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Polymeric poly[[decaaquabis(μ_6-1,8-disulfonato-9*H*-carbazole-3,6-dicarboxylato)di-μ_3-hydroxy-pentazinc] decahydrate]

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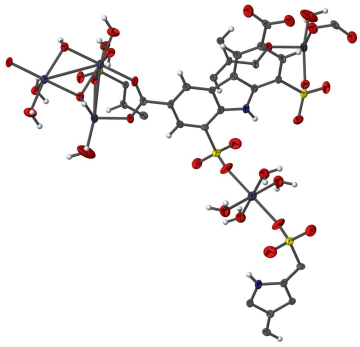
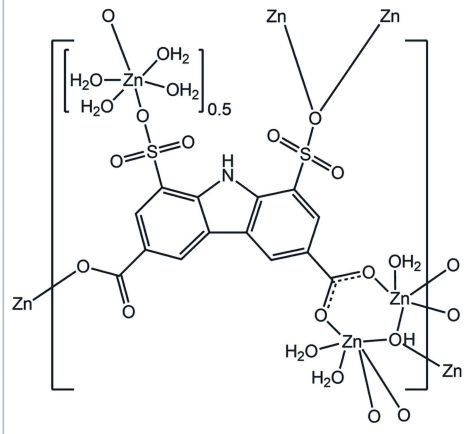
The asymmetric unit of the title MOF, $[Zn_5(C_{14}H_5NO_{10}S_2)_2(OH)_2(H_2O)_{10}]_n$ comprises three Zn^{II} atoms, one of which is located on a centre of inversion, a tetra-negative carboxylate ligand, one μ_3-hydroxide and five water molecules, each of which is coordinated. The Zn^{II} atom, lying on a centre of inversion, is coordinated by *trans* sulfoxide-O atoms and four water molecules in an octahedral geometry. Another Zn^{II} atom is coordinated by two carboxylate-O atoms, one hydroxy-O, one sulfoxide-O and a water-O atom to define a distorted trigonal–bipyramidal geometry; a close Zn···O(carboxylate) interaction derived from an asymmetrically coordinating ligand (Zn—O = 1.95 and 3.07 Å) suggests a 5 + 1 coordination geometry. The third Zn^{II} atom is coordinated in an octahedral fashion by two hydroxy-O atoms, one carboxylate-O, one sulfoxide-O and two water-O atoms, the latter being mutually *cis*. In all, the carboxylate ligand binds six Zn^{II} ions leading to a three-dimensional architecture. In the crystal, all acidic donors form hydrogen bonds to oxygen acceptors to contribute to the stability of the three-dimensional architecture.

3D view



Chemical scheme



Structure description

In recent years, metal–organic frameworks (MOF's) have attracted much attention because of their fascinating architectures as well as their great potential applications in the areas of gas adsorption (Suh *et al.*, 2012), gas separation (Li *et al.*, 2012), heterogeneous catalysis (Liu *et al.*, 2014), sensing (Kreno *et al.*, 2012), *etc*. In this context, the synthesis and structure of a new Zn^{II}-based MOF, $[Zn_5(\mu_3\text{-OH})_2$(1,8-disulfo-9*H*-carba-

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O13^{i}	1.00	1.83	2.804 (5)	163
O4—H4A···O12^{i}	0.87	1.86	2.632 (4)	147
O4—H4B···O16^{ii}	0.87	1.85	2.608 (3)	145
O5—H5A···O12^{iii}	0.97	1.81	2.736 (3)	160
O5—H5B···O7^{iv}	0.96	2.09	2.818 (4)	131
O6—H6A···O13^{i}	0.97	2.09	2.976 (5)	151
O6—H6B···O7^{v}	0.97	2.24	3.156 (7)	157
O10—H10A···O7^{vi}	0.96	2.20	2.941 (5)	133
O10—H10B···O16^{i}	0.96	1.72	2.666 (5)	166
O11—H11A···O4^{i}	0.87	1.96	2.837 (3)	179
O11—H11B···O9^{vi}	0.87	1.89	2.757 (5)	171
N1—H1···O9	0.88	2.46	2.962 (4)	117
N1—H1···O12	0.88	2.40	2.908	117

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

zole-3,6-dicarboxylate)$_2$(H_2O)$_{10}$]$_n$, (I), is reported herein. This MOF was constructed by the solvothermal reaction between 1,8-disulfo-9*H*-carbazole-3,6-dicarboxylic acid and $Zn(NO_3)_2$ in the presence of HBF_4, as a competing reagent, in dimethylformamide (DMF).

Single-crystal X-ray diffraction reveals that (I) crystallizes in the triclinic space group $P\overline{1}$. The asymmetric unit, Fig. 1, comprises comprises three Zn^{II} atoms, one of which (Zn3) is located on a centre of inversion, a tetra-negative carboxylate ligand, one μ_3-hydroxide and five water molecules; each water molecule is coordinated. The hydroxide bridges three Zn atoms. A pair of centrosymmetrically related Zn2 atoms is connected by two hydroxide bridges with each hydroxide also bridging a Zn1 atom. Additional links between the Zn1 and Zn2 atoms are provided by bidentate bridging carboxylate ligands and sulfoxide-oxygen atoms. The coordination geometry for the Zn1 atom is completed by oxygen atoms derived from an asymmetrically coordinating (Zn1—O3, O4 = 1.95 and 3.07 Å) carboxylate residue and a water molecule. If the weak interaction were ignored, the Zn1 atom would be considered five-coordinate, distorted trigonal–bipyramidal with the sulfoxide-oxygen and the water-oxygen atoms occupying axial positions. The distorted octahedral coordination geometry for the Zn2 atom is completed by two water molecules which occupy mutually *cis* positions. A distinct distorted octahedral geometry is found for the Zn3 atom. This atom lies on a centre of inversion and is coordinated by two sulfoxide-oxygen atoms and four water molecules; from symmetry the sulfoxide-oxygen atoms are *trans*.

The carboxylate ligand binds six Zn^{II} ions with one carboxylate residue (O1, O2) bridging two Zn^{II} atoms (Zn1 and Zn2) and the other (O15, O16) being connected to a single Zn^{II} atom (Zn2). One of the sulfoxide-oxygen atoms (O8) connects to a single Zn^{II} centre (Zn3) while the other (O14) bridges two Zn^{II} atoms (Zn1 and Zn2). In this way a three-dimensional architecture is generated, Fig. 2.

As anticipated from the chemical composition, there are extensive hydrogen-bonding interactions in the crystal, which contribute to the stability of the three-dimensional architecture, Table 1. All acidic donors form hydrogen bonds to oxygen acceptors.

Synthesis and crystallization

1,8-Disulfo-9*H*-carbazole-3,6-dicarboxylic acid (10 mg), $Zn(NO_3)_2$ (20 mg), and HBF_4 (4 drops) were ultrasonically dissolved in DMF (2 ml) in a 4 ml Pyrex vial and sealed. The reaction system was then heated at 80°C for 24 h in an oven. Colourless crystals of the title complex suitable for single-crystal X-ray analysis were obtained from the reaction vessel.

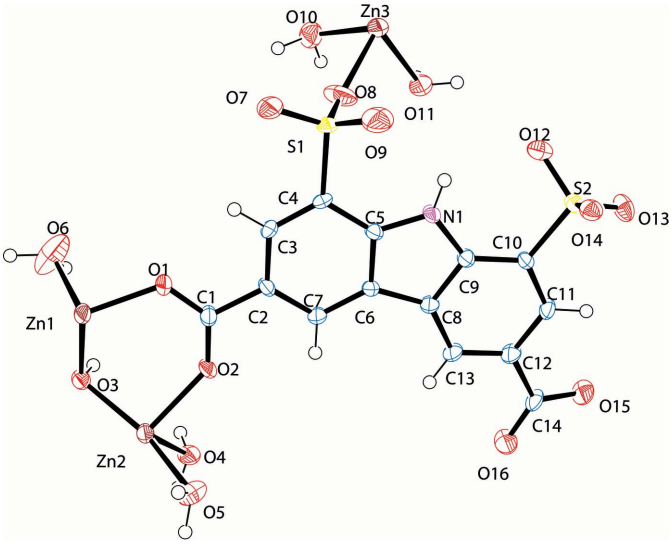


Figure 1
A view of the asymmetric unit of (I), showing the atom numbering, with displacement ellipsoids drawn at the 50% probability level.

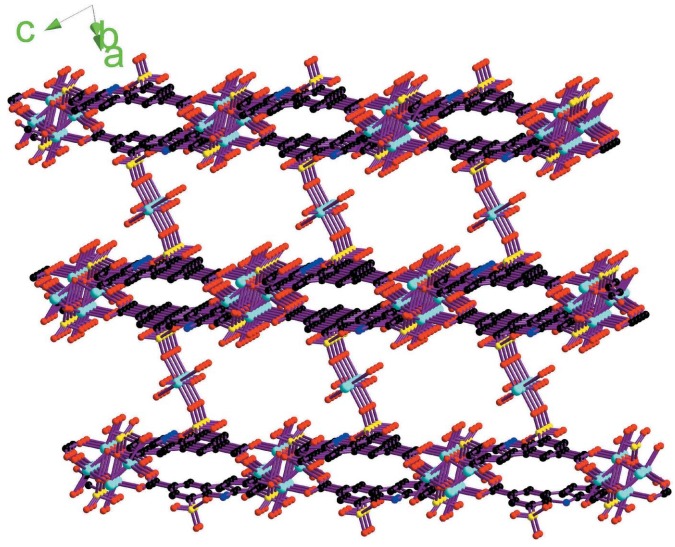


Figure 2
A view of the three-dimensional structure of (I); H atoms have been omitted for reasons of clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Zn_5(C_{14}H_5NO_{10}S_2)_2(OH)_2(H_2O)_{10}]$
M_r	1363.64
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	289
a, b, c (Å)	7.3573 (3), 11.2345 (5), 12.9215 (5)
α, β, γ (°)	74.215 (4), 78.085 (4), 85.178 (4)
V (Å^3)	1005.17 (8)
Z	1
Radiation type	Cu $K\alpha$
μ (mm^{-1})	6.36
Crystal size (mm)	0.10 × 0.08 × 0.04
Data collection	
Diffractometer	Rigaku Oxford Diffraction SuperNova, Dual, Cu at home/near, AtlasS2
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2017)
T_{min}, T_{max}	0.674, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6682, 3966, 3348
R_{int}	0.037
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.129, 1.08
No. of reflections	3966
No. of parameters	303
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.73, −0.82

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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References

Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Gruene, T., Hahn, H. W., Luebben, A. V., Meilleur, F. & Sheldrick, G. M. (2014). *J. Appl. Cryst.* **47**, 462–466.

Kreno, L. E., Leong, K., Farha, O. K., Allendorf, M., Van Duyne, R. P. & Hupp, J. T. (2012). *Chem. Rev.* **112**, 1105–1125.

Li, J. R., Sculley, J. & Zhou, H.-C. (2012). *Chem. Rev.* **112**, 869–932.

Liu, J., Chen, L., Cui, H., Zhang, J., Zhang, L. & Su, C. Y. (2014). *Chem. Soc. Rev.* **43**, 6011–6061.

Rigaku OD (2017). *CrysAlis PRO*. Rigaku Oxford Diffraction, Oxford, England.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Suh, M. P., Park, H. J., Prasad, T. K. & Lim, D. W. (2012). *Chem. Rev.* **112**, 782–835.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2019). **4**, x190667 [https://doi.org/10.1107/S2414314619006679]

Polymeric poly[[decaaquabis(μ_6-1,8-disulfonato-9*H*-carbazole-3,6-dicarboxylato)di-μ_3-hydroxy-pentazinc] decahydrate]

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Poly[[decaaquabis(μ_6-1,8-disulfonato-9*H*-carbazole-3,6-dicarboxylato)di-μ_3-hydroxy-pentazinc] decahydrate]

Crystal data

$[Zn_5(C_{14}H_5NO_{10}S_2)_2(OH)_2(H_2O)_{10}]$
M_r = 1363.64
Triclinic, $P\overline{1}$
a = 7.3573 (3) Å
b = 11.2345 (5) Å
c = 12.9215 (5) Å
α = 74.215 (4)°
β = 78.085 (4)°
γ = 85.178 (4)°
V = 1005.17 (8) Å^3
Z = 1
$F(000)$ = 684
D_x = 2.253 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 3065 reflections
θ = 4.1–74.3°
μ = 6.36 mm^{-1}
T = 289 K
Prism, colourless
0.10 × 0.08 × 0.04 mm

Data collection

Rigaku Oxford Diffraction SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer
Radiation source: micro-focus sealed X-ray tube
Detector resolution: 10.3376 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2017)
T_{min} = 0.674, T_{max} = 1.000
6682 measured reflections
3966 independent reflections
3348 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 74.6°, θ_{min} = 3.6°
h = −9→5
k = −13→13
l = −16→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.129
S = 1.08
3966 reflections
303 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0715P)^2 + 0.7146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 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.

Refinement. The H atoms bound to the O5, O6 and O10 atoms were located from difference Fourier maps and had O—H bond lengths in the vicinity of 0.96 Å, Table 1. The H atoms bound to the O4 and O11 atoms were included in their idealized positions at 0.87 Å; U_{iso}(water-H) = 1.5U_{eq}(water-O). The hydroxide-H (1.00 Å) and amine-H (0.88 Å) atoms were included in their idealized positions with U_{iso}(hydroxide-H) = 1.2U_{eq}(hydroxide-O) and U_{iso}(amine-H) = 1.2U_{eq}(amine-N), respectively.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	1.06687 (8)	0.72625 (5)	0.00084 (4)	0.02631 (17)
Zn2	0.98180 (8)	0.93578 (5)	0.12468 (4)	0.02273 (16)
Zn3	0.5000	0.0000	0.5000	0.0297 (2)
S1	0.88904 (14)	0.18599 (9)	0.43688 (8)	0.0250 (2)
S2	0.56934 (13)	0.19518 (9)	0.89732 (8)	0.0214 (2)
O1	0.9726 (4)	0.6195 (3)	0.1462 (2)	0.0303 (7)
O2	0.8944 (4)	0.7689 (3)	0.2326 (2)	0.0291 (7)
O3	0.9412 (4)	0.8915 (3)	−0.0134 (2)	0.0225 (6)
H3	0.8051	0.8818	−0.0069	0.027*
O4	0.7293 (3)	1.0051 (3)	0.1876 (2)	0.0276 (6)
H4A	0.6418	0.9868	0.1588	0.041*
H4B	0.7277	1.0855	0.1679	0.041*
O5	1.1075 (3)	0.9847 (3)	0.2343 (2)	0.0385 (8)
H5A	1.2378	0.9611	0.2212	0.058*
H5B	1.0955	1.0728	0.2237	0.058*
O6	0.8903 (6)	0.6684 (6)	−0.0892 (4)	0.0745 (16)
H6A	0.7701	0.7101	−0.0773	0.112*
H6B	0.9440	0.6955	−0.1668	0.112*
O7	1.0117 (5)	0.1789 (3)	0.3367 (3)	0.0460 (9)
O8	0.7056 (5)	0.1419 (3)	0.4474 (3)	0.0455 (9)
O9	0.9671 (6)	0.1283 (3)	0.5341 (3)	0.0492 (10)
O10	0.3873 (5)	0.0789 (3)	0.3613 (3)	0.0379 (8)
H10A	0.2901	0.1378	0.3779	0.057*
H10B	0.4828	0.1215	0.3034	0.057*
O11	0.31752 (19)	0.1047 (2)	0.58355 (17)	0.0359 (8)
H11A	0.3019	0.0719	0.6543	0.054*
H11B	0.2063	0.1035	0.5700	0.054*
O12	0.54981 (19)	0.11779 (12)	0.82671 (10)	0.0304 (7)
O13	0.4211 (2)	0.18488 (12)	0.99171 (10)	0.0323 (7)
O14	0.75275 (18)	0.17111 (12)	0.92851 (10)	0.0253 (6)
O15	0.26713 (18)	0.62313 (11)	0.94248 (11)	0.0356 (8)
O16	0.3823 (2)	0.77209 (11)	0.79901 (12)	0.0471 (10)
N1	0.7207 (2)	0.30507 (11)	0.63530 (12)	0.0236 (7)
H1	0.7368	0.2242	0.6561	0.028*
C1	0.9111 (5)	0.6577 (4)	0.2306 (3)	0.0218 (8)
C2	0.8569 (5)	0.5611 (3)	0.3364 (3)	0.0201 (8)
C3	0.8957 (5)	0.4361 (4)	0.3383 (3)	0.0209 (8)
H3A	0.9520	0.4147	0.2724	0.025*
C4	0.8535 (6)	0.3441 (3)	0.4338 (3)	0.0205 (8)

C5	0.7718 (5)	0.3775 (3)	0.5303 (3)	0.0201 (8)
C6	0.7261 (5)	0.5026 (3)	0.5283 (3)	0.0186 (7)
C7	0.7709 (6)	0.5942 (4)	0.4308 (3)	0.0233 (8)
H7	0.7426	0.6787	0.4290	0.028*
C8	0.6395 (6)	0.5024 (4)	0.6396 (3)	0.0210 (8)
C9	0.6405 (5)	0.3788 (4)	0.7030 (3)	0.0197 (8)
C10	0.5641 (5)	0.3480 (3)	0.8149 (3)	0.0194 (7)
C11	0.4823 (6)	0.4419 (4)	0.8617 (3)	0.0232 (8)
H11	0.4295	0.4227	0.9377	0.028*
C12	0.4767 (6)	0.5649 (4)	0.7983 (3)	0.0245 (8)
C13	0.5567 (6)	0.5963 (4)	0.6876 (3)	0.0240 (8)
H13	0.5553	0.6799	0.6453	0.029*
C14	0.3707 (6)	0.6619 (4)	0.8495 (3)	0.0265 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0359 (3)	0.0189 (3)	0.0183 (3)	0.0028 (2)	0.0066 (2)	−0.0050 (2)
Zn2	0.0299 (3)	0.0173 (3)	0.0177 (3)	0.0015 (2)	0.0006 (2)	−0.0036 (2)
Zn3	0.0381 (5)	0.0205 (4)	0.0279 (4)	−0.0003 (3)	0.0019 (3)	−0.0084 (3)
S1	0.0335 (5)	0.0142 (4)	0.0261 (5)	0.0018 (4)	0.0006 (4)	−0.0088 (4)
S2	0.0232 (5)	0.0173 (4)	0.0198 (5)	−0.0003 (3)	−0.0010 (4)	−0.0006 (3)
O1	0.0453 (18)	0.0229 (15)	0.0173 (14)	−0.0038 (13)	0.0070 (12)	−0.0053 (12)
O2	0.0465 (18)	0.0125 (13)	0.0203 (14)	0.0000 (12)	0.0062 (13)	−0.0004 (11)
O3	0.0238 (13)	0.0195 (13)	0.0212 (14)	0.0006 (11)	−0.0008 (11)	−0.0032 (11)
O4	0.0287 (15)	0.0199 (14)	0.0324 (16)	0.0031 (11)	0.0003 (12)	−0.0094 (12)
O5	0.046 (2)	0.0373 (18)	0.0413 (19)	0.0059 (15)	−0.0161 (16)	−0.0212 (16)
O6	0.049 (2)	0.128 (5)	0.068 (3)	−0.002 (3)	−0.006 (2)	−0.067 (3)
O7	0.061 (2)	0.0268 (17)	0.042 (2)	−0.0013 (16)	0.0201 (17)	−0.0166 (15)
O8	0.0417 (19)	0.0243 (17)	0.067 (3)	−0.0139 (14)	0.0021 (18)	−0.0107 (17)
O9	0.073 (3)	0.0278 (18)	0.050 (2)	0.0151 (18)	−0.024 (2)	−0.0111 (16)
O10	0.0384 (18)	0.0402 (19)	0.0323 (18)	0.0020 (15)	−0.0001 (14)	−0.0104 (15)
O11	0.0463 (19)	0.0264 (16)	0.0323 (17)	0.0051 (14)	0.0016 (14)	−0.0117 (14)
O12	0.0344 (17)	0.0204 (15)	0.0368 (17)	−0.0019 (12)	−0.0084 (14)	−0.0066 (13)
O13	0.0268 (15)	0.0342 (17)	0.0261 (16)	−0.0007 (13)	0.0051 (12)	0.0007 (13)
O14	0.0258 (14)	0.0206 (14)	0.0281 (15)	0.0018 (11)	−0.0038 (12)	−0.0056 (12)
O15	0.0427 (18)	0.0313 (17)	0.0282 (16)	0.0121 (14)	0.0052 (14)	−0.0132 (14)
O16	0.076 (3)	0.0220 (16)	0.0325 (18)	0.0126 (16)	0.0118 (17)	−0.0102 (14)
N1	0.0336 (18)	0.0126 (15)	0.0187 (16)	0.0036 (13)	0.0039 (14)	−0.0022 (13)
C1	0.0249 (19)	0.0219 (19)	0.0157 (18)	0.0010 (15)	0.0000 (15)	−0.0034 (15)
C2	0.0243 (18)	0.0138 (17)	0.0172 (18)	−0.0015 (14)	0.0014 (15)	0.0006 (14)
C3	0.0242 (19)	0.0202 (19)	0.0172 (18)	−0.0009 (15)	0.0043 (14)	−0.0091 (15)
C4	0.0269 (19)	0.0153 (18)	0.0210 (19)	0.0017 (14)	−0.0015 (15)	−0.0105 (15)
C5	0.0228 (18)	0.0136 (17)	0.0204 (19)	−0.0001 (14)	0.0018 (15)	−0.0029 (14)
C6	0.0226 (18)	0.0143 (17)	0.0178 (18)	−0.0025 (14)	0.0005 (14)	−0.0051 (14)
C7	0.034 (2)	0.0146 (18)	0.020 (2)	0.0030 (15)	−0.0026 (16)	−0.0063 (15)
C8	0.028 (2)	0.0151 (18)	0.0197 (19)	0.0041 (15)	−0.0037 (15)	−0.0052 (15)
C9	0.0211 (18)	0.0173 (18)	0.0181 (19)	0.0007 (14)	0.0007 (14)	−0.0042 (14)

C10	0.0263 (19)	0.0138 (17)	0.0154 (18)	0.0004 (14)	−0.0013 (14)	−0.0016 (14)
C11	0.030 (2)	0.024 (2)	0.0141 (18)	0.0059 (16)	−0.0011 (15)	−0.0064 (15)
C12	0.030 (2)	0.020 (2)	0.023 (2)	0.0072 (16)	−0.0041 (16)	−0.0087 (16)
C13	0.032 (2)	0.0180 (19)	0.022 (2)	0.0062 (16)	−0.0029 (16)	−0.0100 (16)
C14	0.037 (2)	0.026 (2)	0.0175 (19)	0.0120 (17)	−0.0044 (17)	−0.0115 (16)

Geometric parameters (Å, º)

Zn1—O15^{i}	1.9523 (14)	O5—H5B	0.9610
Zn1—O1	1.956 (3)	O6—H6A	0.9687
Zn1—O3	1.983 (3)	O6—H6B	0.9721
Zn1—O6	2.155 (4)	O10—H10A	0.9642
Zn1—O14^{ii}	2.292 (3)	O10—H10B	0.9623
Zn1—Zn2	3.1435 (8)	O11—H11A	0.8742
Zn2—O4	2.048 (2)	O11—H11B	0.8734
Zn2—O5	2.052 (2)	O14—Zn2^{ii}	2.2868 (13)
Zn2—O3	2.061 (3)	O14—Zn1^{ii}	2.2922 (15)
Zn2—O2	2.069 (3)	O15—C14	1.268 (4)
Zn2—O3^{iii}	2.118 (3)	O15—Zn1^{v}	1.9522 (13)
Zn2—O14^{ii}	2.2868 (15)	O16—C14	1.233 (5)
Zn2—Zn2^{iii}	3.1170 (10)	N1—C5	1.373 (4)
Zn3—O11	2.0438 (12)	N1—C9	1.378 (4)
Zn3—O11^{iv}	2.0438 (12)	N1—H1	0.8800
Zn3—O10^{iv}	2.076 (3)	C1—C2	1.499 (5)
Zn3—O10	2.077 (3)	C2—C7	1.384 (5)
Zn3—O8^{iv}	2.164 (3)	C2—C3	1.404 (5)
Zn3—O8	2.164 (3)	C3—C4	1.375 (5)
S1—O7	1.434 (3)	C3—H3A	0.9500
S1—O8	1.444 (4)	C4—C5	1.401 (5)
S1—O9	1.456 (4)	C5—C6	1.413 (5)
S1—C4	1.764 (4)	C6—C7	1.391 (5)
S2—O13	1.4443 (15)	C6—C8	1.447 (5)
S2—O12	1.4546 (17)	C7—H7	0.9500
S2—O14	1.4698 (16)	C8—C13	1.400 (5)
S2—C10	1.759 (4)	C8—C9	1.407 (5)
O1—C1	1.263 (5)	C9—C10	1.397 (5)
O2—C1	1.252 (5)	C10—C11	1.390 (5)
O3—Zn2^{iii}	2.118 (3)	C11—C12	1.404 (6)
O3—H3	1.0000	C11—H11	0.9500
O4—H4A	0.8700	C12—C13	1.389 (6)
O4—H4B	0.8695	C12—C14	1.507 (5)
O5—H5A	0.9653	C13—H13	0.9500

O15^{i}—Zn1—O1	102.03 (10)	Zn1—O3—Zn2	102.04 (12)
O15^{i}—Zn1—O3	148.20 (10)	Zn1—O3—Zn2^{iii}	130.19 (14)
O1—Zn1—O3	109.11 (12)	Zn2—O3—Zn2^{iii}	96.46 (12)
O15^{i}—Zn1—O6	88.49 (16)	Zn1—O3—H3	108.5
O1—Zn1—O6	98.54 (18)	Zn2—O3—H3	108.5

O3—Zn1—O6	93.05 (18)	$Zn2^{iii}$—O3—H3	108.5
$O15^{i}$—Zn1—$O14^{ii}$	96.53 (8)	Zn2—O4—H4A	110.9
O1—Zn1—$O14^{ii}$	91.47 (10)	Zn2—O4—H4B	110.3
O3—Zn1—$O14^{ii}$	76.75 (9)	H4A—O4—H4B	103.3
O6—Zn1—$O14^{ii}$	167.65 (17)	Zn2—O5—H5A	109.1
$O15^{i}$—Zn1—Zn2	143.08 (10)	Zn2—O5—H5B	109.3
O1—Zn1—Zn2	82.99 (9)	H5A—O5—H5B	108.9
O3—Zn1—Zn2	39.88 (8)	Zn1—O6—H6A	108.4
O6—Zn1—Zn2	127.35 (14)	Zn1—O6—H6B	108.2
$O14^{ii}$—Zn1—Zn2	46.57 (4)	H6A—O6—H6B	107.8
O4—Zn2—O5	91.79 (9)	S1—O8—Zn3	153.0 (2)
O4—Zn2—O3	104.80 (10)	Zn3—O10—H10A	109.0
O5—Zn2—O3	161.66 (11)	Zn3—O10—H10B	109.1
O4—Zn2—O2	85.16 (12)	H10A—O10—H10B	108.9
O5—Zn2—O2	93.54 (14)	Zn3—O11—H11A	111.1
O3—Zn2—O2	95.59 (12)	Zn3—O11—H11B	110.4
O4—Zn2—$O3^{iii}$	92.72 (11)	H11A—O11—H11B	103.0
O5—Zn2—$O3^{iii}$	87.98 (13)	S2—O14—$Zn2^{ii}$	135.38 (9)
O3—Zn2—$O3^{iii}$	83.54 (12)	S2—O14—$Zn1^{ii}$	134.74 (8)
O2—Zn2—$O3^{iii}$	177.43 (12)	$Zn2^{ii}$—O14—$Zn1^{ii}$	86.71 (5)
O4—Zn2—$O14^{ii}$	170.98 (10)	C14—O15—$Zn1^{v}$	121.9 (2)
O5—Zn2—$O14^{ii}$	89.45 (9)	C5—N1—C9	109.4 (2)
O3—Zn2—$O14^{ii}$	75.40 (10)	C5—N1—H1	125.3
O2—Zn2—$O14^{ii}$	85.85 (10)	C9—N1—H1	125.3
$O3^{iii}$—Zn2—$O14^{ii}$	96.25 (9)	O2—C1—O1	125.2 (4)
O4—Zn2—$Zn2^{iii}$	101.60 (8)	O2—C1—C2	118.0 (4)
O5—Zn2—$Zn2^{iii}$	127.12 (11)	O1—C1—C2	116.8 (4)
O3—Zn2—$Zn2^{iii}$	42.47 (8)	C7—C2—C3	120.4 (3)
O2—Zn2—$Zn2^{iii}$	138.00 (9)	C7—C2—C1	120.8 (3)
$O3^{iii}$—Zn2—$Zn2^{iii}$	41.07 (8)	C3—C2—C1	118.8 (4)
$O14^{ii}$—Zn2—$Zn2^{iii}$	84.68 (4)	C4—C3—C2	121.2 (4)
O4—Zn2—Zn1	128.73 (7)	C4—C3—H3A	119.4
O5—Zn2—Zn1	133.03 (7)	C2—C3—H3A	119.4
O3—Zn2—Zn1	38.08 (8)	C3—C4—C5	118.6 (3)
O2—Zn2—Zn1	70.94 (8)	C3—C4—S1	122.0 (3)
$O3^{iii}$—Zn2—Zn1	109.46 (8)	C5—C4—S1	119.4 (3)
$O14^{ii}$—Zn2—Zn1	46.72 (7)	N1—C5—C4	130.1 (3)
$Zn2^{iii}$—Zn2—Zn1	72.90 (2)	N1—C5—C6	109.3 (3)
O11—Zn3—$O11^{iv}$	180.00 (10)	C4—C5—C6	120.6 (3)
O11—Zn3—$O10^{iv}$	90.50 (11)	C7—C6—C5	119.7 (4)
$O11^{iv}$—Zn3—$O10^{iv}$	89.50 (11)	C7—C6—C8	134.6 (4)
O11—Zn3—O10	89.50 (11)	C5—C6—C8	105.7 (3)
$O11^{iv}$—Zn3—O10	90.50 (11)	C2—C7—C6	119.5 (4)
$O10^{iv}$—Zn3—O10	180.0	C2—C7—H7	120.3
O11—Zn3—$O8^{iv}$	88.12 (12)	C6—C7—H7	120.3
$O11^{iv}$—Zn3—$O8^{iv}$	91.88 (12)	C13—C8—C9	120.2 (4)
$O10^{iv}$—Zn3—$O8^{iv}$	90.07 (15)	C13—C8—C6	132.6 (4)
O10—Zn3—$O8^{iv}$	89.93 (15)	C9—C8—C6	107.2 (3)

O11—Zn3—O8	91.88 (12)	N1—C9—C10	130.6 (3)
O11^{iv}—Zn3—O8	88.12 (12)	N1—C9—C8	108.4 (3)
O10^{iv}—Zn3—O8	89.93 (15)	C10—C9—C8	120.9 (4)
O10—Zn3—O8	90.07 (15)	C11—C10—C9	118.4 (3)
O8^{iv}—Zn3—O8	180.0	C11—C10—S2	119.5 (3)
O7—S1—O8	113.5 (2)	C9—C10—S2	122.1 (3)
O7—S1—O9	113.3 (2)	C10—C11—C12	120.9 (4)
O8—S1—O9	111.2 (3)	C10—C11—H11	119.6
O7—S1—C4	107.3 (2)	C12—C11—H11	119.6
O8—S1—C4	104.8 (2)	C13—C12—C11	120.9 (4)
O9—S1—C4	106.1 (2)	C13—C12—C14	119.8 (4)
O13—S2—O12	114.31 (12)	C11—C12—C14	119.2 (4)
O13—S2—O14	111.87 (10)	C12—C13—C8	118.7 (4)
O12—S2—O14	109.57 (9)	C12—C13—H13	120.7
O13—S2—C10	107.86 (14)	C8—C13—H13	120.7
O12—S2—C10	105.17 (14)	O16—C14—O15	123.6 (3)
O14—S2—C10	107.63 (15)	O16—C14—C12	119.8 (4)
C1—O1—Zn1	124.5 (3)	O15—C14—C12	116.5 (4)
C1—O2—Zn2	135.7 (3)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O13^{vi}	1.00	1.83	2.804 (5)	163
O4—H4*A*···O12^{vi}	0.87	1.86	2.632 (4)	147
O4—H4*B*···O16^{vii}	0.87	1.85	2.608 (3)	145
O5—H5*A*···O12^{ii}	0.97	1.81	2.736 (3)	160
O5—H5*B*···O7^{viii}	0.96	2.09	2.818 (4)	131
O6—H6*A*···O13^{vi}	0.97	2.09	2.976 (5)	151
O6—H6*B*···O7^{ix}	0.97	2.24	3.156 (7)	157
O10—H10*A*···O7^{x}	0.96	2.20	2.941 (5)	133
O10—H10*B*···O16^{vi}	0.96	1.72	2.666 (5)	166
O11—H11*A*···O4^{vi}	0.87	1.96	2.837 (3)	179
O11—H11*B*···O9^{x}	0.87	1.89	2.757 (5)	171
N1—H1···O9	0.88	2.46	2.962 (4)	117
N1—H1···O12	0.88	2.40	2.908	117

Symmetry codes: (ii) $-x+2, -y+1, -z+1$; (vi) $-x+1, -y+1, -z+1$; (vii) $-x+1, -y+2, -z+1$; (viii) $x, y+1, z$; (ix) $-x+2, -y+1, -z$; (x) $x-1, y, z$.