metal-organic compounds

catena-Poly[4,4′-bipyridinium [[diaqua-disulfatocadmium(II)]-μ-4,4′-bipyridine-κ²N:N′] dihydrate]

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The title compound, $\{(C_{10}H_{10}N_2)[Cd(SO_4)_2(C_{10}H_8N_2)(H_2O)_2]\cdot 2H_2O\}_n$, consists of anionic chains of the Cd complex, diprotonated 4,4′-bipyridinium cations and uncoordinated water molecules. In the anionic chain, the Cd atom lies on a center of inversion in an octahedral geometry. The midpoint of the coordinated bipyridine also resides on a center of inversion, as does the non-coordinated bipyridinium counterion. O—H···O and N—H···O hydrogen bonding interactions and π–π stacking interactions in the structure are responsible for the supramolecular assembly.

Related literature

For background to the structures, topologies and potential applications of metal-organic frameworks, see: Batten & Robson (1998). For the use of 4,4′-bipyridine (bpy) in the construction of supramolecular architectures, see: Biradha *et al.* (2006). For the isostructural complex $\{(H_2bpy)[Mn(SO_4)_2(bpy)(H_2O)_2]\cdot 2H_2O\}_n$, see: Fan & Zhu (2005).
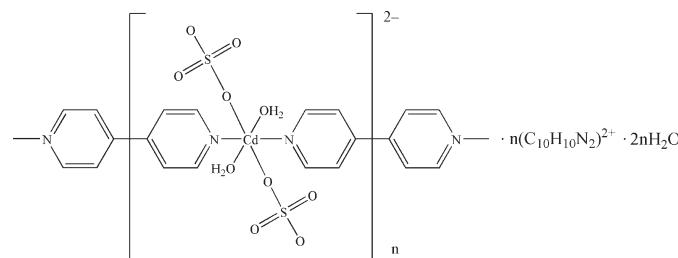
Experimental

Crystal data

$(C_{10}H_{10}N_2)[Cd(SO_4)_2(C_{10}H_8N_2)(H_2O)_2]\cdot 2H_2O$

M_r = 690.97

Triclinic, $P\bar{1}$

a = 7.0150 (14) Å
b = 9.4166 (19) Å
c = 10.020 (2) Å
α = 74.69 (3)°
β = 88.95 (3)°
γ = 77.89 (3)°

V = 623.7 (2) Å³
Z = 1
Mo $K\alpha$ radiation
μ = 1.12 mm⁻¹
T = 295 K
$0.25 \times 0.23 \times 0.17$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.760, T_{max} = 0.830

6106 measured reflections
2797 independent reflections
2572 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.058
S = 1.06
2797 reflections
198 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.61 e Å⁻³
$\Delta\rho_{min}$ = −0.35 e Å⁻³

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O4ⁱ	0.76 (4)	2.11 (4)	2.797 (2)	150
O1—H1B···O5ⁱⁱ	0.84 (3)	1.93 (3)	2.765 (2)	177
O6—H6A···O4	0.83 (3)	2.14 (3)	2.955 (3)	165
O6—H6B···O5ⁱⁱⁱ	0.87 (4)	2.04 (4)	2.788 (6)	144
N2—H2A···O3ⁱᵛ	0.79 (3)	1.82 (3)	2.602 (6)	170

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

References

Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
Biradha, K., Sarkar, M. & Rajput, L. (2006). *Chem. Commun.* pp. 4169–4179.
Fan, S.-R. & Zhu, L.-G. (2005). *Acta Cryst.* E**61**, m1689–m1691.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

catena-Poly[4,4′-bipyridinium [[diaquadisulfatocadmium(II)]-*μ*-4,4′-bipyridine-*κ²N:N′*] dihydrate]

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S1. Comment

Over the past few decades, much attention has been devoted to the research of novel materials based on metal-organic frameworks (MOFs), motivated by their intriguing structures, new topologies, and potential applications (Batten & Robson, 1998). Since the onset, 4,4′-bipyridine (bpy) has been widely used to construct supramolecular architectures, for it has two potential binding sites which are arranged in a divergent (*exo*) fashion and has a rigid structure which will help in the predictability of network geometries (Biradha, *et al.*, 2006). In the present contribution, we report a new cadmium complex, $\{(H_2bpy)[Cd(SO_4)_2(bpy)(H_2O)_2].2H_2O\}_n$, which is isostructural with the previously reported complex $\{(H_2bpy)[Mn(SO_4)_2(bpy)(H_2O)_2].2H_2O\}_n$ (Fan & Zhu, 2005).

As shown in Fig. 1, the structure consists of $\{[Cd(SO_4)_2(bpy)(H_2O)_2)]^{2-}\}_n$ complex anionic chains, 4,4′-bipyridinium dications and hydrate molecules. The unique Cd atom is coordinated in a slightly distorted octahdedral environment by two N atoms from two bridging 4,4′-bipyridine ligands, two O atoms from two sulfate ligands and two O atoms from two water ligands with Cd—O = 2.282 (1) Å, 2.332 (2) Å and Cd—N = 2.356 (2) Å. The Cd ions are bridged by bpy ligands to give linear –Cd-bpy-Cd- chains, in which the neighbouring cadmium ions are seperated by 11.80 Å. Each sulfate anion acts as a monodentate ligand, and through intra- and intermolecular hydrogen bond interactions with coordinating H_2O ligands, hydrate molecules and 4,4′-bipyridinium dications to form the three-dimensional network ($d(O\cdots O)$ = 2.765–2.955 Å and d(O···N) = 2.602 Å) (Fig.2 and Table 1). The 4,4′-bipyridinium dications with the neighboring bpy in the one-dimensional chains form π-π stacking interactions with a distance of about 3.42 Å.

S2. Experimental

0.156 g (1 mmol) 4,4′-bipyridine and 0.151 g (1 mmol) DL-mercaptosuccinic acid were dissolved with stirring in aqueous methanol (20 ml, 1:1 *v/v*). A total of 0.256 g (1 mmol) $CdSO_4.8/3H_2O$ was added to the above solution to obtain a cloudy solution (pH = 3.74), which was filtered. The resulting colorless filtrate was maintained at room temperature and afforded colorless crystals two week later by slow evaporation (yield 18% based on the initial $CdSO_4.8/3H_2O$ input).

S3. Refinement

H atoms bonded to C atoms were placed in geometrically calculated positions and were refined using a riding model, with $U_{iso}(H) = 1.2\ U_{eq}(C)$. H atoms attached to O atoms were found in a difference Fourier synthesis and refined freely.
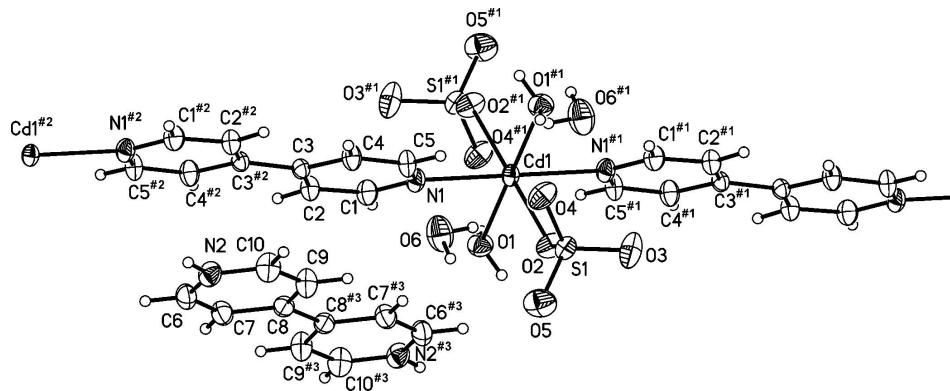
Figure 1

View of the title compound with displacement ellipsoids drawn at the 40% probability level. [Symmetry code: #1 = -*x* + 1, -*y* + 2, -*z* + 1; #2 = -*x*, -*y* + 1, -*z* + 1; #3 = -*x* + 1, -*y* + 1, -*z* + 1]
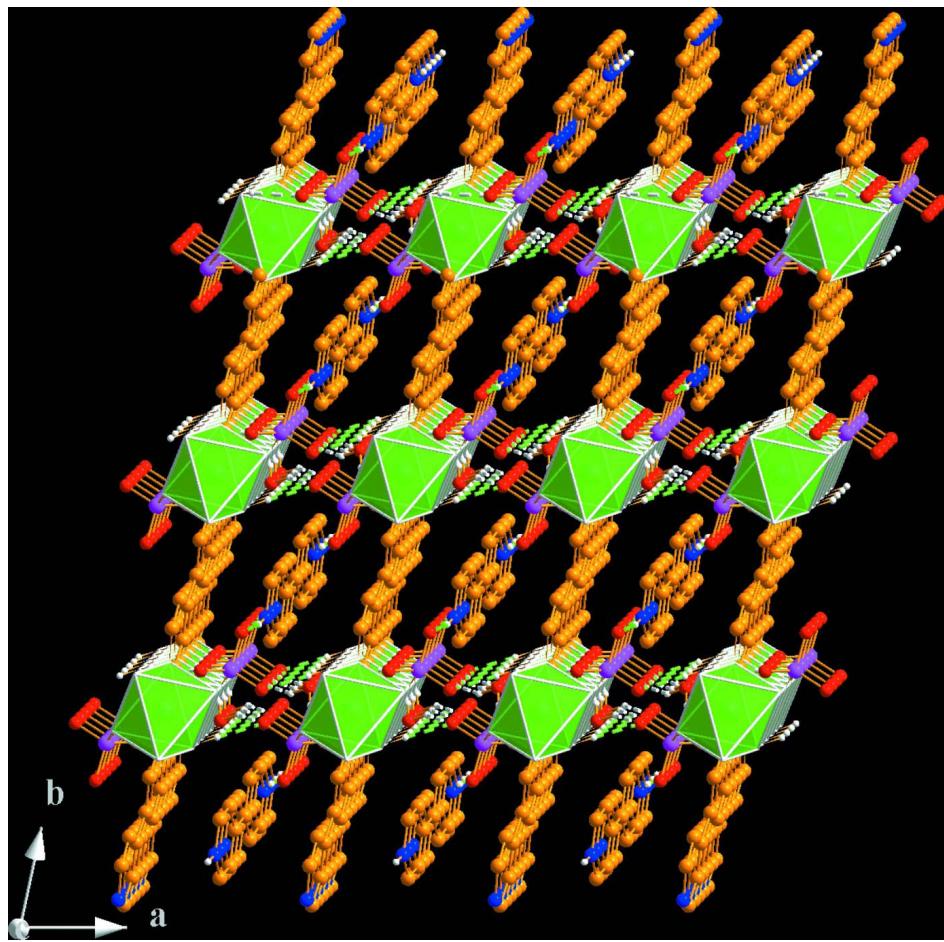
Figure 2

A perspective view of the crystal structure, with hydrogen bonds shown as dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity.

catena-Poly[4,4′-bipyridinium [[diaquadisulfatocadmium(II)]-_µ_-4,4′- bipyridine-_κ²N:N′_] dihydrate]

Crystal data
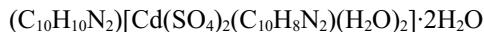
$(C_{10}H_{10}N_2)[Cd(SO_4)_2(C_{10}H_8N_2)(H_2O)_2]\cdot2H_2O$	$Z = 1$
$M_r = 690.97$	$F(000) = 350$
Triclinic, $P\overline{1}$	$D_x = 1.840$ Mg m⁻³
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.0150$ (14) Å	Cell parameters from 5820 reflections
$b = 9.4166$ (19) Å	$\theta = 3.4–27.5°$
$c = 10.020$ (2) Å	$\mu = 1.12$ mm⁻¹
$\alpha = 74.69$ (3)°	$T = 295$ K
$\beta = 88.95$ (3)°	Block, light-yellow
$\gamma = 77.89$ (3)°	$0.25 \times 0.23 \times 0.17$ mm
$V = 623.7$ (2) Å³	

Data collection

Rigaku R-AXIS RAPID diffractometer	6106 measured reflections
Radiation source: fine-focus sealed tube	2797 independent reflections
Graphite monochromator	2572 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.028$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$
$T_{min} = 0.760$, $T_{max} = 0.830$	$h = -8\rightarrow9$
	$k = -12\rightarrow12$
	$l = -12\rightarrow12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.023$	
$wR(F^2) = 0.058$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.06$	
2797 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2]$
198 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.61$ e Å⁻³
	$\Delta\rho_{min} = -0.35$ 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. 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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Cd1	0.0000	1.0000	0.0000	0.01975 (7)
S1	0.29197 (7)	1.15768 (5)	0.17257 (4)	0.02264 (11)
O1	0.1945 (2)	0.84005 (18)	−0.11454 (17)	0.0314 (3)

H1A	0.136 (6)	0.833 (4)	−0.175 (4)	0.088 (14)*
H1B	0.290 (4)	0.868 (3)	−0.157 (3)	0.043 (8)*
O2	0.2561 (2)	1.08582 (18)	0.06347 (15)	0.0317 (3)
O3	0.3055 (3)	1.31472 (19)	0.10627 (17)	0.0436 (4)
O4	0.1344 (2)	1.15595 (19)	0.27022 (15)	0.0368 (4)
O5	0.4799 (2)	1.0756 (2)	0.24417 (17)	0.0450 (4)
N1	0.0296 (2)	0.79779 (18)	0.20108 (16)	0.0239 (3)
C1	0.0538 (3)	0.6552 (2)	0.19390 (19)	0.0256 (4)
H1	0.0766	0.6356	0.1081	0.031*
C2	0.0466 (3)	0.5356 (2)	0.30742 (19)	0.0243 (4)
H2	0.0672	0.4381	0.2975	0.029*
C3	0.0080 (3)	0.56194 (19)	0.43746 (18)	0.0196 (3)
C4	−0.0128 (3)	0.7102 (2)	0.44466 (19)	0.0252 (4)
H4	−0.0347	0.7334	0.5290	0.030*
C5	−0.0006 (3)	0.8224 (2)	0.3263 (2)	0.0262 (4)
H5	−0.0140	0.9204	0.3338	0.031*
N2	0.4126 (3)	0.3731 (2)	0.85093 (18)	0.0298 (4)
H2A	0.385 (4)	0.344 (3)	0.929 (3)	0.036 (7)*
C6	0.4633 (3)	0.2724 (2)	0.7777 (2)	0.0308 (4)
H6	0.4744	0.1704	0.8203	0.037*
C7	0.4990 (3)	0.3192 (2)	0.6395 (2)	0.0284 (4)
H7	0.5344	0.2489	0.5886	0.034*
C8	0.4823 (3)	0.4724 (2)	0.57526 (19)	0.0237 (4)
C9	0.4306 (3)	0.5733 (2)	0.6567 (2)	0.0331 (5)
H9	0.4192	0.6761	0.6178	0.040*
C10	0.3968 (3)	0.5197 (3)	0.7943 (2)	0.0346 (5)
H10	0.3624	0.5867	0.8486	0.041*
O6	0.2828 (3)	0.9313 (2)	0.5331 (2)	0.0477 (4)
H6A	0.257 (5)	1.003 (4)	0.462 (3)	0.057 (9)*
H6B	0.376 (5)	0.956 (4)	0.572 (4)	0.064 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.02501 (11)	0.01778 (10)	0.01586 (10)	−0.00645 (7)	−0.00012 (7)	−0.00191 (7)
S1	0.0271 (2)	0.0267 (3)	0.0168 (2)	−0.01104 (19)	0.00086 (18)	−0.00635 (18)
O1	0.0293 (8)	0.0344 (8)	0.0308 (8)	−0.0052 (6)	0.0055 (7)	−0.0106 (6)
O2	0.0315 (7)	0.0432 (9)	0.0301 (8)	−0.0156 (6)	0.0030 (6)	−0.0206 (7)
O3	0.0716 (11)	0.0319 (9)	0.0338 (8)	−0.0240 (8)	0.0179 (8)	−0.0110 (7)
O4	0.0407 (8)	0.0481 (10)	0.0286 (8)	−0.0195 (7)	0.0121 (7)	−0.0154 (7)
O5	0.0375 (8)	0.0620 (12)	0.0330 (9)	−0.0084 (8)	−0.0092 (7)	−0.0093 (8)
N1	0.0291 (8)	0.0226 (8)	0.0183 (7)	−0.0080 (6)	−0.0015 (7)	−0.0005 (6)
C1	0.0338 (10)	0.0258 (10)	0.0164 (8)	−0.0068 (8)	0.0011 (8)	−0.0037 (7)
C2	0.0332 (10)	0.0187 (9)	0.0208 (9)	−0.0060 (7)	0.0016 (8)	−0.0048 (7)
C3	0.0207 (8)	0.0179 (9)	0.0177 (8)	−0.0035 (7)	−0.0011 (7)	−0.0010 (7)
C4	0.0368 (10)	0.0207 (9)	0.0179 (8)	−0.0064 (8)	0.0009 (8)	−0.0043 (7)
C5	0.0383 (10)	0.0175 (9)	0.0214 (9)	−0.0072 (8)	−0.0010 (8)	−0.0014 (7)
N2	0.0336 (9)	0.0325 (10)	0.0217 (9)	−0.0090 (7)	0.0035 (8)	−0.0031 (7)

C6	0.0348 (10)	0.0243 (10)	0.0290 (10)	−0.0048 (8)	0.0015 (9)	−0.0007 (8)
C7	0.0317 (10)	0.0235 (10)	0.0284 (10)	−0.0033 (8)	0.0025 (8)	−0.0062 (8)
C8	0.0219 (8)	0.0244 (10)	0.0233 (10)	−0.0054 (7)	−0.0015 (7)	−0.0033 (7)
C9	0.0461 (12)	0.0251 (11)	0.0285 (10)	−0.0098 (9)	0.0034 (9)	−0.0059 (8)
C10	0.0466 (12)	0.0317 (11)	0.0279 (10)	−0.0106 (9)	0.0039 (10)	−0.0107 (8)
O6	0.0668 (12)	0.0383 (10)	0.0360 (10)	−0.0107 (9)	−0.0098 (9)	−0.0058 (8)

Geometric parameters (Å, º)

Cd1—O2	2.2821 (14)	C3—C3ⁱⁱ	1.491 (3)
Cd1—O2ⁱ	2.2821 (14)	C4—C5	1.379 (3)
Cd1—O1	2.3324 (17)	C4—H4	0.9300
Cd1—O1ⁱ	2.3324 (17)	C5—H5	0.9300
Cd1—N1	2.3562 (18)	N2—C10	1.328 (3)
Cd1—N1ⁱ	2.3562 (18)	N2—C6	1.334 (3)
S1—O4	1.4625 (16)	N2—H2A	0.80 (3)
S1—O5	1.4713 (17)	C6—C7	1.373 (3)
S1—O3	1.4747 (17)	C6—H6	0.9300
S1—O2	1.4793 (14)	C7—C8	1.397 (3)
O1—H1A	0.77 (4)	C7—H7	0.9300
O1—H1B	0.84 (3)	C8—C9	1.397 (3)
N1—C1	1.338 (2)	C8—C8ⁱⁱⁱ	1.494 (4)
N1—C5	1.341 (2)	C9—C10	1.373 (3)
C1—C2	1.382 (3)	C9—H9	0.9300
C1—H1	0.9300	C10—H10	0.9300
C2—C3	1.401 (3)	O6—H6A	0.84 (3)
C2—H2	0.9300	O6—H6B	0.87 (3)
C3—C4	1.394 (3)		
O2—Cd1—O2ⁱ	180.0	C1—C2—C3	119.64 (17)
O2—Cd1—O1	93.80 (6)	C1—C2—H2	120.2
O2ⁱ—Cd1—O1	86.20 (6)	C3—C2—H2	120.2
O2—Cd1—O1ⁱ	86.20 (6)	C4—C3—C2	116.60 (16)
O2ⁱ—Cd1—O1ⁱ	93.80 (6)	C4—C3—C3ⁱⁱ	121.4 (2)
O1—Cd1—O1ⁱ	180.0	C2—C3—C3ⁱⁱ	122.0 (2)
O2—Cd1—N1	94.14 (6)	C5—C4—C3	119.85 (17)
O2ⁱ—Cd1—N1	85.86 (6)	C5—C4—H4	120.1
O1—Cd1—N1	89.48 (6)	C3—C4—H4	120.1
O1ⁱ—Cd1—N1	90.52 (6)	N1—C5—C4	123.46 (18)
O2—Cd1—N1ⁱ	85.86 (6)	N1—C5—H5	118.3
O2ⁱ—Cd1—N1ⁱ	94.14 (6)	C4—C5—H5	118.3
O1—Cd1—N1ⁱ	90.52 (6)	C10—N2—C6	121.81 (19)
O1ⁱ—Cd1—N1ⁱ	89.48 (6)	C10—N2—H2A	119.5 (19)
N1—Cd1—N1ⁱ	180.00 (7)	C6—N2—H2A	118.6 (19)
O4—S1—O5	110.73 (10)	N2—C6—C7	120.1 (2)
O4—S1—O3	109.56 (11)	N2—C6—H6	119.9
O5—S1—O3	108.83 (11)	C7—C6—H6	119.9
O4—S1—O2	110.99 (9)	C6—C7—C8	120.0 (2)

O5—S1—O2	108.04 (10)	C6—C7—H7	120.0
O3—S1—O2	108.62 (9)	C8—C7—H7	120.0
Cd1—O1—H1A	110 (3)	C7—C8—C9	117.66 (19)
Cd1—O1—H1B	118.7 (19)	C7—C8—C8iii	121.5 (2)
H1A—O1—H1B	100 (3)	C9—C8—C8iii	120.8 (2)
S1—O2—Cd1	134.77 (9)	C10—C9—C8	119.6 (2)
C1—N1—C5	117.01 (16)	C10—C9—H9	120.2
C1—N1—Cd1	121.51 (12)	C8—C9—H9	120.2
C5—N1—Cd1	121.00 (13)	N2—C10—C9	120.7 (2)
N1—C1—C2	123.39 (17)	N2—C10—H10	119.6
N1—C1—H1	118.3	C9—C10—H10	119.6
C2—C1—H1	118.3	H6A—O6—H6B	101 (3)

Symmetry codes: (i) −*x*, −*y*+2, −*z*; (ii) −*x*, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O4i	0.76 (4)	2.11 (4)	2.797 (2)	150
O1—H1*B*···O5iv	0.84 (3)	1.93 (3)	2.765 (2)	177
O6—H6*A*···O4	0.83 (3)	2.14 (3)	2.955 (3)	165
O6—H6*B*···O5v	0.87 (4)	2.04 (4)	2.788 (6)	144
N2—H2*A*···O3vi	0.79 (3)	1.82 (3)	2.602 (6)	170

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