3)	−0.0098 (3)	0.0049 (3)
O1	0.0354 (9)	0.0444 (10)	0.0579 (11)	−0.0242 (8)	−0.0256 (8)	0.0275 (9)
O2	0.0373 (10)	0.0506 (11)	0.0721 (13)	−0.0245 (9)	−0.0374 (9)	0.0357 (10)
O3	0.0427 (10)	0.0491 (11)	0.0498 (11)	−0.0300 (9)	−0.0231 (8)	0.0265 (9)
O4	0.0234 (8)	0.0453 (10)	0.0338 (8)	−0.0185 (7)	−0.0139 (7)	0.0095 (7)
O5	0.0248 (8)	0.0393 (10)	0.0456 (10)	−0.0101 (7)	−0.0213 (7)	0.0103 (8)
O6	0.0235 (8)	0.0425 (10)	0.0624 (12)	−0.0158 (8)	−0.0162 (8)	0.0160 (9)
O7	0.0253 (8)	0.0427 (10)	0.0341 (9)	−0.0126 (8)	−0.0118 (7)	0.0031 (7)
N1	0.0269 (9)	0.0250 (10)	0.0312 (10)	−0.0107 (8)	−0.0105 (8)	0.0052 (8)
N2	0.0330 (10)	0.0268 (10)	0.0317 (10)	−0.0117 (8)	−0.0139 (8)	0.0063 (8)
C1	0.0190 (10)	0.0273 (11)	0.0252 (11)	−0.0090 (8)	−0.0079 (8)	0.0016 (9)
C2	0.0242 (10)	0.0282 (12)	0.0284 (11)	−0.0122 (9)	−0.0098 (9)	0.0058 (9)
C3	0.050 (4)	0.046 (4)	0.073 (5)	−0.026 (3)	−0.039 (3)	0.035 (4)
C4	0.051 (3)	0.065 (3)	0.061 (3)	−0.032 (3)	−0.036 (3)	0.039 (3)
C3A	0.046 (5)	0.049 (6)	0.061 (7)	−0.020 (4)	−0.027 (5)	0.034 (5)
C4A	0.046 (4)	0.047 (5)	0.083 (6)	−0.016 (4)	−0.038 (4)	0.036 (4)
C6	0.0228 (10)	0.0326 (12)	0.0329 (12)	−0.0108 (9)	−0.0152 (9)	0.0084 (9)
C7	0.0208 (10)	0.0295 (12)	0.0270 (11)	−0.0091 (9)	−0.0112 (8)	0.0032 (9)
C8	0.0198 (10)	0.0305 (12)	0.0317 (12)	−0.0075 (9)	−0.0098 (9)	−0.0006 (9)
C9	0.0236 (11)	0.0298 (12)	0.0308 (12)	−0.0131 (9)	−0.0090 (9)	0.0024 (9)
C10	0.0284 (12)	0.0387 (14)	0.0433 (14)	−0.0120 (10)	−0.0137 (10)	0.0111 (11)
C11	0.0338 (13)	0.0492 (16)	0.0473 (15)	−0.0228 (12)	−0.0132 (11)	0.0147 (12)
C12	0.0457 (14)	0.0235 (12)	0.0271 (12)	−0.0130 (10)	−0.0069 (10)	0.0013 (9)
C13	0.0433 (15)	0.0397 (15)	0.0514 (16)	−0.0093 (12)	−0.0215 (12)	0.0172 (12)
C14	0.0315 (13)	0.0500 (16)	0.0605 (17)	−0.0187 (12)	−0.0208 (12)	0.0225 (13)
C15	0.0398 (13)	0.0285 (12)	0.0360 (13)	−0.0141 (10)	−0.0168 (11)	0.0114 (10)
C16	0.0429 (14)	0.0339 (13)	0.0292 (12)	−0.0141 (11)	−0.0136 (10)	0.0078 (10)

C17	0.0396 (13)	0.0279 (12)	0.0324 (12)	−0.0116 (10)	−0.0126 (10)	0.0036 (9)
C18	0.0727 (19)	0.0260 (13)	0.0367 (14)	−0.0166 (13)	−0.0206 (13)	0.0100 (10)
C19	0.0594 (17)	0.0330 (14)	0.0293 (13)	−0.0135 (12)	−0.0169 (12)	0.0072 (10)
O8	0.138 (13)	0.101 (10)	0.094 (10)	−0.032 (8)	0.007 (8)	0.002 (7)

Geometric parameters (Å, º)

Zn1—O5	1.9835 (15)	C2—C6	1.424 (3)
Zn1—O4^i	2.0285 (15)	C3—C4	1.512 (8)
Zn1—N1	2.1131 (18)	C3—H3A	0.9700
Zn1—O7	2.1375 (17)	C3—H3B	0.9700
Zn1—N2^{ii}	2.2107 (18)	C4—H4A	0.9700
S1—C1	1.718 (2)	C4—H4B	0.9700
S1—C7	1.721 (2)	C3A—C4A	1.506 (9)
S2—C17	1.768 (2)	C3A—H3C	0.9700
S2—C12	1.781 (2)	C3A—H3D	0.9700
O1—C2	1.358 (3)	C4A—H4C	0.9700
O1—C3	1.441 (5)	C4A—H4D	0.9700
O1—C3A	1.446 (7)	C6—C7	1.364 (3)
O2—C6	1.367 (3)	C7—C9	1.477 (3)
O2—C4	1.456 (4)	C10—C11	1.371 (3)
O2—C4A	1.474 (6)	C10—H10A	0.9300
O3—C9	1.236 (3)	C11—C12	1.363 (3)
O4—C9	1.271 (3)	C11—H11A	0.9300
O4—Zn1^{iii}	2.0285 (15)	C12—C13	1.372 (4)
O5—C8	1.275 (3)	C13—C14	1.382 (4)
O6—C8	1.226 (3)	C13—H13A	0.9300
O7—H7A	0.827 (9)	C14—H14A	0.9300
O7—H7B	0.828 (9)	C15—C16	1.380 (3)
N1—C14	1.323 (3)	C15—H15A	0.9300
N1—C10	1.336 (3)	C16—C17	1.383 (3)
N2—C15	1.331 (3)	C16—H16A	0.9300
N2—C19	1.339 (3)	C17—C18	1.384 (3)
N2—Zn1^{iv}	2.2107 (18)	C18—C19	1.379 (3)
C1—C2	1.372 (3)	C18—H18A	0.9300
C1—C8	1.484 (3)	C19—H19A	0.9300
O5—Zn1—O4^i	117.56 (6)	H3C—C3A—H3D	107.8
O5—Zn1—N1	95.66 (7)	O2—C4A—C3A	108.1 (11)
O4^i—Zn1—N1	146.78 (7)	O2—C4A—H4C	110.1
O5—Zn1—O7	93.06 (6)	C3A—C4A—H4C	110.1
O4^i—Zn1—O7	92.61 (6)	O2—C4A—H4D	110.1
N1—Zn1—O7	85.43 (7)	C3A—C4A—H4D	110.1
O5—Zn1—N2^{ii}	95.24 (7)	H4C—C4A—H4D	108.4
O4^i—Zn1—N2^{ii}	85.85 (7)	C7—C6—O2	124.33 (19)
N1—Zn1—N2^{ii}	91.17 (7)	C7—C6—C2	113.23 (19)
O7—Zn1—N2^{ii}	171.31 (6)	O2—C6—C2	122.4 (2)
C1—S1—C7	92.49 (10)	C6—C7—C9	129.87 (19)

C17—S2—C12	101.52 (11)	C6—C7—S1	110.81 (15)
C2—O1—C3	111.8 (4)	C9—C7—S1	119.32 (17)
C2—O1—C3A	113.7 (7)	O6—C8—O5	126.4 (2)
C6—O2—C4	111.1 (2)	O6—C8—C1	119.5 (2)
C6—O2—C4A	110.1 (3)	O5—C8—C1	114.1 (2)
C9—O4—Zn1ⁱⁱⁱ	101.88 (14)	O3—C9—O4	122.8 (2)
C8—O5—Zn1	126.61 (15)	O3—C9—C7	120.0 (2)
Zn1—O7—H7A	106.5 (19)	O4—C9—C7	117.1 (2)
Zn1—O7—H7B	110.6 (19)	N1—C10—C11	122.7 (2)
H7A—O7—H7B	111.7 (16)	N1—C10—H10A	118.7
C14—N1—C10	117.0 (2)	C11—C10—H10A	118.7
C14—N1—Zn1	122.99 (16)	C12—C11—C10	119.6 (2)
C10—N1—Zn1	119.57 (16)	C12—C11—H11A	120.2
C15—N2—C19	116.8 (2)	C10—C11—H11A	120.2
C15—N2—Zn1ⁱᵛ	125.22 (15)	C11—C12—C13	118.6 (2)
C19—N2—Zn1ⁱᵛ	117.37 (15)	C11—C12—S2	121.1 (2)
C2—C1—C8	129.8 (2)	C13—C12—S2	120.2 (2)
C2—C1—S1	111.10 (15)	C12—C13—C14	118.2 (2)
C8—C1—S1	119.09 (16)	C12—C13—H13A	120.9
O1—C2—C1	124.96 (19)	C14—C13—H13A	120.9
O1—C2—C6	122.68 (19)	N1—C14—C13	123.7 (2)
C1—C2—C6	112.4 (2)	N1—C14—H14A	118.2
O1—C3—C4	110.7 (6)	C13—C14—H14A	118.2
O1—C3—H3A	109.5	N2—C15—C16	124.0 (2)
C4—C3—H3A	109.5	N2—C15—H15A	118.0
O1—C3—H3B	109.5	C16—C15—H15A	118.0
C4—C3—H3B	109.5	C15—C16—C17	118.6 (2)
H3A—C3—H3B	108.1	C15—C16—H16A	120.7
O2—C4—C3	108.1 (6)	C17—C16—H16A	120.7
O2—C4—H4A	110.1	C16—C17—C18	118.0 (2)
C3—C4—H4A	110.1	C16—C17—S2	116.68 (18)
O2—C4—H4B	110.1	C18—C17—S2	125.28 (19)
C3—C4—H4B	110.1	C19—C18—C17	119.2 (2)
H4A—C4—H4B	108.4	C19—C18—H18A	120.4
O1—C3A—C4A	112.5 (8)	C17—C18—H18A	120.4
O1—C3A—H3C	109.1	N2—C19—C18	123.3 (2)
C4A—C3A—H3C	109.1	N2—C19—H19A	118.4
O1—C3A—H3D	109.1	C18—C19—H19A	118.4
C4A—C3A—H3D	109.1		
C7—S1—C1—C2	−0.11 (17)	Zn1—O5—C8—C1	−170.36 (13)
C7—S1—C1—C8	−179.57 (17)	C2—C1—C8—O6	−1.2 (3)
C3—O1—C2—C1	−165.4 (5)	S1—C1—C8—O6	178.18 (17)
C3A—O1—C2—C1	174.9 (8)	C2—C1—C8—O5	177.9 (2)
C3—O1—C2—C6	14.9 (5)	S1—C1—C8—O5	−2.7 (3)
C3A—O1—C2—C6	−4.7 (8)	Zn1ⁱⁱⁱ—O4—C9—O3	3.9 (3)
C8—C1—C2—O1	−0.2 (4)	Zn1ⁱⁱⁱ—O4—C9—C7	−175.43 (15)
S1—C1—C2—O1	−179.60 (17)	C6—C7—C9—O3	−166.0 (2)

C8—C1—C2—C6	179.5 (2)	S1—C7—C9—O3	13.6 (3)
S1—C1—C2—C6	0.1 (2)	C6—C7—C9—O4	13.4 (3)
C2—O1—C3—C4	−46.5 (8)	S1—C7—C9—O4	−167.03 (16)
C3A—O1—C3—C4	53 (3)	C14—N1—C10—C11	−1.1 (4)
C6—O2—C4—C3	−50.6 (6)	Zn1—N1—C10—C11	171.90 (19)
C4A—O2—C4—C3	46.4 (6)	N1—C10—C11—C12	−1.5 (4)
O1—C3—C4—O2	66.3 (9)	C10—C11—C12—C13	3.1 (4)
C2—O1—C3A—C4A	36.5 (17)	C10—C11—C12—S2	−178.43 (19)
C3—O1—C3A—C4A	−51 (2)	C17—S2—C12—C11	83.8 (2)
C6—O2—C4A—C3A	54.2 (9)	C17—S2—C12—C13	−97.7 (2)
C4—O2—C4A—C3A	−45.6 (7)	C11—C12—C13—C14	−2.1 (4)
O1—C3A—C4A—O2	−62.5 (17)	S2—C12—C13—C14	179.4 (2)
C4—O2—C6—C7	−160.5 (4)	C10—N1—C14—C13	2.1 (4)
C4A—O2—C6—C7	154.0 (5)	Zn1—N1—C14—C13	−170.6 (2)
C4—O2—C6—C2	20.7 (4)	C12—C13—C14—N1	−0.5 (4)
C4A—O2—C6—C2	−24.9 (6)	C19—N2—C15—C16	−0.1 (4)
O1—C2—C6—C7	179.7 (2)	Zn1iv—N2—C15—C16	170.64 (18)
C1—C2—C6—C7	0.0 (3)	N2—C15—C16—C17	−1.5 (4)
O1—C2—C6—O2	−1.4 (3)	C15—C16—C17—C18	2.2 (4)
C1—C2—C6—O2	179.0 (2)	C15—C16—C17—S2	−177.25 (19)
O2—C6—C7—C9	0.6 (4)	C12—S2—C17—C16	167.2 (2)
C2—C6—C7—C9	179.5 (2)	C12—S2—C17—C18	−12.2 (3)
O2—C6—C7—S1	−179.02 (18)	C16—C17—C18—C19	−1.4 (4)
C2—C6—C7—S1	−0.1 (2)	S2—C17—C18—C19	178.0 (2)
C1—S1—C7—C6	0.11 (17)	C15—N2—C19—C18	1.0 (4)
C1—S1—C7—C9	−179.53 (17)	Zn1iv—N2—C19—C18	−170.5 (2)
Zn1—O5—C8—O6	8.7 (3)	C17—C18—C19—N2	−0.2 (4)

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

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7A···O2v	0.83 (1)	2.48 (2)	3.123 (2)	135 (2)
O7—H7A···O4v	0.83 (1)	2.04 (2)	2.746 (2)	143 (2)
O7—H7B···O6vi	0.83 (1)	1.94 (1)	2.733 (2)	159 (2)
C3—H3A···O6vii	0.97	2.66	3.275 (9)	122
C4—H4A···O8v	0.97	2.27	3.015 (17)	133
C3A—H3D···O6vii	0.97	2.60	3.473 (19)	150
C4A—H4C···O8viii	0.97	1.93	2.566 (16)	121
C10—H10A···O5	0.93	2.50	3.079 (3)	121
C14—H14A···O3i	0.93	2.51	3.213 (3)	133
C15—H15A···S1ix	0.93	3.01	3.768 (2)	140
C15—H15A···O3ix	0.93	2.57	3.096 (3)	116
C15—H15A···N1iv	0.93	2.67	3.227 (3)	119
C18—H18A···O8	0.93	2.58	3.190 (13)	123

Symmetry codes: (i) x+1, y, z; (iv) x, y−1, z; (v) −x+1, −y+1, −z; (vi) −x+2, −y+1, −z; (vii) −x+1, −y+2, −z; (viii) x−1, y+1, z; (ix) −x+1, −y, −z+1.