

Poly[[bis[3-(1*H*-tetrazol-1-yl)propanoic acid- κ N⁴]cadmium]-di- μ -thiocyanato- κ^2 N:S; κ^2 S:N]

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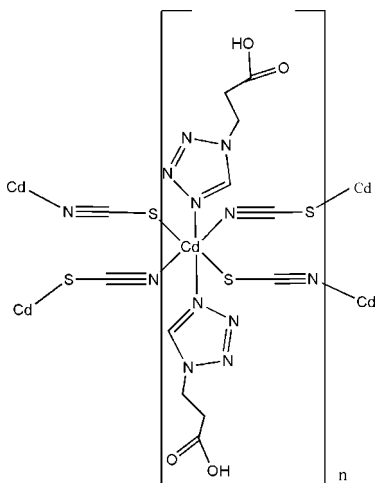
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.021; wR factor = 0.052; data-to-parameter ratio = 13.2.

In the title compound, $[\text{Cd}(\text{NCS})_2(\text{C}_4\text{H}_6\text{N}_4\text{O}_2)_2]_n$, the Cd^{II} cation is located on an inversion center and is coordinated by two N and two S atoms from four SCN^- anions and two N atoms from two 3-(1*H*-tetrazol-1-yl)propanoic acid (Htzp) ligands in a distorted octahedral geometry. The SCN^- anions bridge the Cd^{II} cations into a layer structure parallel to (100). A weak intramolecular $\text{C}-\text{H}\cdots\text{N}$ interaction occurs. The layers are further assembled into a three-dimensional supramolecular structure *via* classical $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For general background to carboxylate-tetrazole complexes, see: Yang *et al.* (2009); He *et al.* (2005); Yu *et al.* (2008); Dong *et al.* (2008); Zhang *et al.* (2009); Li *et al.* (2008, 2010); Xie *et al.* (2010); Bai *et al.* (2008); Voitekhovich *et al.* (2010).



Experimental

Crystal data

$[\text{Cd}(\text{NCS})_2(\text{C}_4\text{H}_6\text{N}_4\text{O}_2)_2]$
 $M_r = 512.81$
 Monoclinic, $P2_1/c$
 $a = 12.7402$ (19) Å
 $b = 6.9555$ (11) Å
 $c = 10.7549$ (16) Å
 $\beta = 106.809$ (1)°
 $V = 912.3$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.47$ mm⁻¹
 $T = 296$ K
 $0.23 \times 0.22 \times 0.20$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
 $T_{\min} = 0.729$, $T_{\max} = 0.758$
 5775 measured reflections
 1695 independent reflections
 1505 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.052$
 $S = 1.07$
 1695 reflections
 128 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.59$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.51$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O}2-\text{H}1\text{O}\cdots\text{O}1^{\text{i}}$	0.94 (4)	1.70 (4)	2.631 (3)	170 (4)
$\text{C}1-\text{H}1\cdots\text{N}5^{\text{ii}}$	0.93	2.62	3.404 (3)	142

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); 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: XU5497).

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Zhang, X.-Q., Yu, Q., Bian, H.-D., Bao, X.-G. & Liang, H. (2009). *J. Coord. Chem.* **62**, 2108–2117.

supplementary materials

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Poly[[bis[3-(1*H*-tetrazol-1-yl)propanoic acid- κ N⁴]]cadmium]-di- μ -thiocyanato- κ^2 N:S; κ^2 S:N]

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Comment

Recently, the design and synthesis of carboxylate-tetrazole coordination compounds have been of an attractive area of research due to their intriguing topological structures as well as their novel physical properties such as anion exchange, photoluminescence, magnetism behavior and biological activities *etc.* (Yang *et al.*, 2009; Yu *et al.*, 2008; Li *et al.*, 2010; He *et al.*, 2005; Li *et al.*, 2008; Dong *et al.*, 2008; Xie *et al.*, 2010; Bai *et al.*, 2008; Voitekhovich *et al.*, 2010). Herein, we report the structure of the title coordination polymer based on a flexible ligand tetrazole-1-propanoic acid (Htzip).

The title coordination polymer crystallizes in the monoclinic space group $P2_1/c$ and the asymmetric unit contains half of the $[\text{Cd}(\text{Htzip})_2(\text{SCN})_2]$ molecule (Fig. 1). Each Cd^{2+} ion lies on the inversion center of an octahedral environment and is coordinated by two N atoms from two Htzip, two N and two O atoms from four different SCN^- ions. Each Cd^{2+} center is linked to four adjacent Cd^{2+} centers by four SCN^- ions, resulting in a two-dimensional layer structure with $\text{Cd}\cdots\text{Cd}$ distance of 6.404 Å (Fig. 2). The adjacent two-dimensional layers are further linked through intermolecular hydrogen-bonding interaction between two not coordinated carboxylate group ($\text{O2}\cdots\text{H1}\cdots\text{O1} = 2.631$ Å) to afford a three-dimensional supramolecular structure (Fig. 3). In addition, weak intramolecular hydrogen bonds ($\text{C1}\cdots\text{H1}\cdots\text{N5} = 3.404$ Å) are present in the crystal structure.

Experimental

The Htzip (0.0284 g, 0.2 mmol) and NH_4SCN (0.0152 g, 0.2 mmol) were mixed in distilled water (5 ml) and ethanol (3 ml). Then, CdCl_2 (0.0367 g, 0.2 mmol) dissolved in distilled water (5 ml) was added slowly to the mixture. The mixture was allowed to slowly concentrate by evaporation at room temperature. Several days later, colorless block crystals suitable for X-ray diffraction were obtained with yield 63% on the basis of Htzip.

Refinement

Carboxyl H atom was located in a difference Fourier map and refined isotropically. Other H atoms were positioned geometrically and treated in a riding-model approximation, with $\text{C}\cdots\text{H} = 0.93$ Å (aromatic) and 0.97 Å (CH_2) and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE* (Bruker, 2007); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

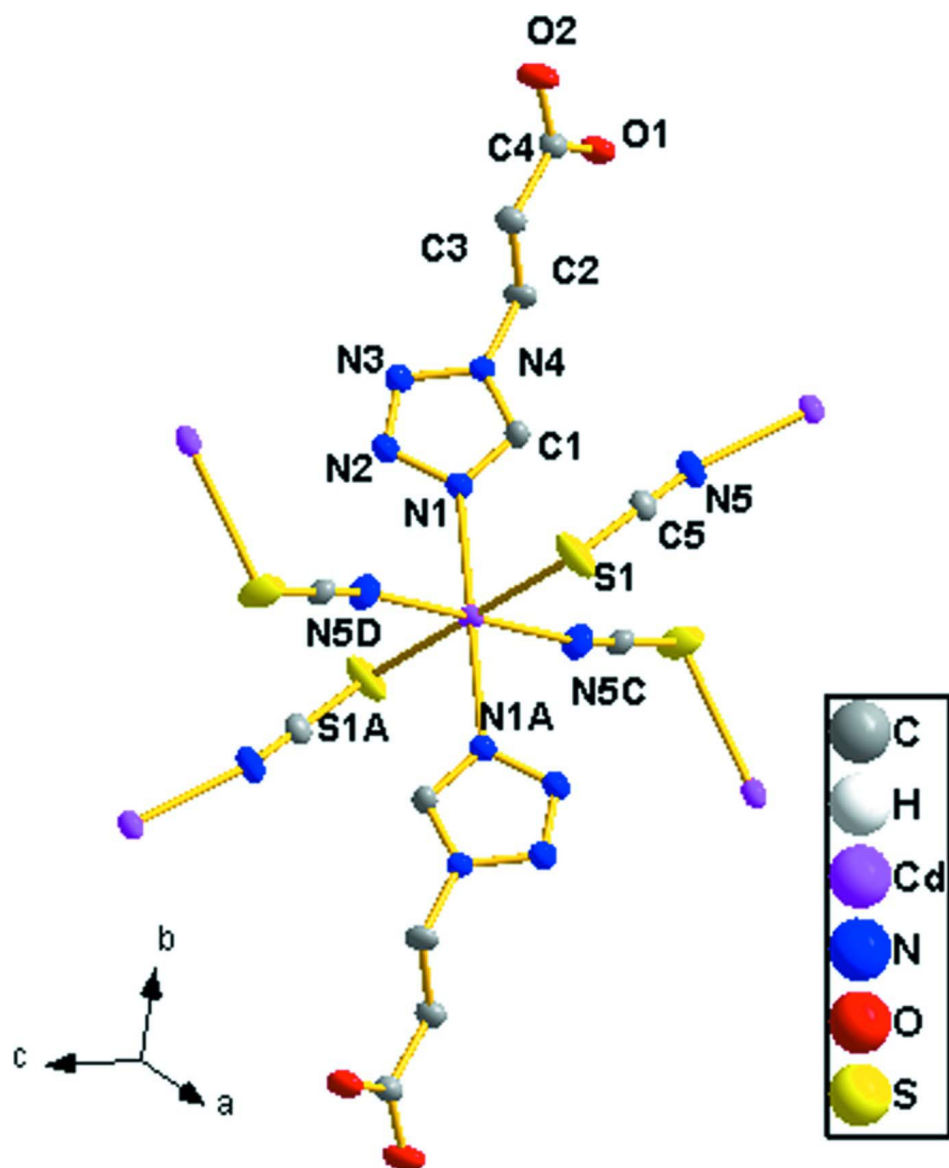


Figure 1

coordination environments of cadmium atoms in the title coordination polymer. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

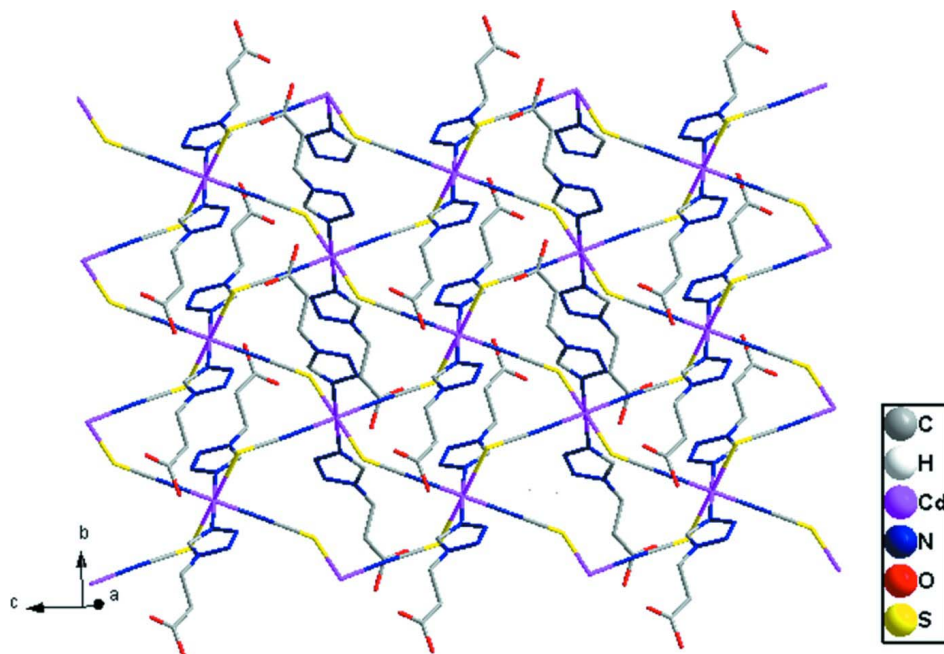


Figure 2

The two-dimensional layer structure of the title coordination polymer along the *bc* plane. H atoms have been omitted for clarity.

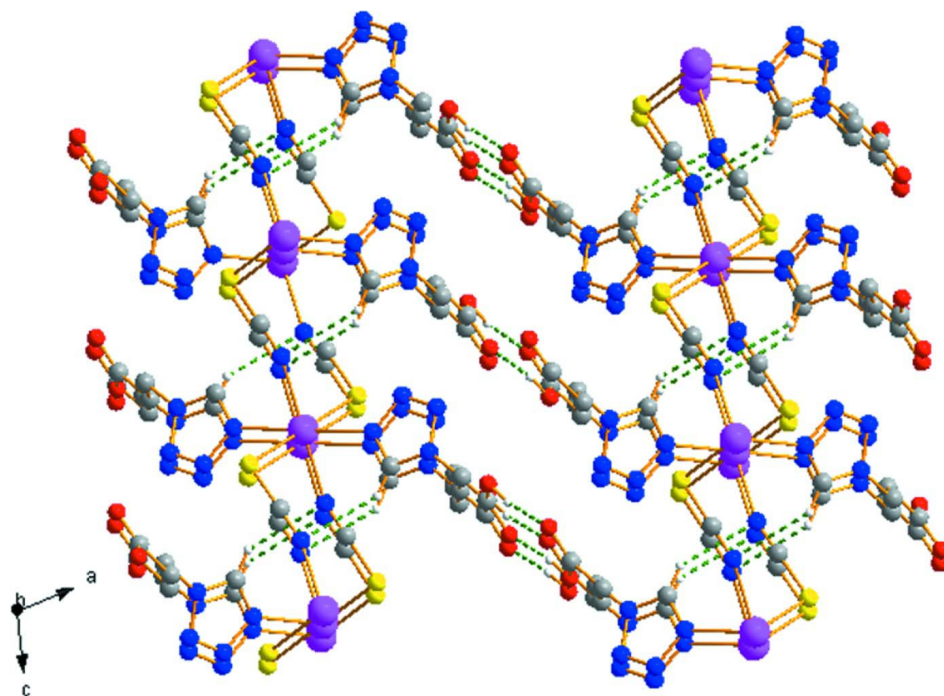


Figure 3

The three-dimensional supramolecular structure of the title coordination polymer. Hydrogen bonds are shown as dashed lines.

Poly[[bis[3-(1*H*-tetrazol-1-yl)propanoic acid- κ N⁴]cadmium]- di- μ -thiocyanato- κ^2 N:S; κ^2 S:N]

Crystal data

[Cd(NCS)₂(C₄H₆N₄O₂)₂]
M_r = 512.81
 Monoclinic, *P*2₁/*c*
 Hall symbol: -*P* 2ybc
a = 12.7402 (19) Å
b = 6.9555 (11) Å
c = 10.7549 (16) Å
 β = 106.809 (1)°
V = 912.3 (2) Å³
Z = 2

F(000) = 508
D_x = 1.863 Mg m⁻³
 Mo *K* α radiation, λ = 0.71073 Å
 Cell parameters from 4116 reflections
 θ = 3.3–28.3°
 μ = 1.47 mm⁻¹
T = 296 K
 Block, blue
 0.23 × 0.22 × 0.20 mm

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2001)
T_{min} = 0.729, *T_{max}* = 0.758

5775 measured reflections
 1695 independent reflections
 1505 reflections with *I* > 2 σ (*I*)
R_{int} = 0.021
 θ_{\max} = 25.5°, θ_{\min} = 3.3°
h = -15→15
k = -8→8
l = -13→13

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2 σ (*F*²)] = 0.021
wR(*F*²) = 0.052
S = 1.07
 1695 reflections
 128 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0245P)^2 + 0.480P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.59 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.51 \text{ e } \text{Å}^{-3}$

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 > σ (*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)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}</i> */ <i>U_{eq}</i>
C1	0.30765 (19)	0.2887 (4)	0.3041 (2)	0.0348 (5)
H1	0.3447	0.2929	0.2412	0.042*
C2	0.1466 (2)	0.4991 (3)	0.1939 (2)	0.0370 (6)
H2A	0.0708	0.4582	0.1737	0.044*

H2B	0.1698	0.4853	0.1160	0.044*
C3	0.1555 (2)	0.7069 (3)	0.2350 (2)	0.0342 (5)
H3A	0.1298	0.7213	0.3110	0.041*
H3B	0.2318	0.7463	0.2584	0.041*
C4	0.08935 (19)	0.8341 (3)	0.1283 (2)	0.0314 (5)
C5	0.42494 (19)	−0.3428 (4)	0.6880 (2)	0.0337 (5)
Cd1	0.5000	0.0000	0.5000	0.02720 (9)
N1	0.33986 (16)	0.1944 (3)	0.41393 (17)	0.0345 (5)
N2	0.26241 (18)	0.2267 (3)	0.4749 (2)	0.0426 (5)
N3	0.18639 (17)	0.3363 (3)	0.4049 (2)	0.0419 (5)
N4	0.21474 (15)	0.3766 (3)	0.29673 (17)	0.0289 (4)
N5	0.46640 (18)	−0.3889 (3)	0.79258 (19)	0.0447 (6)
O1	0.04537 (15)	0.7745 (3)	0.01892 (15)	0.0402 (4)
O2	0.08335 (18)	1.0111 (3)	0.16420 (19)	0.0493 (5)
S1	0.36445 (7)	−0.27644 (12)	0.53866 (6)	0.0594 (2)
H1O	0.042 (3)	1.083 (6)	0.093 (4)	0.080 (11)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0356 (13)	0.0419 (15)	0.0290 (11)	0.0104 (11)	0.0129 (10)	0.0079 (10)
C2	0.0396 (13)	0.0343 (14)	0.0302 (12)	0.0123 (11)	−0.0007 (10)	0.0047 (10)
C3	0.0360 (13)	0.0327 (14)	0.0299 (11)	0.0036 (11)	0.0032 (10)	0.0038 (10)
C4	0.0322 (12)	0.0298 (14)	0.0303 (11)	0.0015 (10)	0.0061 (10)	0.0033 (10)
C5	0.0348 (12)	0.0343 (14)	0.0324 (13)	−0.0070 (11)	0.0101 (10)	0.0043 (10)
Cd1	0.03311 (14)	0.02849 (15)	0.01786 (12)	0.00767 (10)	0.00396 (9)	0.00081 (9)
N1	0.0377 (11)	0.0369 (12)	0.0300 (9)	0.0113 (9)	0.0113 (8)	0.0079 (9)
N2	0.0506 (13)	0.0425 (13)	0.0407 (11)	0.0153 (11)	0.0227 (10)	0.0164 (10)
N3	0.0435 (12)	0.0452 (14)	0.0424 (12)	0.0132 (10)	0.0209 (10)	0.0129 (10)
N4	0.0304 (10)	0.0281 (11)	0.0271 (9)	0.0063 (8)	0.0064 (8)	0.0041 (8)
N5	0.0533 (13)	0.0522 (15)	0.0279 (11)	−0.0044 (11)	0.0105 (10)	0.0109 (10)
O1	0.0462 (10)	0.0340 (10)	0.0322 (8)	0.0089 (8)	−0.0018 (7)	0.0016 (7)
O2	0.0655 (13)	0.0303 (11)	0.0379 (10)	0.0106 (9)	−0.0076 (9)	−0.0006 (8)
S1	0.0620 (5)	0.0644 (5)	0.0352 (3)	−0.0248 (4)	−0.0121 (3)	0.0207 (3)

Geometric parameters (\AA , $^\circ$)

C1—N1	1.310 (3)	C5—S1	1.634 (2)
C1—N4	1.314 (3)	Cd1—N5 ⁱ	2.281 (2)
C1—H1	0.9300	Cd1—N5 ⁱⁱ	2.281 (2)
C2—N4	1.466 (3)	Cd1—N1 ⁱⁱⁱ	2.3989 (19)
C2—C3	1.506 (3)	Cd1—N1	2.3990 (19)
C2—H2A	0.9700	Cd1—S1 ⁱⁱⁱ	2.6958 (8)
C2—H2B	0.9700	Cd1—S1	2.6958 (8)
C3—C4	1.500 (3)	N1—N2	1.352 (3)
C3—H3A	0.9700	N2—N3	1.290 (3)
C3—H3B	0.9700	N3—N4	1.343 (3)
C4—O1	1.220 (3)	N5—Cd1 ^{iv}	2.281 (2)
C4—O2	1.299 (3)	O2—H1O	0.94 (4)
C5—N5	1.142 (3)		

N1—C1—N4	109.2 (2)	N5 ⁱⁱ —Cd1—N1	94.85 (7)
N1—C1—H1	125.4	N1 ⁱⁱⁱ —Cd1—N1	180.0
N4—C1—H1	125.4	N5 ⁱ —Cd1—S1 ⁱⁱⁱ	92.19 (6)
N4—C2—C3	111.01 (19)	N5 ⁱⁱ —Cd1—S1 ⁱⁱⁱ	87.81 (6)
N4—C2—H2A	109.4	N1 ⁱⁱⁱ —Cd1—S1 ⁱⁱⁱ	87.15 (5)
C3—C2—H2A	109.4	N1—Cd1—S1 ⁱⁱⁱ	92.85 (5)
N4—C2—H2B	109.4	N5 ⁱ —Cd1—S1	87.81 (6)
C3—C2—H2B	109.4	N5 ⁱⁱ —Cd1—S1	92.19 (6)
H2A—C2—H2B	108.0	N1 ⁱⁱⁱ —Cd1—S1	92.85 (5)
C4—C3—C2	111.32 (19)	N1—Cd1—S1	87.15 (5)
C4—C3—H3A	109.4	S1 ⁱⁱⁱ —Cd1—S1	180.0
C2—C3—H3A	109.4	C1—N1—N2	105.79 (19)
C4—C3—H3B	109.4	C1—N1—Cd1	129.80 (16)
C2—C3—H3B	109.4	N2—N1—Cd1	124.41 (14)
H3A—C3—H3B	108.0	N3—N2—N1	110.18 (18)
O1—C4—O2	123.9 (2)	N2—N3—N4	106.52 (18)
O1—C4—C3	122.5 (2)	C1—N4—N3	108.31 (18)
O2—C4—C3	113.6 (2)	C1—N4—C2	130.0 (2)
N5—C5—S1	179.4 (2)	N3—N4—C2	121.74 (19)
N5 ⁱ —Cd1—N5 ⁱⁱ	180.0	C5—N5—Cd1 ^{iv}	164.0 (2)
N5 ⁱ —Cd1—N1 ⁱⁱⁱ	94.85 (7)	C4—O2—H1O	109 (2)
N5 ⁱⁱ —Cd1—N1 ⁱⁱⁱ	85.15 (7)	C5—S1—Cd1	102.24 (9)
N5 ⁱ —Cd1—N1	85.15 (7)		
N4—C2—C3—C4	177.9 (2)	Cd1—N1—N2—N3	-179.93 (16)
C2—C3—C4—O1	-7.7 (3)	N1—N2—N3—N4	-0.2 (3)
C2—C3—C4—O2	171.9 (2)	N1—C1—N4—N3	-0.4 (3)
N4—C1—N1—N2	0.2 (3)	N1—C1—N4—C2	180.0 (2)
N4—C1—N1—Cd1	-179.88 (15)	N2—N3—N4—C1	0.3 (3)
N5 ⁱ —Cd1—N1—C1	-40.8 (2)	N2—N3—N4—C2	-180.0 (2)
N5 ⁱⁱ —Cd1—N1—C1	139.2 (2)	C3—C2—N4—C1	-106.9 (3)
N1 ⁱⁱⁱ —Cd1—N1—C1	-19 (32)	C3—C2—N4—N3	73.4 (3)
S1 ⁱⁱⁱ —Cd1—N1—C1	51.2 (2)	S1—C5—N5—Cd1 ^{iv}	23 (27)
S1—Cd1—N1—C1	-128.8 (2)	N5—C5—S1—Cd1	128 (26)
N5 ⁱ —Cd1—N1—N2	139.1 (2)	N5 ⁱ —Cd1—S1—C5	142.55 (11)
N5 ⁱⁱ —Cd1—N1—N2	-40.9 (2)	N5 ⁱⁱ —Cd1—S1—C5	-37.45 (11)
N1 ⁱⁱⁱ —Cd1—N1—N2	161 (32)	N1 ⁱⁱⁱ —Cd1—S1—C5	47.80 (11)
S1 ⁱⁱⁱ —Cd1—N1—N2	-128.94 (19)	N1—Cd1—S1—C5	-132.20 (11)
S1—Cd1—N1—N2	51.05 (19)	S1 ⁱⁱⁱ —Cd1—S1—C5	-57 (10)
C1—N1—N2—N3	0.0 (3)		

Symmetry codes: (i) $x, -y-1/2, z-1/2$; (ii) $-x+1, y+1/2, -z+3/2$; (iii) $-x+1, -y, -z+1$; (iv) $-x+1, y-1/2, -z+3/2$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H1O \cdots O1 ^v	0.94 (4)	1.70 (4)	2.631 (3)	170 (4)
C1—H1 \cdots N5 ⁱⁱⁱ	0.93	2.62	3.404 (3)	142

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