

# Crystal structure of polymeric bis(3-amino-1*H*-pyrazole)cadmium dibromide

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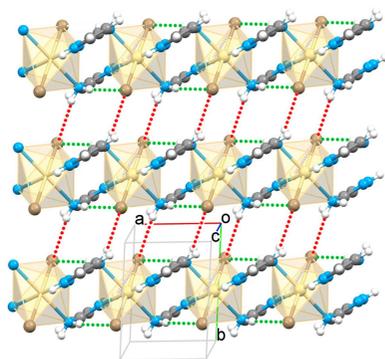
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The reaction of cadmium bromide tetrahydrate with 3-aminopyrazole (3-apz) in ethanolic solution leads to tautomerization of the ligand and the formation of crystals of the title compound, *catena*-poly[[dibromidocadmium(II)]-bis( $\mu$ -3-amino-1*H*-pyrazole)- $\kappa^2 N^3:N^2$ ;  $\kappa^2 N^2:N^3$ ], [CdBr<sub>2</sub>(C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>)<sub>2</sub>]<sub>n</sub> or [CdBr<sub>2</sub>(3-apz)<sub>2</sub>]<sub>n</sub>. Its asymmetric unit consists of a half of a Cd<sup>2+</sup> cation, a bromide anion and a 3-apz molecule. The Cd<sup>2+</sup> cations are coordinated by two bromide anions and two 3-apz ligands, generating *trans*-CdN<sub>4</sub>Br<sub>2</sub> octahedra, which are linked into chains by pairs of the bridging ligands. In the crystal, the ligand molecules and bromide anions of neighboring chains are linked through interchain hydrogen bonds into a two-dimensional network. The intermolecular contacts were quantified using Hirshfeld surface analysis and two-dimensional fingerprint plots, revealing the relative quantitative contributions of the weak intermolecular contacts.

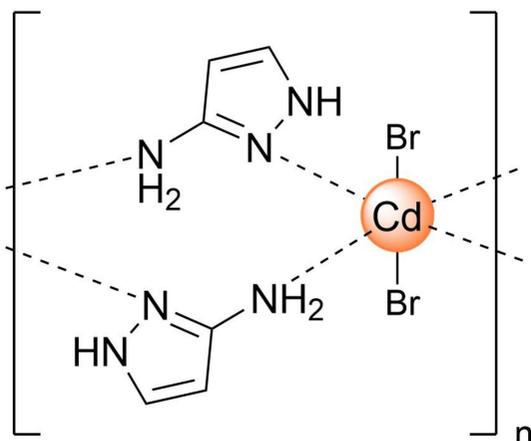
## 1. Chemical context

Inorganic–organic coordination polymers, an active field of investigation in chemistry, attract attention for their intriguing structures and applications. Inorganic components may introduce magnetic, optical, and mechanical attributes, while organic ligands offer versatility and luminescence. Combining these attributes yields novel materials with diverse properties such as catalysis, separation, luminescence, spin transition and more (Seredyuk *et al.*, 2015; Piñeiro-López *et al.*, 2021). The formation of a coordination polymer involves the self-assembly of organic ligands and metal ions, driven by strong and directional interactions such as metal–ligand coordination bonds, as well as weaker hydrogen bonds,  $\pi$ – $\pi$  stacking, halogen–halogen, and C–H...*X* interactions (*X* = O, N, halogen, *etc.*). Engineering polymeric networks is a challenge that demands further exploration of metal–organic interactions.

The pyrazole is known to be a good linker to bind metal ions and play a key role in the design of new functional coordination polymers. It can serve as a monodentate ligand or upon deprotonation as a bridging ligand, effectively linking metal ions into polynuclear or polymeric moieties (Parshad *et al.*, 2024). We have discovered that 3-aminopyrazole (3-apz) can form coordination polymers without the need to deprotonate the pyrazole moiety, due to the participation of the amino group in the coordination of the metal ion. Having an interest in polymeric complexes formed by bridging ligands

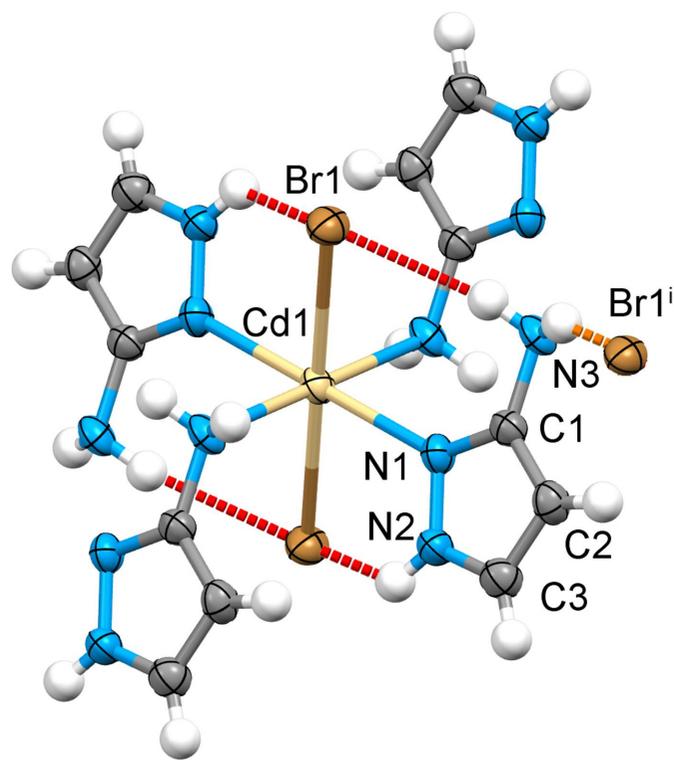


(Piñeiro-López *et al.*, 2018, 2021; Seredyuk *et al.*, 2007), we report here on the coordination polymer of the apz ligand with a Cd<sup>2+</sup> cation and Br<sup>−</sup> anions as co-ligands.



## 2. Structural commentary

The asymmetric unit comprises half of the monomeric neutral unit [Cd(3-apz)<sub>2</sub>Br<sub>2</sub>], which is composed of a Cd<sup>2+</sup> cation, two 3-apz bridging ligands and two Br<sup>−</sup> anions, balancing the charge (Fig. 1). The tautomerism of the ligand molecule, which can interconvert between 3- and 5-aminopyrazole in solution, is blocked, and only the first form is observed in the structure.

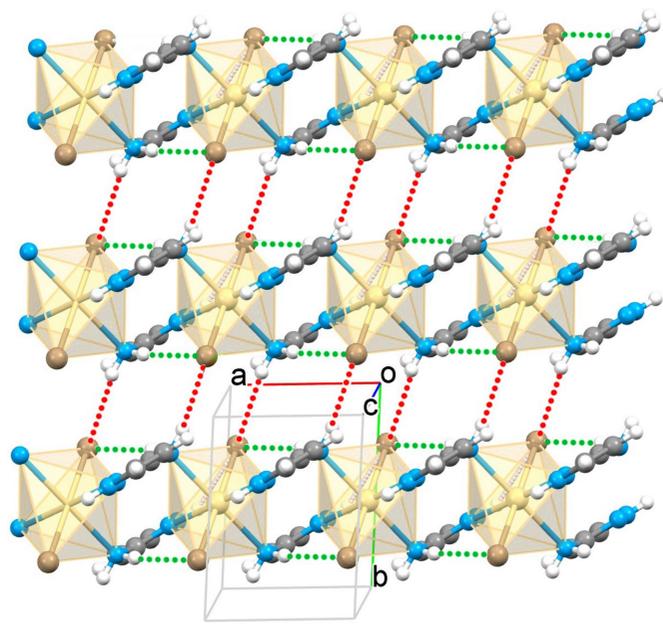


**Figure 1**  
Crystal structure of the title compound with labelling and displacement ellipsoids drawn at the 50% probability level. The strong intra- and interchain N—H⋯Br hydrogen bonds are shown as dashed red and orange lines, respectively. Symmetry code: (i) 1 − x, −y, 1 − z.

The coordination geometry around the central ion can be described as an elongated octahedron with the Br atoms being in axial positions [Cd—Br1 = 2.7379 (11) Å] and the amino nitrogen atom of the 3-apz ligand [Cd—N1 = 2.358 (9) Å, Cd—N3 = 2.446 (9) Å] in the equatorial plane. The average trigonal distortion parameters  $\Sigma = \Sigma_1^{12}(|90 - \varphi_i|)$ , where  $\varphi_i$  is the angle N/Br—Cd—N'/Br' (Drew *et al.*, 1995), and  $\Theta = \Sigma_1^{24}(|60 - \theta_i|)$ , where  $\theta_i$  is the angle generated by superposition of two opposite faces of an octahedron (Chang *et al.*, 1990) are 34.6 and 112.4°, respectively. The values reveal a deviation of the coordination environment from an ideal octahedron (where  $\Sigma = \Theta = 0$ ). The calculated continuous shape measure (CShM) value relative to the ideal *O<sub>h</sub>* symmetry is 0.578 (Kershaw Cook *et al.*, 2015). The volume of the [CdN<sub>4</sub>Br<sub>2</sub>] coordination polyhedron is equal to 20.952 Å<sup>3</sup>. The 3-apz ligand is close to planarity with a maximum deviation of 0.19 (1) Å from the plane of the pyrazole ring for the amino N3 atom.

## 3. Supramolecular features

The [Cd(3-apz)<sub>2</sub>Br<sub>2</sub>] units are linked by alternating amino/pyrazole nitrogen atoms of the 3-apz ligand to give an infinite one-dimensional linear chain propagating along the *a*-axis direction (Figs. 1 and 2). The Cd⋯Cd distance separated by 5-aminopyrazole within the chain is 5.051 (1) Å. The N2 atom and one hydrogen of the NH<sub>2</sub> groups of pyrazole are involved in interactions within the coordination chain, forming intrachain hydrogen bonds with the Br atom (Table 1). The second hydrogen atom of the NH<sub>2</sub> group forms a hydrogen bond with the Br atom of a neighboring chain. This interaction expands



**Figure 2**  
Fragment of the two-dimensional supramolecular network formed by polymeric chains of {[CdBr<sub>2</sub>(3-apz)<sub>2</sub>]}<sub>n</sub> with intrachain hydrogen bonds (green dashed lines) linked by interchain hydrogen bonds (red dashed lines).

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

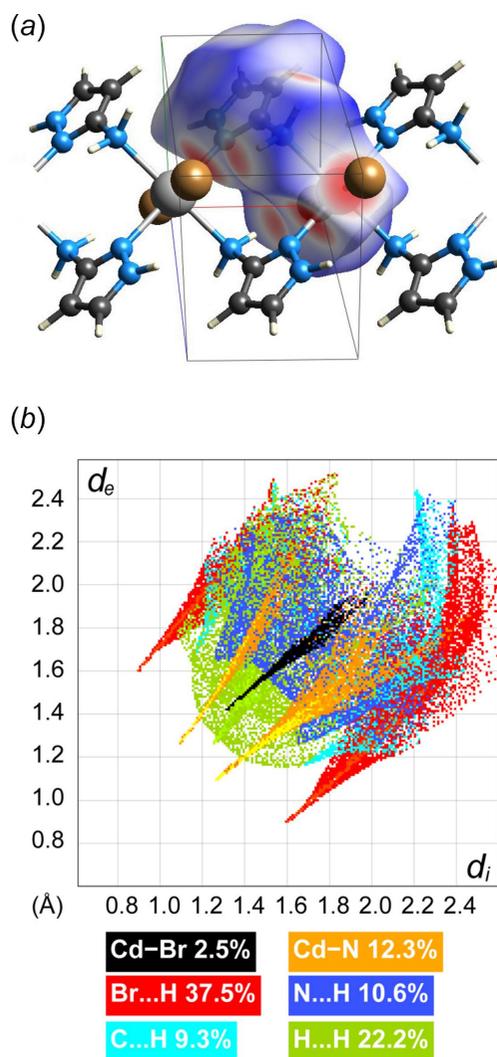
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2–H2 $\cdots$ Br1 <sup>i</sup>	0.86	2.80	3.377 (9)	126
N3–H3A $\cdots$ Br1 <sup>ii</sup>	0.89	2.61	3.484 (9)	169
N3–H3B $\cdots$ Br1 <sup>iii</sup>	0.89	2.79	3.640 (9)	160

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

the chains to a two-dimensional supramolecular network (Fig. 2). The planes stack along the  $c$  axis with no interactions below the van der Waals radii.

#### 4. Hirshfeld surface and two-dimensional fingerprint plots

Hirshfeld surface analysis was performed and the associated two-dimensional fingerprint plots were generated using



**Figure 3**

(a) A projection of  $d_{\text{norm}}$  mapped on the Hirshfeld surface onto a fragment of the polymeric chain in the asymmetric unit, visualizing intra- and intermolecular interactions. Red/blue and white areas represent regions where contacts are shorter/longer than the sum and close to the sum of the van der Waals radii, respectively; (b) decomposition of the two-dimensional fingerprint plot into specific interactions.

*CrystalExplorer* (Spackman *et al.*, 2021), with a standard resolution of the three-dimensional  $d_{\text{norm}}$  surfaces plotted over a fixed colour scale of  $-0.4941$  (red) to  $1.0389$  (blue) a.u. (Fig. 3a). Since the title compound is a coordination polymer, this analysis also includes the bonding information at the edge of the asymmetric unit. The overall two-dimensional fingerprint plot is depicted in Fig. 3b decomposed into specific interactions. The central spike with the tip at  $(d_i, d_e) = (1.30, 1.41)$  directly represents the Cd–Br bond length with the relative contribution of 2.5%, while two other closely lying spikes with tips at  $(d_i, d_e) = (1.10, 1.30)/(1.30/1.10)$  correspond to the shorter Cd–N bond length with the contribution of 12.3%. The rest of the contacts belong to weak hydrogen bonds. At 37.5%, the largest contribution to the overall crystal packing is from Br $\cdots$ H/H $\cdots$ Br interactions, which form characteristic wings of the plot with tips at  $(d_i, d_e) = (0.90, 1.60)/(1.60/0.90)$ . Other interactions, H $\cdots$ H (22.2%), H $\cdots$ C/C $\cdots$ H (9.3%) and H $\cdots$ N/N $\cdots$ H (10.6%), are mainly distributed in the middle part of the plot.

#### 5. Database survey

A search of the Cambridge Structural Database (CSD version 5.43, update of November 2022; Groom *et al.*, 2016) reveals one hit with the 3-apz bridging ligand in a binuclear Cu<sup>2+</sup> complex TIXDAH with oxalyl anions as coligands (Świtlicka-Olszewska *et al.*, 2014). In the complex, the same coordination mode of the ligand is observed, but with a shorter intermetallic separation (4.583 Å) than in the title compound, which is due to the different chemical nature and square-pyramidal coordination geometry of the central ion.

#### 6. Synthesis and crystallization

CdBr<sub>2</sub>·4H<sub>2</sub>O and 3-apz were purchased from Sigma Aldrich and were used without further purification. Colourless crystals were obtained by the reaction of 1 mmol of CdBr<sub>2</sub>·4H<sub>2</sub>O (344 mg) and 2 mmol of 3-apz (166 mg) in 10 ml of ethanol (96%). The reaction mixture was left overnight in an open vial, leading to the formation of crystals suitable for single-crystal X-ray analysis. Elemental analysis calculated for C<sub>6</sub>H<sub>10</sub>Br<sub>2</sub>CdN<sub>6</sub>: C, 16.44; H, 2.30; N, 19.17. Found: C, 16.56; H, 2.18; N, 19.33. IR (KBr; cm<sup>-1</sup>): 3321(s)  $\nu$ (NH); 1592(m), 1554(m) and 1528(s)  $\nu$ (C=N/C<sub>3</sub>-apz).

#### 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were refined as riding [C–H = 0.83–0.92 Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C/N})$ ].

#### Acknowledgements

Author contributions are as follows: Conceptualization, VAP and IOF; methodology, OSV; formal analysis, SOM; synthesis, ISK, OSV; single-crystal measurements, SS; writing (original draft), MS; writing (review and editing of the manuscript),

SOM, MS; visualization and calculations, MS; funding acquisition, MS, IOF.

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**Table 2**

Experimental details.

Crystal data	
Chemical formula	[CdBr <sub>2</sub> (C <sub>3</sub> H <sub>5</sub> N <sub>3</sub> ) <sub>2</sub> ]
<i>M<sub>r</sub></i>	438.42
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.0515 (2), 6.7912 (3), 8.7083 (6)
$\alpha$ , $\beta$ , $\gamma$ (°)	83.585 (4), 79.907 (4), 86.833 (3)
<i>V</i> (Å <sup>3</sup> )	292.09 (3)
<i>Z</i>	1
Radiation type	Cu <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	22.83
Crystal size (mm)	0.15 × 0.02 × 0.02
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2020)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.212, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	5241, 1122, 1114
<i>R<sub>int</sub></i>	0.036
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.631
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.045, 0.134, 1.27
No. of reflections	1122
No. of parameters	71
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.94, -0.84

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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## supporting information

*Acta Cryst.* (2023). E79, 1151-1154 [https://doi.org/10.1107/S2056989023009751]

Crystal structure of polymeric bis(3-amino-1*H*-pyrazole)cadmium dibromide

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Sergiu Shova, Igor O. Fritsky and Maksym Seredyuk

## Computing details

catena-Poly[[dibromidocadmium(II)]-bis( $\mu$ -3-amino-1*H*-pyrazole)- $\kappa^2 N^3:N^2;\kappa^2 N^2:N^3$ ]

## Crystal data

[CdBr<sub>2</sub>(C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>)<sub>2</sub>]

$M_r = 438.42$

Triclinic,  $P\bar{1}$

$a = 5.0515$  (2) Å

$b = 6.7912$  (3) Å

$c = 8.7083$  (6) Å

$\alpha = 83.585$  (4)°

$\beta = 79.907$  (4)°

$\gamma = 86.833$  (3)°

$V = 292.09$  (3) Å<sup>3</sup>

$Z = 1$

$F(000) = 206$

$D_x = 2.492$  Mg m<sup>-3</sup>

Cu  $K\alpha$  radiation,  $\lambda = 1.54184$  Å

Cell parameters from 4554 reflections

$\theta = 5.2$ – $76.6$ °

$\mu = 22.83$  mm<sup>-1</sup>

$T = 293$  K

Needle, clear light colourless

$0.15 \times 0.02 \times 0.02$  mm

## Data collection

XtaLAB Synergy, Dualflex, HyPix  
diffractometer

Radiation source: micro-focus sealed X-ray  
tube, PhotonJet (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
(CrysAlisPro; Rigaku OD, 2020)

$T_{\min} = 0.212$ ,  $T_{\max} = 1.000$

5241 measured reflections

1122 independent reflections

1114 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 76.8$ °,  $\theta_{\min} = 5.2$ °

$h = -6 \rightarrow 6$

$k = -8 \rightarrow 8$

$l = -10 \rightarrow 10$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.134$

$S = 1.27$

1122 reflections

71 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 5.2025P]$

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

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.94$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.84$  e Å<sup>-3</sup>

Extinction correction: *SHELXL2018/3*

(Sheldrick, 2015b),

$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0028 (7)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	1.000000	0.500000	0.500000	0.0316 (4)
Br1	0.9072 (2)	0.25426 (18)	0.28787 (13)	0.0413 (4)
N2	0.3030 (18)	0.6427 (14)	0.1530 (10)	0.037 (2)
H2	0.171982	0.587161	0.125640	0.044*
N1	0.3397 (17)	0.6397 (13)	0.3036 (10)	0.0336 (19)
N3	0.6733 (17)	0.7584 (13)	0.4288 (11)	0.0341 (19)
H3A	0.539337	0.762302	0.509882	0.041*
H3B	0.752934	0.874184	0.416228	0.041*
C3	0.491 (2)	0.7406 (17)	0.0522 (14)	0.040 (2)
H3	0.503093	0.760630	−0.056213	0.048*
C2	0.664 (2)	0.8068 (16)	0.1397 (13)	0.036 (2)
H2A	0.818189	0.878515	0.103040	0.043*
C1	0.559 (2)	0.7436 (15)	0.2937 (12)	0.032 (2)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cd1	0.0268 (6)	0.0368 (6)	0.0324 (6)	−0.0077 (4)	−0.0069 (4)	−0.0032 (4)
Br1	0.0427 (7)	0.0449 (7)	0.0387 (7)	−0.0148 (5)	−0.0056 (5)	−0.0109 (5)
N2	0.031 (5)	0.048 (5)	0.032 (5)	−0.007 (4)	−0.008 (4)	−0.003 (4)
N1	0.026 (4)	0.040 (5)	0.036 (5)	−0.010 (4)	−0.004 (4)	−0.002 (4)
N3	0.030 (4)	0.033 (4)	0.043 (5)	−0.009 (4)	−0.014 (4)	−0.003 (4)
C3	0.040 (6)	0.042 (6)	0.038 (6)	−0.006 (5)	−0.009 (5)	0.001 (5)
C2	0.032 (5)	0.035 (6)	0.041 (6)	−0.007 (4)	−0.007 (5)	0.003 (4)
C1	0.031 (5)	0.035 (5)	0.032 (5)	0.000 (4)	−0.009 (4)	−0.002 (4)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

Cd1—Br1 <sup>i</sup>	2.7379 (11)	N1—C1	1.332 (13)
Cd1—Br1	2.7379 (11)	N3—H3A	0.8900
Cd1—N1 <sup>ii</sup>	2.358 (9)	N3—H3B	0.8900
Cd1—N1 <sup>iii</sup>	2.358 (9)	N3—C1	1.413 (13)
Cd1—N3	2.446 (9)	C3—H3	0.9300
Cd1—N3 <sup>i</sup>	2.446 (9)	C3—C2	1.380 (15)
N2—H2	0.8600	C2—H2A	0.9300
N2—N1	1.355 (12)	C2—C1	1.382 (15)
N2—C3	1.326 (15)		
Br1—Cd1—Br1 <sup>i</sup>	180.0	N2—N1—Cd1 <sup>iv</sup>	117.1 (6)

N1 <sup>iii</sup> —Cd1—Br1 <sup>i</sup>	92.6 (2)	C1—N1—Cd1 <sup>iv</sup>	138.2 (7)
N1 <sup>ii</sup> —Cd1—Br1	92.6 (2)	C1—N1—N2	104.1 (8)
N1 <sup>ii</sup> —Cd1—Br1 <sup>i</sup>	87.4 (2)	Cd1—N3—H3A	107.7
N1 <sup>iii</sup> —Cd1—Br1	87.4 (2)	Cd1—N3—H3B	107.7
N1 <sup>ii</sup> —Cd1—N1 <sup>iii</sup>	180.0	H3A—N3—H3B	107.1
N1 <sup>iii</sup> —Cd1—N3 <sup>i</sup>	88.8 (3)	C1—N3—Cd1	118.3 (7)
N1 <sup>ii</sup> —Cd1—N3	88.8 (3)	C1—N3—H3A	107.7
N1 <sup>ii</sup> —Cd1—N3 <sup>i</sup>	91.2 (3)	C1—N3—H3B	107.7
N1 <sup>iii</sup> —Cd1—N3	91.2 (3)	N2—C3—H3	126.7
N3—Cd1—Br1 <sup>i</sup>	85.2 (2)	N2—C3—C2	106.5 (10)
N3 <sup>i</sup> —Cd1—Br1	85.2 (2)	C2—C3—H3	126.7
N3 <sup>i</sup> —Cd1—Br1 <sup>i</sup>	94.8 (2)	C3—C2—H2A	127.4
N3—Cd1—Br1	94.8 (2)	C3—C2—C1	105.1 (10)
N3 <sup>i</sup> —Cd1—N3	180.0	C1—C2—H2A	127.4
N1—N2—H2	123.6	N1—C1—N3	120.3 (9)
C3—N2—H2	123.6	N1—C1—C2	111.5 (9)
C3—N2—N1	112.7 (9)	C2—C1—N3	127.8 (10)
Cd1 <sup>iv</sup> —N1—C1—N3	14.7 (16)	N2—C3—C2—C1	-1.1 (13)
Cd1 <sup>iv</sup> —N1—C1—C2	-172.3 (8)	N1—N2—C3—C2	0.1 (13)
Cd1—N3—C1—N1	87.2 (11)	C3—N2—N1—Cd1 <sup>iv</sup>	173.9 (7)
Cd1—N3—C1—C2	-84.6 (12)	C3—N2—N1—C1	0.9 (12)
N2—N1—C1—N3	-174.6 (9)	C3—C2—C1—N1	1.7 (13)
N2—N1—C1—C2	-1.6 (12)	C3—C2—C1—N3	174.1 (10)

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

*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>
N2—H2 $\cdots$ Br1 <sup>iv</sup>	0.86	2.80	3.377 (9)	126
N3—H3A $\cdots$ Br1 <sup>ii</sup>	0.89	2.61	3.484 (9)	169
N3—H3B $\cdots$ Br1 <sup>v</sup>	0.89	2.79	3.640 (9)	160

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

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

<i>D</i> —H $\cdots$ <i>A</i>	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N2H $\cdots$ Br <sup>i</sup>	3.377 (1)	2.803 (1)	125.63 (1)
N3—H $\cdots$ Br <sup>ii</sup>	3.848 (1)	2.607 (1)	168.92 (1)
N3—H $\cdots$ Br <sup>iii</sup>	3.640 (1)	2.791 (1)	159.89 (1)

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