

Bis(1,10-phenanthroline- κ^2N,N')bis(thiocyanato- κN)cadmium

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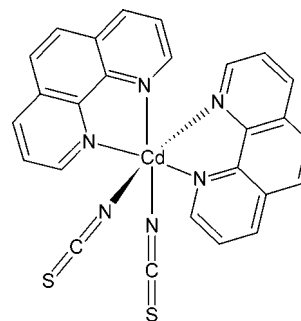
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.040; wR factor = 0.117; data-to-parameter ratio = 21.7.

The title compound, $[Cd(NCS)_2(C_{12}H_8N_2)_2]$, has been obtained from the decomposition reaction of dithiooxamide in a dimethylformamide solution containing 1,10-phenanthroline (phen) and $Cd(NO_3)_2 \cdot 4H_2O$. Its crystal structure is formed by monuclear Cd^{II} entities in which the metal atom is sited on a twofold rotation axis. The Cd^{II} atom is six-coordinated in the form of a distorted octahedron by two chelating phenanthroline molecules and two thiocyanate anions coordinated through their N atoms. In the crystal, $C-H \cdots N$ hydrogen bonds are established between the phenanthroline and thiocyanate ligands of neighbouring complexes.

Related literature

For the coordination versatility of the thiocyanate anion in transition metal complexes, see: Goher *et al.* (2000). For isotypic Mn(II), Fe(II), Co(II), Cu(II) and Zn(II) structures, see: Holleman *et al.* (1994); Gallois *et al.* (1990); Yin (2007); Parker *et al.* (1996); Liu *et al.* (2005). For another Cd^{II} -phen complex with a CdN_6 coordination environment, see: He *et al.* (2004). For $Cd-N$ bond lengths in related structures, see: Moon *et al.* (2000).



Experimental

Crystal data

$[Cd(NCS)_2(C_{12}H_8N_2)_2]$	$V = 2351.62$ (6) Å ³
$M_r = 588.97$	$Z = 4$
Orthorhombic, $Pbcn$	Mo $K\alpha$ radiation
$a = 13.5295$ (2) Å	$\mu = 1.14$ mm ⁻¹
$b = 9.91538$ (18) Å	$T = 100$ K
$c = 17.5297$ (2) Å	$0.32 \times 0.22 \times 0.21$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer	19593 measured reflections
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2003)	3444 independent reflections
$T_{min} = 0.757$, $T_{max} = 0.826$	2606 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	159 parameters
$wR(F^2) = 0.117$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{max} = 1.56$ e Å ⁻³
3444 reflections	$\Delta\rho_{min} = -0.83$ e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Cd—N3	2.262 (3)	Cd—N1	2.372 (3)
Cd—N2	2.369 (3)		
N3—Cd—N3 ⁱ	95.97 (15)	N2—Cd—N1 ⁱ	90.48 (8)
N3—Cd—N2 ⁱ	108.26 (9)	N3—Cd—N1	160.29 (9)
N3—Cd—N2	89.42 (10)	N2—Cd—N1	70.87 (8)
N2 ⁱ —Cd—N2	153.81 (12)	N1 ⁱ —Cd—N1	90.34 (13)
N3—Cd—N1 ⁱ	90.14 (10)		

Symmetry code: (i) $-x, y, -z + \frac{3}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C8-H8 \cdots N3^{ii}$	0.93	2.54	3.373 (4)	149

Symmetry code: (ii) $x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Financial support from the Ministerio de Ciencia e Innovación (Project MAT2008–05690/MAT) and the Gobierno Vasco (IT477–10) is gratefully acknowledged. We are also thankful for the technical and human support provided by SGIker (UPV/EHU, MICINN, GV/EJ, ESF).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZJ2006).

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supporting information

Acta Cryst. (2011). E67, m704–m705 [doi:10.1107/S160053681101289X]

Bis(1,10-phenanthroline- κ^2 N,N')bis(thiocyanato- κ N)cadmium**Daniel Vallejo, Garikoitz Beobide, Oscar Castillo and Antonio Luque****S1. Comment**

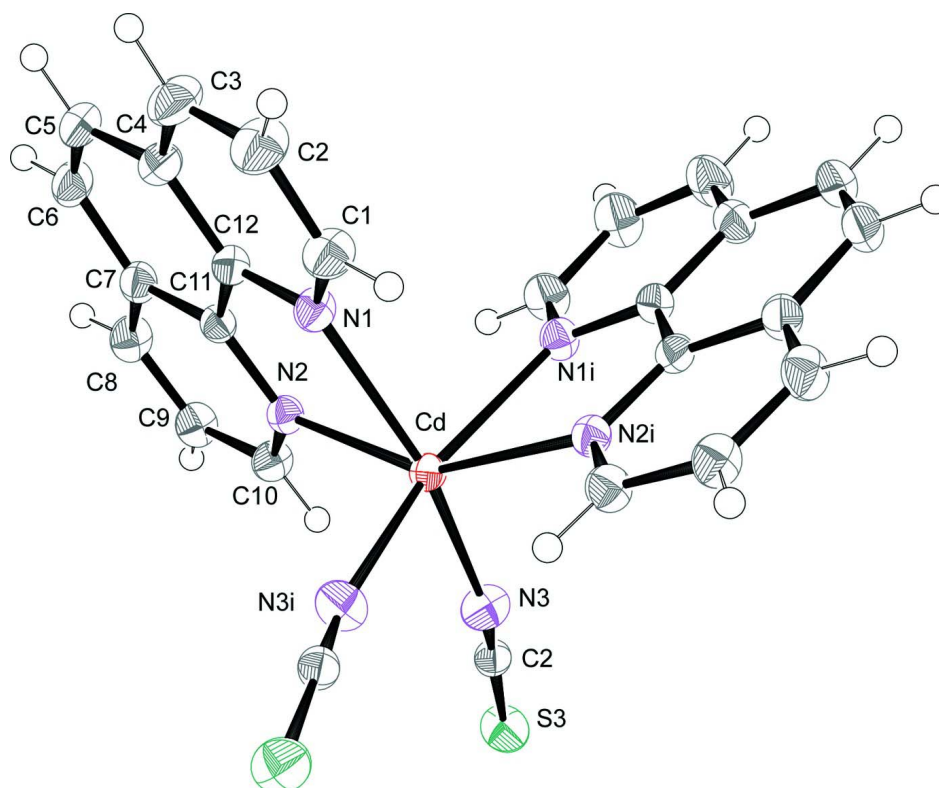
Transition metal complexes based on thiocyanate anion have been widely studied due the coordination versatility of this ligand (Goher *et al.*, 2000). Regarding to the title compound, it deserves to note that isostructural compounds of Mn(II), Fe(II), Co(II), Cu(II) and Zn(II) have been previously reported (Holleman *et al.*, 1994; Gallois *et al.*, 1990; Yin, 2007; Parker *et al.*, 1996; Liu *et al.*, 2005). However, to the best of our knowledge, the crystal structure described herein represents the first example of the Cd^{II} analogue (*I*). The cadmium(II) cation is placed on a twofold rotation axis showing a distorted octahedral coordination geometry. The coordination environment is completed by four N atoms of two chelating phen ligands in *cis* arrangement and by two N atoms of two thiocyanate anions (Fig. 1). The two phen ligands are almost perpendicular to each other, with a dihedral angle of 84.8 (1)°. The Cd—N distances corresponding to chelating phen ligands (*ca* 2.37 Å) are comparable to values found in other Cd^{II}-phen complex with CdN₆ coordination environment (He *et al.*, 2004). While the bond Cd—N distance (2.262 (3) Å) corresponding to thiocyanate N atoms is slightly shorter and similar to those found in related compounds (Moon *et al.*, 2000). In the crystal structure, neighbouring complexes interact by means of C—H \cdots N hydrogen bondings (Table 2). Figure 2 shows a view of the crystal packing with the hydrogen bonding interaction scheme.

S2. Experimental

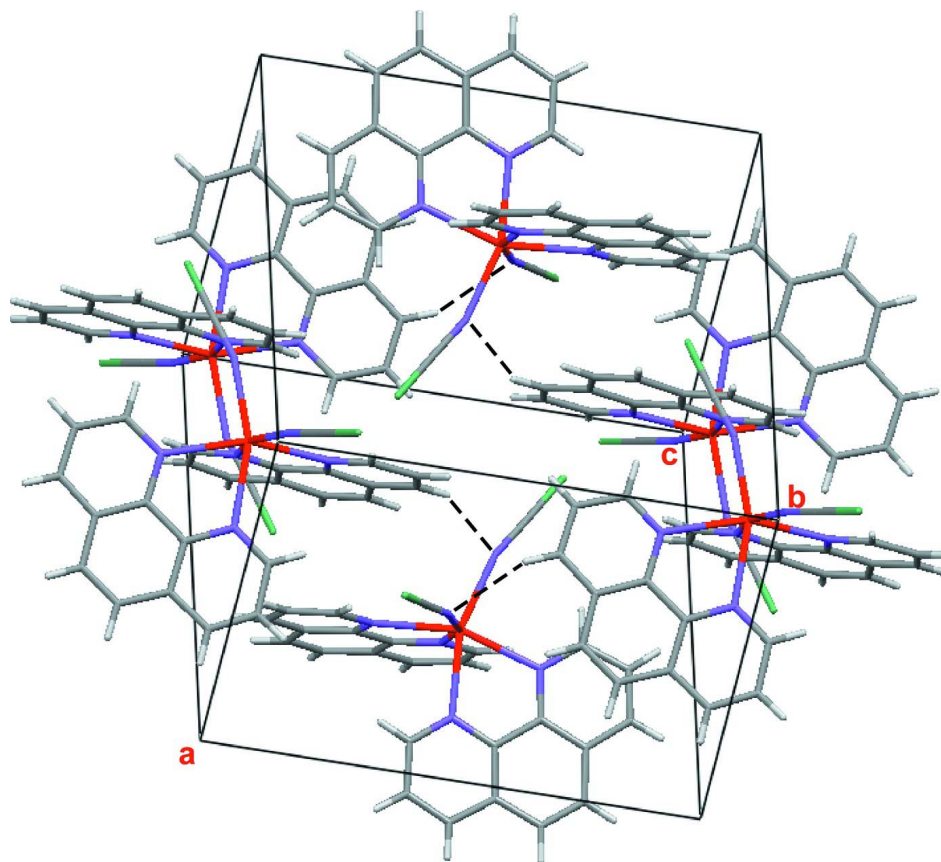
Cd(NO₃)₂·4H₂O (43.3 mg, 0.140 mmol), phen (66.4 mg, 0.368 mmol) and dithiooxamide (18.4 mg, 0.153 mmol) were mixed in 30 ml of dimethylformamide. The reaction mixture was stirred for 30 min and subsequently it was allowed to stand in air. Rhombohedral yellow crystals were obtained three weeks later. They were filtered out, washed with ethanol and dried at room temperature (yield 40%). Elemental analysis calculated for C₂₆H₁₆CdN₆S₂: C 53.02, H 2.74, Cd 19.08, N 14.27, S 10.89%; found: C 53.96, H 3.01, Cd 18.75, N 13.87, S 10.63%.

S3. Refinement

H atoms were included at geometrically calculated positions and refined as riding atoms [C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

**Figure 1**

The molecular structure of (I) showing atom labels and 50% probability displacement ellipsoids for non-H atoms. Atoms with suffix *i* are generated by the symmetry operator $(-x, y, 3/2 - z)$.

**Figure 2**

View of the crystal packing of (I) showing the hydrogen bonding scheme.

Bis(1,10-phenanthroline- κ^2N,N')bis(thiocyanato- κN)cadmium

Crystal data

$[\text{Cd}(\text{NCS})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]$

$M_r = 588.97$

Orthorhombic, *Pbcn*

Hall symbol: -P 2n 2ab

$a = 13.5295 (2) \text{ \AA}$

$b = 9.91538 (18) \text{ \AA}$

$c = 17.5297 (2) \text{ \AA}$

$V = 2351.62 (6) \text{ \AA}^3$

$Z = 4$

$F(000) = 1176$

$D_x = 1.664 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 19593 reflections

$\theta = 3.0\text{--}30.1^\circ$

$\mu = 1.14 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Rhombohedral, yellow

$0.32 \times 0.22 \times 0.21 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: analytical

(*CrysAlis RED*; Oxford Diffraction, 2003)

$T_{\min} = 0.757$, $T_{\max} = 0.826$

19593 measured reflections

3444 independent reflections

2606 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 30.1^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -18 \rightarrow 19$

$k = -13 \rightarrow 10$

$l = -24 \rightarrow 23$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.117$
 $S = 1.11$
 3444 reflections
 159 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-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 3.0087P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.56 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.83 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. CrysAlis RED, Oxford Diffraction Ltd., Version 1.170.32 (release 06.06.2003 CrysAlis170 VC++) (compiled Jun 6 2003,13:53:32). Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid.

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd	0.0000	0.31999 (3)	0.7500	0.01949 (10)
S1	-0.16408 (7)	0.01037 (9)	0.56558 (5)	0.0346 (2)
N1	-0.00666 (17)	0.4887 (3)	0.84583 (15)	0.0237 (5)
N2	-0.16737 (19)	0.3741 (3)	0.77514 (14)	0.0213 (5)
N3	-0.0504 (2)	0.1673 (3)	0.66235 (16)	0.0308 (6)
C13	-0.0980 (2)	0.1038 (3)	0.62292 (16)	0.0224 (5)
C12	-0.0987 (2)	0.5344 (3)	0.86435 (16)	0.0226 (6)
C9	-0.3426 (2)	0.3557 (4)	0.75684 (17)	0.0283 (6)
H9	-0.3950	0.3137	0.7321	0.034*
C11	-0.1831 (2)	0.4731 (3)	0.82731 (15)	0.0215 (5)
C7	-0.2791 (2)	0.5182 (3)	0.84580 (16)	0.0254 (6)
C8	-0.3593 (2)	0.4548 (4)	0.80914 (18)	0.0303 (7)
H8	-0.4236	0.4806	0.8206	0.036*
C1	0.0703 (3)	0.5433 (3)	0.88069 (19)	0.0313 (7)
H1	0.1330	0.5104	0.8695	0.038*
C4	-0.1141 (2)	0.6393 (3)	0.91695 (18)	0.0283 (6)
C10	-0.2452 (3)	0.3186 (3)	0.74108 (16)	0.0256 (6)
H10	-0.2342	0.2517	0.7049	0.031*
C3	-0.0296 (3)	0.6967 (4)	0.9512 (2)	0.0370 (8)
H3	-0.0362	0.7674	0.9857	0.044*
C2	0.0618 (3)	0.6478 (4)	0.9335 (2)	0.0381 (8)
H2	0.1179	0.6839	0.9564	0.046*

C6	-0.2909 (2)	0.6262 (4)	0.89896 (18)	0.0313 (7)
H6	-0.3541	0.6573	0.9103	0.038*
C5	-0.2122 (3)	0.6839 (3)	0.93295 (19)	0.0315 (7)
H5	-0.2220	0.7540	0.9674	0.038*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd	0.01802 (15)	0.01969 (16)	0.02076 (15)	0.000	0.00092 (10)	0.000
S1	0.0382 (4)	0.0350 (4)	0.0306 (4)	-0.0064 (4)	-0.0062 (3)	-0.0011 (3)
N1	0.0205 (11)	0.0264 (12)	0.0242 (11)	-0.0014 (10)	0.0004 (9)	-0.0025 (10)
N2	0.0199 (11)	0.0222 (12)	0.0219 (10)	-0.0003 (10)	0.0006 (9)	0.0008 (9)
N3	0.0250 (14)	0.0317 (15)	0.0356 (14)	0.0000 (11)	-0.0032 (11)	-0.0054 (12)
C13	0.0219 (13)	0.0227 (14)	0.0226 (12)	0.0036 (11)	0.0020 (11)	0.0025 (11)
C12	0.0250 (14)	0.0226 (14)	0.0202 (12)	0.0007 (11)	0.0031 (11)	0.0001 (10)
C9	0.0201 (14)	0.0333 (16)	0.0316 (15)	0.0009 (12)	-0.0022 (12)	0.0022 (12)
C11	0.0219 (13)	0.0212 (13)	0.0215 (12)	0.0014 (11)	0.0027 (10)	0.0031 (10)
C7	0.0255 (14)	0.0263 (15)	0.0245 (13)	0.0032 (12)	0.0043 (11)	0.0030 (11)
C8	0.0213 (14)	0.0360 (17)	0.0338 (15)	0.0067 (13)	0.0012 (12)	0.0033 (13)
C1	0.0267 (15)	0.0338 (17)	0.0333 (15)	-0.0048 (13)	-0.0019 (13)	-0.0078 (14)
C4	0.0304 (16)	0.0263 (15)	0.0282 (14)	0.0002 (13)	0.0034 (12)	-0.0042 (12)
C10	0.0217 (14)	0.0267 (15)	0.0284 (14)	0.0004 (11)	-0.0005 (11)	-0.0015 (11)
C3	0.0374 (18)	0.0364 (19)	0.0371 (18)	-0.0039 (15)	0.0022 (15)	-0.0161 (15)
C2	0.0328 (18)	0.042 (2)	0.0391 (18)	-0.0073 (16)	-0.0018 (15)	-0.0142 (16)
C6	0.0302 (16)	0.0330 (17)	0.0308 (16)	0.0081 (14)	0.0085 (13)	0.0008 (13)
C5	0.0373 (18)	0.0292 (17)	0.0279 (15)	0.0038 (14)	0.0072 (13)	-0.0045 (13)

Geometric parameters (Å, °)

Cd—N3	2.262 (3)	C9—H9	0.9300
Cd—N3 ⁱ	2.262 (3)	C11—C7	1.411 (4)
Cd—N2 ⁱ	2.369 (3)	C7—C8	1.409 (5)
Cd—N2	2.369 (3)	C7—C6	1.429 (5)
Cd—N1 ⁱ	2.372 (3)	C8—H8	0.9300
Cd—N1	2.372 (3)	C1—C2	1.394 (5)
S1—C13	1.634 (3)	C1—H1	0.9300
N1—C1	1.323 (4)	C4—C3	1.410 (5)
N1—C12	1.365 (4)	C4—C5	1.428 (5)
N2—C10	1.329 (4)	C10—H10	0.9300
N2—C11	1.358 (4)	C3—C2	1.364 (5)
N3—C13	1.135 (4)	C3—H3	0.9300
C12—C4	1.405 (4)	C2—H2	0.9300
C12—C11	1.448 (4)	C6—C5	1.347 (5)
C9—C8	1.362 (5)	C6—H6	0.9300
C9—C10	1.396 (5)	C5—H5	0.9300
N3—Cd—N3 ⁱ	95.97 (15)	N2—C11—C12	118.8 (3)
N3—Cd—N2 ⁱ	108.26 (9)	C7—C11—C12	119.3 (3)

N3 ⁱ —Cd—N2 ⁱ	89.42 (10)	C8—C7—C11	117.5 (3)
N3—Cd—N2	89.42 (10)	C8—C7—C6	123.1 (3)
N3 ⁱ —Cd—N2	108.26 (9)	C11—C7—C6	119.4 (3)
N2 ⁱ —Cd—N2	153.81 (12)	C9—C8—C7	120.1 (3)
N3—Cd—N1 ⁱ	90.14 (10)	C9—C8—H8	120.0
N3 ⁱ —Cd—N1 ⁱ	160.29 (9)	C7—C8—H8	120.0
N2 ⁱ —Cd—N1 ⁱ	70.87 (8)	N1—C1—C2	123.1 (3)
N2—Cd—N1 ⁱ	90.48 (8)	N1—C1—H1	118.4
N3—Cd—N1	160.29 (9)	C2—C1—H1	118.4
N3 ⁱ —Cd—N1	90.14 (10)	C12—C4—C3	117.3 (3)
N2 ⁱ —Cd—N1	90.48 (8)	C12—C4—C5	119.7 (3)
N2—Cd—N1	70.87 (8)	C3—C4—C5	123.0 (3)
N1 ⁱ —Cd—N1	90.34 (13)	N2—C10—C9	123.3 (3)
C1—N1—C12	118.2 (3)	N2—C10—H10	118.3
C1—N1—Cd	125.9 (2)	C9—C10—H10	118.3
C12—N1—Cd	115.94 (18)	C2—C3—C4	119.6 (3)
C10—N2—C11	118.5 (3)	C2—C3—H3	120.2
C10—N2—Cd	125.4 (2)	C4—C3—H3	120.2
C11—N2—Cd	116.04 (19)	C3—C2—C1	119.3 (3)
C13—N3—Cd	162.9 (3)	C3—C2—H2	120.4
N3—C13—S1	178.6 (3)	C1—C2—H2	120.4
N1—C12—C4	122.5 (3)	C5—C6—C7	121.2 (3)
N1—C12—C11	118.3 (2)	C5—C6—H6	119.4
C4—C12—C11	119.2 (3)	C7—C6—H6	119.4
C8—C9—C10	118.7 (3)	C6—C5—C4	121.1 (3)
C8—C9—H9	120.7	C6—C5—H5	119.5
C10—C9—H9	120.7	C4—C5—H5	119.5
N2—C11—C7	121.9 (3)		

Symmetry code: (i) $-x, y, -z+3/2$.

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

<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>
C8—H8 \cdots N3 ⁱⁱ	0.93	2.54	3.373 (4)	149

Symmetry code: (ii) $x-1/2, y+1/2, -z+3/2$.