



Crystal structure of a cadmium sulfate coordination polymer based on the 3,6-bis(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine ligand

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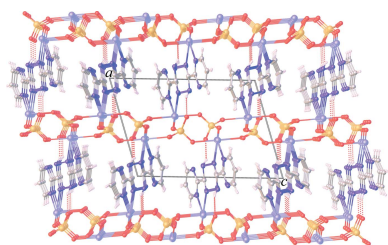
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The polymeric title compound, poly[aquahemi[μ_2 -3,6-bis(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine](μ_3 -sulfato)cadmium(II)], [Cd(SO₄)(C₁₀H₈N₈)_{0.5}(H₂O)]_n, (**I**), represents an example of a three-dimensional coordination polymer resulting from the reaction of CdSO₄·8/3H₂O with 3,6-bis(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine (H₂bmtz, C₁₀H₈N₈) under hydrothermal conditions. The Cd^{II} atom has a distorted octahedral coordination environment defined by two nitrogen atoms from one H₂bmtz ligand, three oxygen atoms from three different sulfate anions, and one oxygen atom from a coordinating water molecule. The 1,4-dihydro-1,2,4,5-tetrazine ring of the H₂bmtz ligand is located about an inversion center, with the NH group being equally disordered over two sites. The sulfate anion acts as a μ_3 -bridging ligand to connect three Cd^{II} atoms, resulting in the formation of [Cd(SO₄)(H₂O)] sheets propagating parallel to the *bc* plane. Adjacent sheets are interconnected across the H₂bmtz ligands, which coordinate the Cd^{II} atoms in a bis-bidentate coordination mode, to form a three-dimensional framework structure. The framework is further stabilized by classical O—H···O hydrogen bonds involving the coordinating water molecules and the sulfate groups, and by N—H···O hydrogen bonds between the disordered tetrazine NH groups and sulfate oxygen atom, along with C—H··· π and π — π stacking [centroid-to-centroid separation = 3.5954 (15) Å] interactions between parallel pyrimidine rings of the H₂bmtz ligand.

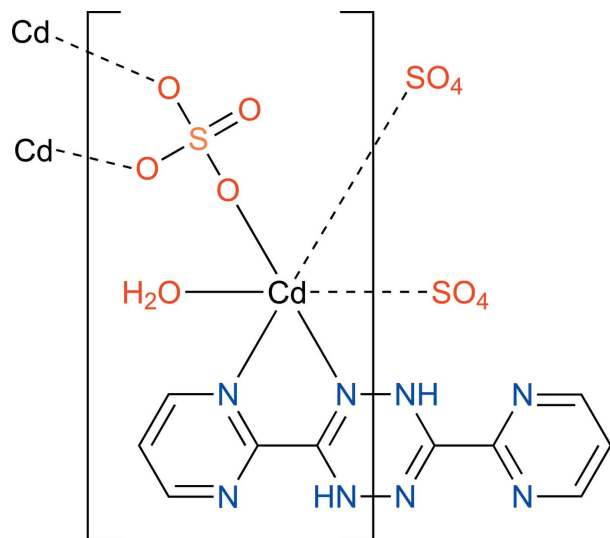
1. Chemical context

Coordination polymers (CPs) are a class of organic–inorganic hybrid materials formed from metal ions or metal clusters and organic linkers through covalent bonds. The structural organization of CPs can result in chains, sheets or three-dimensional frameworks (Batten *et al.*, 2009). These hybrid materials have received extensive attention over the past three decades owing to their structural features and useful applications in the fields of gas storage and separation, catalysis, chemical sensing, magnetism or proton conduction (Furukawa *et al.*, 2010; Ye & Johnson, 2016; Espallargas & Coronado, 2018; Xu *et al.*, 2016; Zhang *et al.*, 2017). Nowadays, many multi-dimensional CPs with structural and topological diversity have been synthesized through the tremendous possibilities of choices for building blocks, and some of them seem promising as candidate materials, for instance, in gas purification (Duan *et al.*, 2015). In the context of the crystal engineering of CPs, the most feasible strategy for the construction of such infinite hybrid networks is by the careful selection of metal coordination arrangements and suitable organic linkers. Among the



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most common ligands, the rigid organic carboxylate- and pyridyl-based ligands have by far been the most widely used to control the structural motifs of these solids (Glöckle *et al.*, 2001).



In this work, to explore the synthesis of novel CPs using 3,6-bis(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine, $C_{10}H_8N_8$ or H_2bmtz (Kaim & Fees, 1995; Chainok *et al.*, 2012) as a polydentate nitrogen-donor ligand with cadmium(II) sulfate, a new CP $[Cd(SO_4)(H_2bmtz)_{0.5}(H_2O)]_n$ (**I**) was isolated under hydrothermal conditions. The crystal structure and supramolecular interactions of (**I**) are reported herein.

2. Structural commentary

The asymmetric unit of the title compound consists of one Cd^{II} cation, one-half of the H_2bmtz ligand, one sulfate anion and one coordinating water molecule. The 1,4-dihydro-1,2,4,5-tetrazine ring of the H_2bmtz ligand is located about an inversion centre, with the NH group (N4) being equally disordered over two sites. As shown in Fig. 1, the Cd^{II} atom exhibits a distorted octahedral $[CdN_2O_4]$ coordination environment with two nitrogen atoms from the H_2bmtz ligand, three oxygen atoms from three different sulfate anions and one oxygen atom from the coordinating water molecule. The bond angles around the central Cd^{II} atom range from 69.69 (5) to 168.46 (5)°. The $Cd-O$ and $Cd-N$ bond lengths fall in the range of 2.2321 (12)– 2.3790 (13) Å, which is comparable with those of reported cadmium(II) sulfate compounds containing additional nitrogen donor ligands such as $[Cd_2(SO_4)_2(C_{16}H_{12}N_6)_2(H_2O)_2] \cdot 4H_2O$ (GADLON; Harvey *et al.*, 2003), $[Cd_2(C_2H_3O_2)_2(S_2O_8)(C_{15}H_{11}N_2)_2(H_2O)_2] \cdot 7H_2O$ (FOMBUF; Díaz de Vivar *et al.*, 2005) and $[Cd_2(C_{15}H_9N_9)(H_2O)_6(SO_4)_2] \cdot H_2O$ (DIQCOX; Safin *et al.*, 2013). The complete H_2bmtz molecule is not planar (r.m.s. deviation = 0.111 Å) with the central six-membered ring of the 1,4-dihydro-1,2,4,5-tetrazine moiety in a twist-boat conformation; the $C5-N3-N4^i-C5^i$ torsion angle is 36.4 (4)° [symmetry code: (i) $2-x, 1-y, 1-z$]. The sulfate anion acts

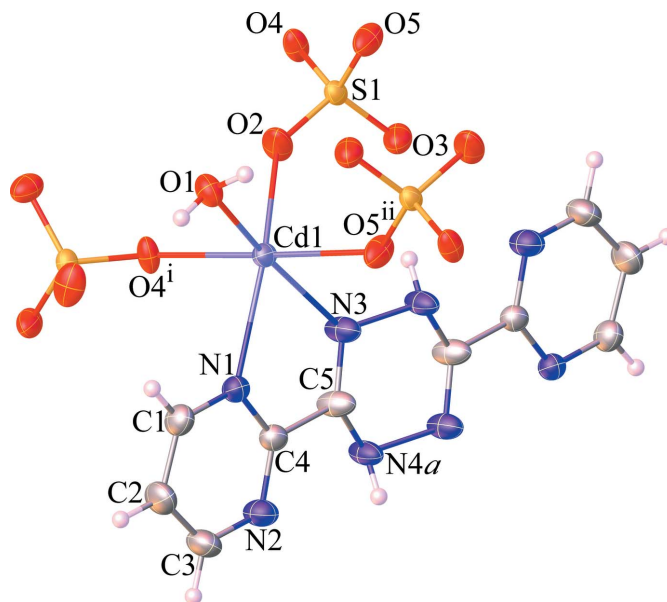


Figure 1
Molecular structure of (**I**), showing the atom-labelling scheme. Only one orientation of the disordered N4–H group is shown. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii) $1-x, 1-y, 1-z$].

as a μ_3 -bridging ligand to connect three Cd^{II} atoms to form a sheet-like structure of $[Cd(SO_4)(H_2O)]$ units, propagating parallel to the bc plane, Fig. 2. Adjacent sheets are interconnected across the H_2bmtz ligands, which exhibit a bis-bidentate coordination mode, giving rise to a three-dimensional framework structure, Fig. 3.

3. Supramolecular features

In the crystal, classical $O-H \cdots O$ hydrogen bonds exist between the coordinating water molecules and the sulfate groups, and $N-H \cdots O$ hydrogen bonds involving the disordered tetrazine NH group and sulfate oxygen atoms. In this

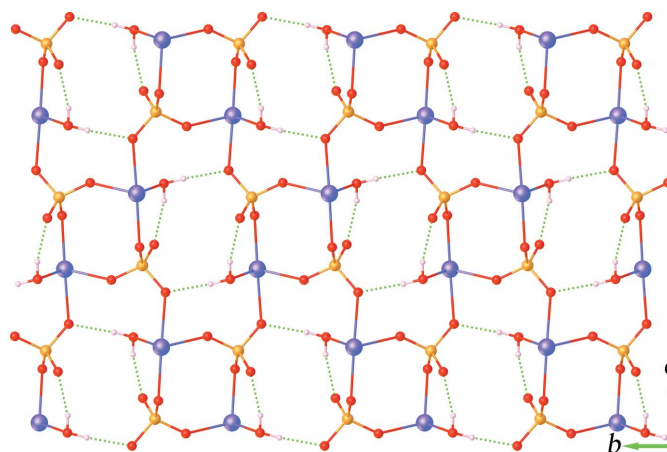


Figure 2
View of the $[Cd(SO_4)(H_2O)]$ sheet in (**I**) propagating parallel to the bc plane. Classical $O-H \cdots O$ hydrogen-bonding interactions are shown as dashed lines.

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

*Cg*₁ is the centroid of the N1/N2/C1–C4 ring.

<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>
O1–H1A···O3 ⁱ	0.84 (2)	1.92 (2)	2.710 (2)	159 (2)
O1–H1B···O4 ⁱⁱ	0.84 (2)	1.91 (2)	2.743 (2)	174 (3)
N4A–H4A···O3 ⁱⁱⁱ	0.87 (2)	2.09 (2)	2.889 (3)	153 (2)
N4B–H4A···O3 ⁱⁱⁱ	0.87 (2)	2.09 (2)	2.828 (3)	143 (2)
C2–H2··· <i>Cg</i> ₁ ^{iv}	0.93	3.34 (2)	4.091 (3)	140 (2)

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

way, rings with $R_1^1(8)$ and $R_4^4(16)$ graph-set motifs are formed, Table 1. Additionally, C–H··· π [H···*Cg* = 3.34 (2) Å; *Cg* is the centroid of the pyrimidine ring] and π – π stacking [centroid-to-centroid separation = 3.5954 (15) Å, slippage between parallel pyrimidine rings = 1.131 Å] interactions between the pyrimidine rings of the H₂bmtz ligand are also observed, Fig. 4.

4. Database survey

A search of the Cambridge Structural Database (CSD version 5.41, November 2019 update; Groom *et al.*, 2016) gave only two hits for H₂bmtz complexes with transition metals ions, *viz.* with Cu^I (QORNAM; Glöckle *et al.*, 2001) and Ag^I (ZASTAQ; Chainok *et al.*, 2012). In these structures, the coordination mode of the H₂bmtz ligands is bis-bidentate through nitrogen atoms.

5. Synthesis and crystallization

All reagents were of analytical grade and were used as received without further purification. The ligand 3,6-bis(-pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine was synthesized according to a literature method (Kaim & Fees, 1995). A mixture solution of CdSO₄·8/3H₂O (41.7 mg, 0.2 mmol) and the H₂bmtz ligand (36.7 mg, 0.1 mmol) in water (5 ml) was added into a 15 ml Teflon-lined reactor, stirred at room

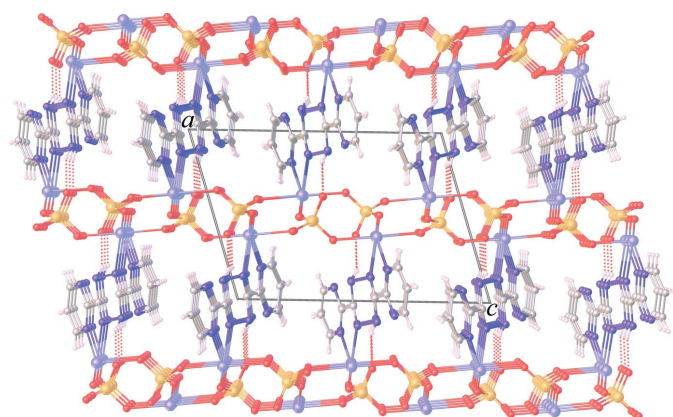


Figure 3
Packing diagram of (I), showing N–H···O hydrogen bonding as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	[Cd(SO ₄)(C ₁₀ H ₈ N ₈) _{0.5} (H ₂ O)]
<i>M_r</i>	346.60
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.3000 (3), 7.9798 (2), 13.2586 (4)
β (°)	106.872 (1)
<i>V</i> (Å ³)	941.60 (5)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.56
Crystal size (mm)	0.28 × 0.24 × 0.18
Data collection	
Diffractometer	Bruker D8 QUEST CMOS
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2016)
<i>T</i> _{min} , <i>T</i> _{max}	0.660, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	24280, 2357, 2338
<i>R</i> _{int}	0.020
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.668
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.014, 0.037, 1.12
No. of reflections	2357
No. of parameters	167
No. of restraints	11
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.41, -0.37

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

temperature for 10 min, sealed in a stainless steel autoclave and placed in an oven. The mixture was heated to 383 K under autogenous pressure for 48 h, and then cooled down to room temperature. After filtration, brown block-shaped crystals were obtained in 80% yield (33.4 mg) based on the cadmium(II) source.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Nitrogen atom N4 of the 1,4-di-

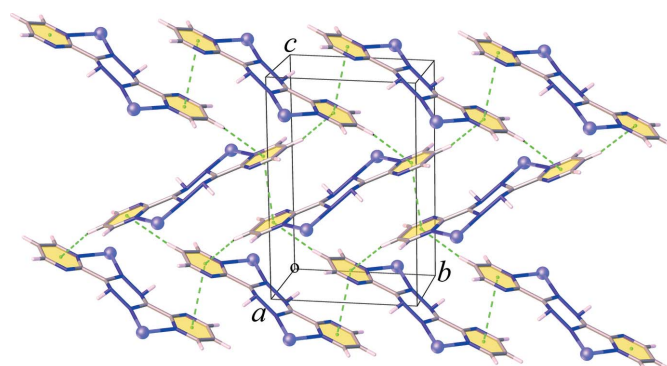


Figure 4
Partial packing diagram of (I), showing C–H··· π and π – π stacking interactions (dashed lines) between the H₂bmtz ligands.

hydro-1,2,4,5-tetrazine ring was found to be disordered about an inversion centre; restraints (SADI and RIGU with $esd(0.001 \text{ \AA}^2)$) were used for its refinement. All hydrogen atoms were found in difference-Fourier maps. H atoms attached to C atoms were refined in the riding-model approximation with $C-H = 0.93 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms bound to O or N atoms were refined with distance restraints of $O-H = 0.84 \pm 0.01 \text{ \AA}$ and $N-H = 0.86 \pm 0.01 \text{ \AA}$ and with $U_{iso}(H) = 1.5U_{eq}(O)$ and $1.2U_{eq}(N)$, respectively.

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Acta Cryst. (2020). E76, 958-961 [https://doi.org/10.1107/S2056989020006830]

Crystal structure of a cadmium sulfate coordination polymer based on the 3,6-bis(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine ligand

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *ShelXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Poly[aquahemi[μ_2 -3,6-bis(pyrimidin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine](μ_3 -sulfato)cadmium(II)]

Crystal data

[Cd(SO₄)(C₁₀H₈N₈)_{0.5}(H₂O)]

$M_r = 346.60$

Monoclinic, $P2_1/c$

$a = 9.3000$ (3) Å

$b = 7.9798$ (2) Å

$c = 13.2586$ (4) Å

$\beta = 106.872$ (1)°

$V = 941.60$ (5) Å³

$Z = 4$

$F(000) = 672$

$D_x = 2.445$ Mg m⁻³

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

Cell parameters from 9940 reflections

$\theta = 3.4$ – 28.4 °

$\mu = 2.56$ mm⁻¹

$T = 296$ K

Block, brown

$0.28 \times 0.24 \times 0.18$ mm

Data collection

Bruker D8 QUEST CMOS
diffractometer

Radiation source: sealed x-ray tube

Graphite monochromator

Detector resolution: 7.39 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2016)

$T_{\min} = 0.660$, $T_{\max} = 0.746$

24280 measured reflections

2357 independent reflections

2338 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 28.4$ °, $\theta_{\min} = 3.2$ °

$h = -12 \rightarrow 12$

$k = -10 \rightarrow 10$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.014$

$wR(F^2) = 0.037$

$S = 1.12$

2357 reflections

167 parameters

11 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0176P)^2 + 0.6173P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.41$ e Å⁻³

$\Delta\rho_{\min} = -0.37$ e Å⁻³

Extinction correction: SHELXL-2018/3
 (Sheldrick 2015b),
 $F_c^* = kF_c [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0013 (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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cd1	0.61850 (2)	0.31497 (2)	0.37692 (2)	0.01977 (5)	
S1	0.46994 (4)	0.71617 (4)	0.38900 (3)	0.01921 (8)	
O1	0.40176 (15)	0.17176 (15)	0.34420 (10)	0.0290 (2)	
H1A	0.378 (3)	0.170 (3)	0.4004 (13)	0.046 (7)*	
H1B	0.408 (3)	0.0706 (15)	0.329 (2)	0.049 (7)*	
O2	0.49134 (16)	0.55557 (15)	0.34172 (10)	0.0389 (3)	
O3	0.61350 (13)	0.77844 (18)	0.45697 (10)	0.0327 (3)	
O4	0.40858 (15)	0.83595 (14)	0.30158 (9)	0.0276 (2)	
O5	0.35993 (14)	0.70011 (18)	0.44827 (9)	0.0338 (3)	
N1	0.81264 (15)	0.12667 (17)	0.37110 (10)	0.0254 (3)	
N2	1.07599 (16)	0.1093 (2)	0.39678 (13)	0.0342 (3)	
N3	0.85731 (15)	0.44436 (17)	0.44639 (13)	0.0321 (3)	
N4A	1.1157 (3)	0.4194 (4)	0.4718 (3)	0.0326 (6)	0.5
H4A	1.180 (2)	0.345 (3)	0.5064 (15)	0.070 (9)*	
N4B	1.1132 (3)	0.3849 (4)	0.5340 (3)	0.0320 (6)	0.5
C1	0.7954 (2)	−0.0244 (2)	0.32666 (14)	0.0337 (4)	
H1	0.699820	−0.071019	0.303463	0.040*	
C2	0.9168 (2)	−0.1135 (3)	0.31425 (17)	0.0427 (4)	
H2	0.904140	−0.217907	0.281657	0.051*	
C3	1.0573 (2)	−0.0420 (3)	0.35194 (17)	0.0410 (4)	
H3	1.140880	−0.100588	0.345972	0.049*	
C4	0.95337 (18)	0.18608 (18)	0.40350 (13)	0.0243 (3)	
C5	0.97378 (19)	0.3543 (2)	0.45278 (17)	0.0354 (4)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.01945 (7)	0.02157 (7)	0.01864 (7)	0.00090 (3)	0.00607 (4)	0.00089 (3)
S1	0.02314 (16)	0.01938 (15)	0.01601 (15)	0.00267 (12)	0.00708 (12)	0.00085 (12)
O1	0.0335 (6)	0.0267 (6)	0.0300 (6)	−0.0058 (4)	0.0145 (5)	−0.0068 (4)
O2	0.0544 (8)	0.0226 (6)	0.0341 (6)	0.0142 (5)	0.0042 (6)	−0.0037 (5)
O3	0.0235 (5)	0.0464 (7)	0.0285 (6)	−0.0025 (5)	0.0081 (5)	−0.0066 (5)
O4	0.0458 (7)	0.0195 (5)	0.0182 (5)	0.0052 (5)	0.0102 (5)	0.0032 (4)
O5	0.0249 (6)	0.0580 (8)	0.0200 (5)	−0.0031 (5)	0.0090 (4)	0.0059 (5)
N1	0.0235 (6)	0.0253 (6)	0.0262 (6)	0.0015 (5)	0.0053 (5)	−0.0010 (5)

N2	0.0250 (6)	0.0319 (7)	0.0456 (8)	0.0029 (6)	0.0101 (6)	-0.0042 (6)
N3	0.0208 (6)	0.0213 (6)	0.0537 (9)	-0.0026 (5)	0.0101 (6)	-0.0076 (6)
N4A	0.0192 (11)	0.0255 (14)	0.0529 (19)	-0.0017 (10)	0.0102 (12)	-0.0135 (14)
N4B	0.0227 (12)	0.0210 (13)	0.0506 (18)	-0.0004 (10)	0.0079 (11)	-0.0084 (13)
C1	0.0292 (8)	0.0321 (8)	0.0356 (9)	-0.0019 (7)	0.0025 (7)	-0.0077 (7)
C2	0.0421 (10)	0.0341 (9)	0.0480 (11)	0.0047 (8)	0.0067 (8)	-0.0178 (8)
C3	0.0331 (9)	0.0400 (10)	0.0498 (11)	0.0091 (8)	0.0119 (8)	-0.0117 (8)
C4	0.0235 (7)	0.0233 (7)	0.0262 (7)	0.0011 (5)	0.0072 (6)	0.0009 (5)
C5	0.0203 (7)	0.0228 (7)	0.0613 (11)	-0.0022 (6)	0.0087 (7)	-0.0069 (7)

Geometric parameters (Å, °)

Cd1—O1	2.2472 (12)	N2—C4	1.320 (2)
Cd1—O2	2.2321 (12)	N3—N4A ⁱⁱⁱ	1.505 (3)
Cd1—O4 ⁱ	2.3122 (11)	N3—N4B ⁱⁱⁱ	1.399 (3)
Cd1—O5 ⁱⁱ	2.2708 (12)	N3—C5	1.282 (2)
Cd1—N1	2.3674 (13)	N4A—H4A	0.871 (10)
Cd1—N3	2.3790 (13)	N4A—C5	1.372 (3)
S1—O2	1.4653 (12)	N4B—H4A	0.866 (10)
S1—O3	1.4640 (12)	N4B—C5	1.445 (3)
S1—O4	1.4828 (11)	C1—H1	0.9300
S1—O5	1.4654 (12)	C1—C2	1.384 (3)
O1—H1A	0.835 (10)	C2—H2	0.9300
O1—H1B	0.839 (10)	C2—C3	1.379 (3)
N1—C1	1.331 (2)	C3—H3	0.9300
N1—C4	1.340 (2)	C4—C5	1.481 (2)
N2—C3	1.335 (2)		
O1—Cd1—O4 ⁱ	90.81 (5)	C4—N2—C3	116.51 (15)
O1—Cd1—O5 ⁱⁱ	88.77 (5)	N4A ⁱⁱⁱ —N3—Cd1	122.32 (13)
O1—Cd1—N1	108.71 (5)	N4B ⁱⁱⁱ —N3—Cd1	127.25 (15)
O1—Cd1—N3	168.46 (5)	C5—N3—Cd1	117.26 (11)
O2—Cd1—O1	90.34 (5)	C5—N3—N4A ⁱⁱⁱ	113.35 (17)
O2—Cd1—O4 ⁱ	80.21 (5)	C5—N3—N4B ⁱⁱⁱ	114.67 (17)
O2—Cd1—O5 ⁱⁱ	98.25 (5)	N3 ⁱⁱⁱ —N4A—H4A	99.5 (18)
O2—Cd1—N1	154.41 (5)	C5—N4A—N3 ⁱⁱⁱ	110.9 (2)
O2—Cd1—N3	94.94 (5)	C5—N4A—H4A	108.3 (19)
O4 ⁱ —Cd1—N1	82.54 (5)	N3 ⁱⁱⁱ —N4B—H4A	108.1 (19)
O4 ⁱ —Cd1—N3	100.19 (5)	N3 ⁱⁱⁱ —N4B—C5	112.9 (2)
O5 ⁱⁱ —Cd1—O4 ⁱ	178.41 (4)	C5—N4B—H4A	102.7 (18)
O5 ⁱⁱ —Cd1—N1	99.05 (5)	N1—C1—H1	119.3
O5 ⁱⁱ —Cd1—N3	80.32 (5)	N1—C1—C2	121.38 (16)
N1—Cd1—N3	69.69 (5)	C2—C1—H1	119.3
O2—S1—O4	107.38 (7)	C1—C2—H2	121.2
O2—S1—O5	110.83 (9)	C3—C2—C1	117.63 (17)
O3—S1—O2	110.33 (8)	C3—C2—H2	121.2
O3—S1—O4	109.74 (8)	N2—C3—C2	121.52 (17)
O3—S1—O5	110.69 (7)	N2—C3—H3	119.2

O5—S1—O4	107.78 (7)	C2—C3—H3	119.2
Cd1—O1—H1A	106.8 (18)	N1—C4—C5	116.76 (14)
Cd1—O1—H1B	114.6 (17)	N2—C4—N1	126.64 (15)
H1A—O1—H1B	105 (2)	N2—C4—C5	116.60 (15)
S1—O2—Cd1	142.41 (8)	N3—C5—N4A	123.30 (19)
S1—O4—Cd1 ^{iv}	131.02 (7)	N3—C5—N4B	120.8 (2)
S1—O5—Cd1 ⁱⁱ	133.11 (8)	N3—C5—C4	118.78 (15)
C1—N1—Cd1	126.47 (11)	N4A—C5—C4	114.68 (18)
C1—N1—C4	116.31 (14)	N4B—C5—C4	117.02 (18)
C4—N1—Cd1	116.63 (10)		
Cd1—N1—C1—C2	170.31 (15)	N2—C4—C5—N3	169.24 (18)
Cd1—N1—C4—N2	-172.52 (14)	N2—C4—C5—N4A	8.9 (3)
Cd1—N1—C4—C5	8.10 (19)	N2—C4—C5—N4B	-31.3 (3)
Cd1—N3—C5—N4A	167.1 (2)	N3 ⁱⁱⁱ —N4A—C5—N3	40.7 (4)
Cd1—N3—C5—N4B	-150.1 (2)	N3 ⁱⁱⁱ —N4A—C5—C4	-160.0 (2)
Cd1—N3—C5—C4	8.5 (2)	N3 ⁱⁱⁱ —N4B—C5—N3	-38.9 (4)
O2—S1—O4—Cd1 ^{iv}	-10.01 (13)	N3 ⁱⁱⁱ —N4B—C5—C4	162.2 (2)
O2—S1—O5—Cd1 ⁱⁱ	103.95 (11)	N4A ⁱⁱⁱ —N3—C5—N4A	-41.6 (4)
O3—S1—O2—Cd1	38.91 (17)	N4A ⁱⁱⁱ —N3—C5—C4	159.9 (2)
O3—S1—O4—Cd1 ^{iv}	109.93 (10)	N4B ⁱⁱⁱ —N3—C5—N4B	39.5 (4)
O3—S1—O5—Cd1 ⁱⁱ	-18.81 (14)	N4B ⁱⁱⁱ —N3—C5—C4	-161.9 (2)
O4—S1—O2—Cd1	158.47 (14)	C1—N1—C4—N2	-0.8 (3)
O4—S1—O5—Cd1 ⁱⁱ	-138.82 (10)	C1—N1—C4—C5	179.83 (16)
O5—S1—O2—Cd1	-84.06 (16)	C1—C2—C3—N2	-1.5 (3)
O5—S1—O4—Cd1 ^{iv}	-129.45 (10)	C3—N2—C4—N1	0.9 (3)
N1—C1—C2—C3	1.5 (3)	C3—N2—C4—C5	-179.74 (18)
N1—C4—C5—N3	-11.3 (3)	C4—N1—C1—C2	-0.5 (3)
N1—C4—C5—N4A	-171.7 (2)	C4—N2—C3—C2	0.3 (3)
N1—C4—C5—N4B	148.1 (2)		

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

Hydrogen-bond geometry (\AA , $^\circ$)

*Cg*1 is the centroid of the N1/N2/C1—C4 ring.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1A \cdots O3 ⁱⁱ	0.84 (2)	1.92 (2)	2.710 (2)	159 (2)
O1—H1B \cdots O4 ^v	0.84 (2)	1.91 (2)	2.743 (2)	174 (3)
N4A—H4A \cdots O3 ⁱⁱⁱ	0.87 (2)	2.09 (2)	2.889 (3)	153 (2)
N4B—H4A \cdots O3 ⁱⁱⁱ	0.87 (2)	2.09 (2)	2.828 (3)	143 (2)
C2—H2 \cdots <i>Cg</i> 1 ^{vi}	0.93	3.34 (2)	4.091 (3)	140 (2)

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