



# Crystal structures of dibromido{*N*-[(pyridin-2-yl- $\kappa$ *N*)methylidene]picolinohydrazide- $\kappa^2$ *N',O*}-cadmium methanol monosolvate and diiodido-{*N*-[(pyridin-2-yl- $\kappa$ *N*)methylidene]picolinohydrazide- $\kappa^2$ *N',O*}cadmium

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**CCDC references:** 1543006; 1543005

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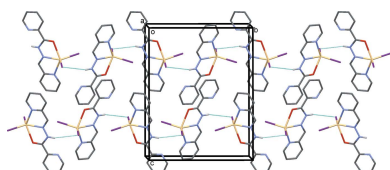
The title compounds, [CdBr<sub>2</sub>(C<sub>12</sub>H<sub>10</sub>N<sub>4</sub>O)]·CH<sub>3</sub>OH, (I), and [CdI<sub>2</sub>(C<sub>12</sub>H<sub>10</sub>N<sub>4</sub>O)], (II), are cadmium bromide and cadmium iodide complexes of the ligand (*E*)-*N'*-(pyridin-2-ylmethylene)picolinohydrazide. Complex (I) crystallizes as the methanol monosolvate. In both compounds, the Cd<sup>2+</sup> cation is ligated by one O atom and two N atoms of the tridentate ligand, and by two bromide anions forming a Br<sub>2</sub>N<sub>2</sub>O pentacoordination sphere for (I), and by two iodide anions forming an I<sub>2</sub>N<sub>2</sub>O pentacoordination sphere for (II), both with a distorted square-pyramidal geometry. In the crystal of complex (I), molecules are linked by pairs of N—H···O and O—H···Br hydrogen bonds, involving the solvent molecule, forming dimeric units, which are linked by C—H···Br hydrogen bonds forming layers parallel to (101). In the crystal of complex (II), molecules are linked by N—H···I hydrogen bonds, forming chains propagating along [010]. In complex (II), measured at room temperature, the two iodide anions are each disordered over two sites; the refined occupancy ratio is 0.75 (2):0.25 (2).

## 1. Chemical context

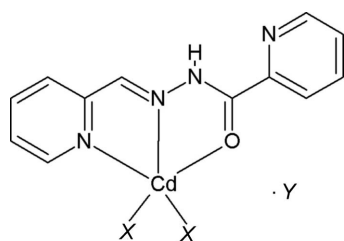
The cadmium(II) ion, has a *d*<sup>10</sup> electronic configuration and exhibits a variety of coordination geometries and modes. Hydrazone ligands are one of the most important classes of flexible and versatile polydentate ligands and show very high efficiency in chelating transition metal ions (Afkhami *et al.*, 2017*a*). Hydrazone ligands obtained from 2-pyridine carboxylic acid can act as ditopic ligands *via* two different donor sites (a tridentate coordination pocket and through an N-donor pyridine group), and have the potential to form mono- and multinuclear structures (Afkhami *et al.*, 2017*b*). Herein, we report on the crystal structures of two new Cd<sup>II</sup> complexes based on the tridentate hydrazone ligand, (*E*)-*N'*-(pyridin-2-ylmethylene)picolinohydrazide, obtained by condensation of an equimolar mixture of 2-pyridinecarbaldehyde and picolinic acid hydrazide in methanol.

## 2. Structural commentary

The molecular structures of compounds (I) and (II) are shown in Figs. 1 and 2, respectively. In compound (I), the ligand is almost planar with a dihedral angle between the pyridine rings

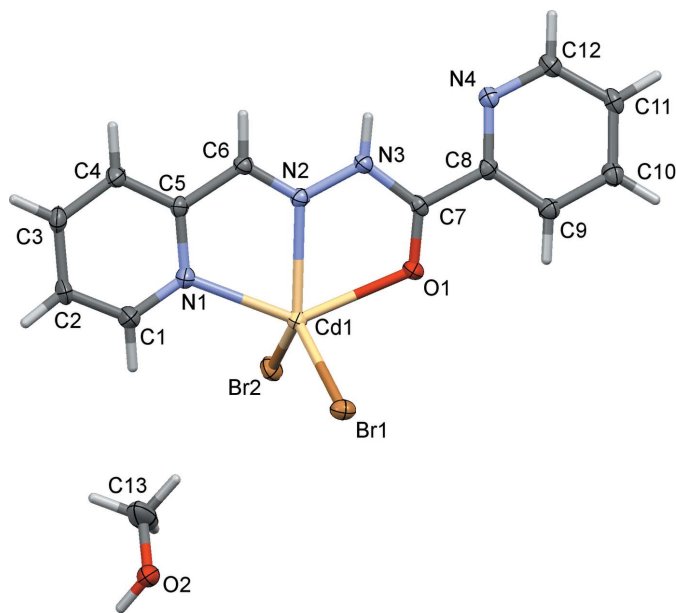


of  $6.9(3)^\circ$ . The Cd1–Br1 and Cd1–Br2 bond lengths are 2.5585(6) and 2.5490(7) Å, respectively, and the Cd1–N2 bond length is 2.336(4) Å. Atom Cd1 is ligated by one O atom (O1) and two N atoms (N1 and N2) of the tridentate ligand, and by two bromide anions, hence the Cd<sup>2+</sup> cation has a fivefold Br<sub>2</sub>N<sub>2</sub>O coordination sphere with a distorted shape and a  $\tau_5$  value of 0.33 ( $\tau_5 = 0$  for an ideal square-pyramidal coordination sphere, and = 1 for an ideal trigonal-pyramidal coordination sphere; Addison *et al.*, 1984).



(I) X = Br, Y = CH<sub>3</sub>OH  
(II) X = I

In compound (II), the ligand is also almost planar with a dihedral angle between the pyridine rings of  $8.0(2)^\circ$ . The two iodide anions are each disordered over two sites; the refined occupancy ratio is 0.75(2):0.25(2) for atoms I1A/I2A:I1B/I2B. Considering the major components only, the Cd1–I1A and Cd1–I2A bond lengths are 2.736(3) and 2.7128(19) Å, respectively, and the Cd1–N2 bond length is 2.336(3) Å. Atom Cd1 is ligated by one O atom (O1) and two N atoms (N1 and N2) of the tridentate ligand, and by two iodide anions. Atom Cd1 has a fivefold I<sub>2</sub>N<sub>2</sub>O coordination sphere with a distorted shape and a  $\tau_5$  value of 0.28.



**Figure 1**  
The molecular components in the structure of compound (I), with atom labelling. Displacement ellipsoids are shown at the 30% probability level.

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

D–H...A	D–H	H...A	D...A	D–H...A
N3–H3N...O2 <sup>i</sup>	0.88	1.96	2.803(5)	161
O2–H2A...Br1 <sup>ii</sup>	0.84	2.70	3.456(4)	150
C2–H2...Br2 <sup>iii</sup>	0.95	2.90	3.734(6)	147
C4–H4...Br2 <sup>iv</sup>	0.95	2.91	3.826(5)	162
C10–H10...Br1 <sup>v</sup>	0.95	2.85	3.703(5)	149

Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x + 1, -y + 1, -z + 1$ ; (iv)  $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (v)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ .

**Table 2**  
Hydrogen-bond geometry (Å, °) for (II).

D–H...A	D–H	H...A	D...A	D–H...A
N3–H3N...I2A <sup>i</sup>	0.87(4)	3.04(4)	3.866(3)	161(3)

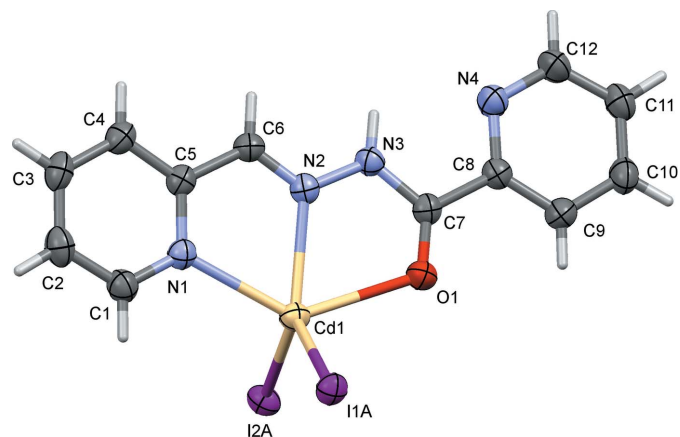
Symmetry code: (i)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ .

### 3. Supramolecular features

In the crystal of compound (I), molecules are linked by pairs of N–H...O and O–H...Br hydrogen bonds, involving the solvent molecule, forming dimeric units, which are linked by C–H...Br hydrogen bonds forming layers parallel to (101); see Table 1 and Fig. 3. In the crystal of complex (II), molecules are linked by N–H...I hydrogen bonds forming chains propagating along [010]; see Table 2 and Fig. 4.

### 4. Database survey

All bond lengths and angles in the title compounds fall within acceptable ranges and are comparable with those reported for related structures, such as bis{*N'*–[(*E*)-4-hydroxybenzylidene]pyridine-4-carbohydrazide- $\kappa$ N<sup>1</sup>}diiododicadmium methanol disolvate (Afkhami *et al.*, 2017c), dibromido{*N'*–[1-(pyridin-2-yl)ethylidene]picolinohydrazide- $\kappa^2$ N',O}cadmium (Akkurt *et al.*, 2012), di- $\mu$ -chlorido-bis(chlorido{*N'*–[phenyl-(pyridin-2-yl)- $\kappa$ N]methylidene]pyridine-2-carbohydrazide- $\kappa^2$ N',O}cadmium)



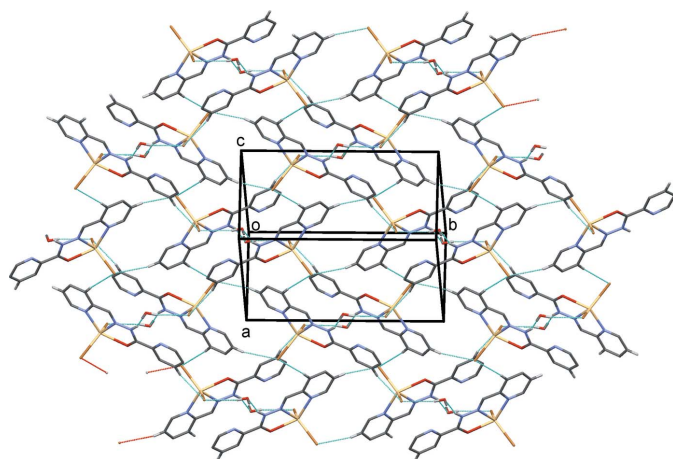
**Figure 2**  
The molecular structure of compound (II), with atom labelling. Displacement ellipsoids are shown at the 30% probability level. Only the major components of the disordered I atoms are shown.

**Table 3**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	[CdBr <sub>2</sub> (C <sub>12</sub> H <sub>10</sub> N <sub>4</sub> O)]·CH <sub>4</sub> O	[CdI <sub>2</sub> (C <sub>12</sub> H <sub>10</sub> N <sub>4</sub> O)]
<i>M<sub>r</sub></i>	530.50	592.44
Crystal system, space group	Monoclinic, <i>P2<sub>1</sub>/n</i>	Monoclinic, <i>P2<sub>1</sub>/n</i>
Temperature (K)	130	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.5482 (4), 15.7571 (8), 14.6407 (6)	7.5264 (7), 13.1325 (12), 16.5718 (15)
$\beta$ (°)	95.132 (4)	94.384 (1)
<i>V</i> (Å <sup>3</sup> )	1734.35 (15)	1633.2 (3)
<i>Z</i>	4	4
Radiation type	Cu <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	15.59	5.12
Crystal size (mm)	0.08 × 0.05 × 0.04	0.48 × 0.20 × 0.02
Data collection		
Diffractometer	Agilent SuperNova, Dual, Cu at zero, Atlas	Bruker D8 Venture diffractometer with Photon 100 CMOS detector
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2011)	Multi-scan ( <i>SADABS</i> ; Bruker, 2016)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.561, 1.000	0.616, 0.903
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	6773, 3458, 2764	3946, 3946, 3193
<i>R<sub>int</sub></i>	0.038	0.023
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.625	0.665
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>	0.034, 0.078, 1.02	0.023, 0.058, 1.06
No. of reflections	3458	3946
No. of parameters	201	204
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.63, -0.76	0.65, -0.39

Computer programs: *CrysAlis PRO* (Agilent, 2011), *APEX3* and *SAINT-Plus* (Bruker, 2016), *SHELXS2014/7* (Sheldrick, 2008), *SHELXT* (Sheldrick, 2015a), *SHELXL2016/6* and *SHELXL2014* (Sheldrick, 2015b), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

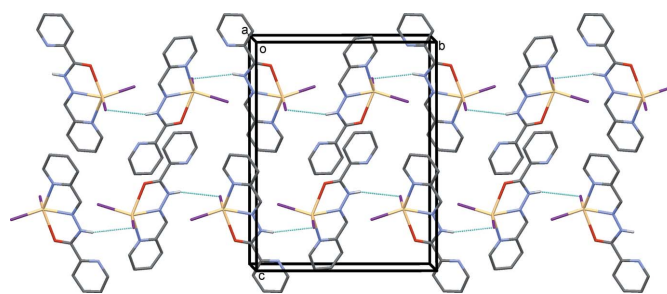
(Akkurt *et al.*, 2014), bis{2-[(2,4-dimethylphenyl)iminomethyl]pyridine- $\kappa^2N,N'$ }bis(thiocyanato- $\kappa N$ )cadmium (Malekshahian *et al.*, 2012), and *cis*-diaquabis-[(*E*)-4-(2-hydroxybenzylideneamino)benzoato- $\kappa^2O,O'$ ]cadmium in which layers are built from strong O—H...O hydrogen bonds (Yao *et al.*, 2006).



**Figure 3**  
A view normal to (101) of the crystal packing of compound (I). The hydrogen bonds are shown as dashed lines (see Table 1). For clarity, only the H atoms involved in hydrogen bonding have been included.

## 5. Synthesis and crystallization

A solution of the ligand *N'*-(pyridin-2-ylmethyl-ene)picolinohydrazide (0.151 g, 0.5 mmol) in 30 ml of methanol was treated with a methanolic solution of the appropriate cadmium(II) salt (0.5 mmol); CdBr<sub>2</sub> for complex (I) and CdI<sub>2</sub> for (II). The solutions were heated under reflux for 4 h and then allowed to stand at room temperature. After slow evaporation of the solvent, single crystals separated out. They were collected, washed with ether and dried over P<sub>4</sub>O<sub>10</sub> in vacuum.



**Figure 4**  
A view along the *a* axis of the crystal packing of compound (II). The hydrogen bonds are shown as dashed lines (see Table 2). For clarity, only the H atoms involved in hydrogen bonding and only the major components of the disordered I atoms have been included.

## 6. Refinement

Crystal data, data collection and structure refinement details for compounds (I) and (II) are summarized in Table 3. For complex (I), measured at 130 K, H atoms were placed in calculated positions (C–H = 0.95–0.98 Å, N–H = 0.88 Å and O–H = 0.84 Å) and included in the refinement in the riding-model approximation, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$  and  $1.2U_{\text{eq}}(\text{N,C})$  for other H atoms. Owing to poor agreement, two reflections, ( $\bar{4}$  4 6 and  $\bar{7}$  10 3), were omitted from the final cycles of refinement. For complex (II), measured at 296 K, the C-bound H atoms were placed in calculated positions (C–H = 0.93 Å) and included in the refinement in the riding-model approximation, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The N-bound H atoms were located in a difference-Fourier map but were refined with a distance restraint of N–H = 0.86 (4) Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ . In complex (II), the two iodide anions (I1 and I2) are each disordered over two sites, and their site-occupation factors refined to 0.75 (2):0.25 (2).

## Acknowledgements

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## Funding information

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## supporting information

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**Crystal structures of dibromido{*N*-[(pyridin-2-yl- $\kappa$ N)methylidene]picolinohydrazide- $\kappa^2$ N',O}cadmium methanol monosolvate and diiodido{*N*-[(pyridin-2-yl- $\kappa$ N)methylidene]picolinohydrazide- $\kappa^2$ N',O}cadmium**

**Ali Akbar Khandar, Farhad Akbari Afkhami, Harald Krautscheid, Kenneth Aase Kristoffersen, Zeliha Atioğlu, Mehmet Akkurt and Carl Henrik Görbitz**

**Computing details**

Data collection: *CrysAlis PRO* (Agilent, 2011) for (I); *APEX3* (Bruker, 2016) for (II). Cell refinement: *CrysAlis PRO* (Agilent, 2011) for (I); *S SAINT-Plus* (Bruker, 2016) for (II). Data reduction: *CrysAlis PRO* (Agilent, 2011) for (I); *S SAINT-Plus* (Bruker, 2016) for (II). Program(s) used to solve structure: *SHELXS2014/7* (Sheldrick, 2008) for (I); *SHELXT* (Sheldrick, 2015a) for (II). Program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015b) for (I); *SHELXL2014* (Sheldrick, 2015b) for (II). Molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) for (I); *Mercury* (Macrae *et al.*, 2008) for (II). Software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009) for (I); *SHELXL2014* (Sheldrick, 2015b) for (II).

**(I) Dibromido{*N*-[(pyridin-2-yl- $\kappa$ N)methylidene]picolinohydrazide- $\kappa^2$ N',O}cadmium methanol monosolvate**

*Crystal data*

[CdBr<sub>2</sub>(C<sub>12</sub>H<sub>10</sub>N<sub>4</sub>O)]·CH<sub>4</sub>O

*M<sub>r</sub>* = 530.50

Monoclinic, *P2<sub>1</sub>/n*

*a* = 7.5482 (4) Å

*b* = 15.7571 (8) Å

*c* = 14.6407 (6) Å

$\beta$  = 95.132 (4)°

*V* = 1734.35 (15) Å<sup>3</sup>

*Z* = 4

*F*(000) = 1016

*D<sub>x</sub>* = 2.032 Mg m<sup>-3</sup>

Cu *K* $\alpha$  radiation,  $\lambda$  = 1.5418 Å

Cell parameters from 2435 reflections

$\theta$  = 3.0–74.4°

$\mu$  = 15.59 mm<sup>-1</sup>

*T* = 130 K

Prism, light yellow

0.08 × 0.05 × 0.04 mm

*Data collection*

Agilent SuperNova, Dual, Cu at zero, Atlas diffractometer

Radiation source: SuperNova (Cu) X-ray

Source

Mirror monochromator

$\omega$  scans

Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2011)

*T<sub>min</sub>* = 0.561, *T<sub>max</sub>* = 1.000

6773 measured reflections

3458 independent reflections

2764 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.038

$\theta_{\max}$  = 74.6°,  $\theta_{\min}$  = 4.1°

*h* = -9→9

*k* = -18→19

*l* = -18→10

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.078$   
 $S = 1.02$   
 3458 reflections  
 201 parameters  
 0 restraints

Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0275P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.63 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.76 \text{ e } \text{\AA}^{-3}$

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3542 (9)	0.3896 (4)	0.5136 (4)	0.0494 (16)
H1	0.3566	0.4180	0.4565	0.059*
C2	0.2666 (9)	0.4292 (4)	0.5819 (4)	0.0482 (16)
H2	0.2058	0.4814	0.5708	0.058*
C3	0.2712 (8)	0.3898 (4)	0.6662 (3)	0.0376 (12)
H3	0.2154	0.4151	0.7150	0.045*
C4	0.3584 (7)	0.3128 (3)	0.6786 (3)	0.0315 (11)
H4	0.3643	0.2850	0.7364	0.038*
C5	0.4375 (6)	0.2763 (3)	0.6056 (3)	0.0259 (10)
C6	0.5190 (6)	0.1927 (3)	0.6130 (3)	0.0257 (9)
H6	0.5270	0.1620	0.6690	0.031*
C7	0.7080 (6)	0.0589 (3)	0.4588 (3)	0.0239 (9)
C8	0.7879 (6)	-0.0271 (3)	0.4567 (3)	0.0261 (10)
C9	0.8393 (6)	-0.0581 (3)	0.3740 (3)	0.0311 (11)
H9	0.8205	-0.0258	0.3192	0.037*
C10	0.9185 (7)	-0.1374 (4)	0.3737 (3)	0.0338 (11)
H10	0.9544	-0.1609	0.3185	0.041*
C11	0.9440 (6)	-0.1815 (3)	0.4546 (3)	0.0306 (11)
H11	1.0005	-0.2354	0.4566	0.037*
C12	0.8857 (7)	-0.1459 (3)	0.5335 (3)	0.0321 (11)
H12	0.9033	-0.1772	0.5890	0.039*
C13	0.2406 (12)	0.4864 (5)	0.2809 (5)	0.083 (3)
H13A	0.3593	0.5002	0.2631	0.124*
H13B	0.2374	0.4268	0.2999	0.124*
H13C	0.2133	0.5229	0.3321	0.124*
N1	0.4340 (6)	0.3153 (3)	0.5234 (3)	0.0333 (10)
N2	0.5791 (5)	0.1625 (3)	0.5414 (2)	0.0240 (8)
N3	0.6507 (5)	0.0828 (3)	0.5400 (2)	0.0265 (8)
H3N	0.6589	0.0495	0.5884	0.032*
N4	0.8071 (5)	-0.0709 (3)	0.5358 (2)	0.0267 (8)

O1	0.6971 (5)	0.1057 (2)	0.3907 (2)	0.0291 (7)
O2	0.1154 (6)	0.4997 (3)	0.2070 (2)	0.0401 (9)
H2A	0.1202	0.5505	0.1898	0.060*
Cd1	0.57044 (5)	0.24361 (2)	0.40754 (2)	0.02814 (10)
Br1	0.34115 (7)	0.21728 (4)	0.27099 (3)	0.03309 (13)
Br2	0.82753 (8)	0.34184 (4)	0.37807 (4)	0.03634 (14)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.081 (5)	0.035 (4)	0.033 (3)	0.020 (3)	0.011 (3)	0.004 (2)
C2	0.076 (4)	0.028 (3)	0.041 (3)	0.024 (3)	0.012 (3)	-0.003 (2)
C3	0.049 (3)	0.027 (3)	0.038 (3)	0.003 (2)	0.009 (2)	-0.011 (2)
C4	0.042 (3)	0.024 (3)	0.029 (2)	-0.004 (2)	0.006 (2)	-0.001 (2)
C5	0.031 (2)	0.021 (3)	0.026 (2)	-0.003 (2)	0.0001 (17)	-0.0046 (18)
C6	0.031 (2)	0.022 (3)	0.024 (2)	-0.003 (2)	0.0019 (17)	0.0018 (18)
C7	0.022 (2)	0.017 (2)	0.032 (2)	-0.0017 (18)	-0.0005 (17)	-0.0006 (19)
C8	0.026 (2)	0.023 (3)	0.029 (2)	-0.0033 (19)	-0.0015 (17)	-0.0036 (19)
C9	0.031 (2)	0.032 (3)	0.030 (2)	0.003 (2)	0.0019 (19)	-0.001 (2)
C10	0.034 (3)	0.030 (3)	0.039 (3)	0.002 (2)	0.008 (2)	-0.001 (2)
C11	0.027 (2)	0.020 (3)	0.045 (3)	0.0005 (19)	0.003 (2)	-0.002 (2)
C12	0.031 (2)	0.025 (3)	0.039 (2)	0.000 (2)	0.001 (2)	0.003 (2)
C13	0.123 (8)	0.050 (5)	0.065 (4)	0.023 (5)	-0.045 (5)	-0.006 (4)
N1	0.050 (3)	0.025 (2)	0.0260 (18)	0.004 (2)	0.0066 (17)	-0.0026 (17)
N2	0.0269 (19)	0.023 (2)	0.0222 (16)	-0.0018 (16)	0.0007 (14)	-0.0002 (15)
N3	0.033 (2)	0.021 (2)	0.0258 (18)	0.0001 (17)	0.0004 (15)	0.0017 (16)
N4	0.0272 (19)	0.024 (2)	0.0295 (18)	0.0008 (17)	0.0035 (15)	-0.0002 (16)
O1	0.0388 (19)	0.0215 (19)	0.0274 (16)	0.0022 (15)	0.0046 (13)	0.0044 (14)
O2	0.060 (2)	0.032 (2)	0.0284 (17)	0.0022 (19)	0.0041 (16)	-0.0001 (15)
Cd1	0.03855 (18)	0.0225 (2)	0.02370 (15)	0.00179 (15)	0.00451 (12)	0.00180 (13)
Br1	0.0344 (3)	0.0331 (3)	0.0313 (2)	-0.0030 (2)	0.00060 (19)	0.0069 (2)
Br2	0.0439 (3)	0.0243 (3)	0.0413 (3)	-0.0036 (2)	0.0063 (2)	-0.0008 (2)

*Geometric parameters (Å, °)*

C1—N1	1.319 (7)	C9—H9	0.9500
C1—C2	1.394 (7)	C10—C11	1.370 (7)
C1—H1	0.9500	C10—H10	0.9500
C2—C3	1.378 (8)	C11—C12	1.391 (7)
C2—H2	0.9500	C11—H11	0.9500
C3—C4	1.385 (8)	C12—N4	1.324 (7)
C3—H3	0.9500	C12—H12	0.9500
C4—C5	1.395 (6)	C13—O2	1.388 (7)
C4—H4	0.9500	C13—H13A	0.9800
C5—N1	1.349 (6)	C13—H13B	0.9800
C5—C6	1.453 (7)	C13—H13C	0.9800
C6—N2	1.271 (6)	N1—Cd1	2.351 (4)
C6—H6	0.9500	N2—N3	1.368 (6)

C7—O1	1.236 (5)	N2—Cd1	2.336 (4)
C7—N3	1.354 (6)	N3—H3N	0.8800
C7—C8	1.485 (7)	O1—Cd1	2.396 (3)
C8—N4	1.344 (6)	O2—H2A	0.8400
C8—C9	1.393 (6)	Cd1—Br2	2.5490 (7)
C9—C10	1.385 (7)	Cd1—Br1	2.5585 (6)
N1—C1—C2	124.1 (5)	C12—C11—H11	120.6
N1—C1—H1	118.0	N4—C12—C11	123.9 (5)
C2—C1—H1	118.0	N4—C12—H12	118.1
C3—C2—C1	117.7 (5)	C11—C12—H12	118.1
C3—C2—H2	121.1	O2—C13—H13A	109.5
C1—C2—H2	121.1	O2—C13—H13B	109.5
C2—C3—C4	119.1 (5)	H13A—C13—H13B	109.5
C2—C3—H3	120.5	O2—C13—H13C	109.5
C4—C3—H3	120.5	H13A—C13—H13C	109.5
C3—C4—C5	119.4 (5)	H13B—C13—H13C	109.5
C3—C4—H4	120.3	C1—N1—C5	118.3 (4)
C5—C4—H4	120.3	C1—N1—Cd1	125.0 (3)
N1—C5—C4	121.3 (5)	C5—N1—Cd1	116.7 (3)
N1—C5—C6	117.0 (4)	C6—N2—N3	121.8 (4)
C4—C5—C6	121.6 (4)	C6—N2—Cd1	120.1 (3)
N2—C6—C5	117.3 (4)	N3—N2—Cd1	118.1 (3)
N2—C6—H6	121.4	C7—N3—N2	115.3 (4)
C5—C6—H6	121.4	C7—N3—H3N	122.4
O1—C7—N3	122.6 (4)	N2—N3—H3N	122.4
O1—C7—C8	121.7 (4)	C12—N4—C8	116.7 (4)
N3—C7—C8	115.7 (4)	C7—O1—Cd1	117.1 (3)
N4—C8—C9	123.5 (5)	C13—O2—H2A	109.5
N4—C8—C7	117.6 (4)	N2—Cd1—N1	68.80 (14)
C9—C8—C7	118.9 (4)	N2—Cd1—O1	66.95 (12)
C10—C9—C8	118.2 (5)	N1—Cd1—O1	135.60 (13)
C10—C9—H9	120.9	N2—Cd1—Br2	120.65 (9)
C8—C9—H9	120.9	N1—Cd1—Br2	102.70 (12)
C11—C10—C9	118.8 (5)	O1—Cd1—Br2	102.51 (8)
C11—C10—H10	120.6	N2—Cd1—Br1	122.22 (9)
C9—C10—H10	120.6	N1—Cd1—Br1	109.42 (11)
C10—C11—C12	118.9 (5)	O1—Cd1—Br1	91.20 (8)
C10—C11—H11	120.6	Br2—Cd1—Br1	115.99 (2)
N1—C1—C2—C3	3.2 (11)	C2—C1—N1—Cd1	176.8 (5)
C1—C2—C3—C4	-1.3 (10)	C4—C5—N1—C1	0.4 (8)
C2—C3—C4—C5	-0.8 (8)	C6—C5—N1—C1	177.2 (5)
C3—C4—C5—N1	1.4 (8)	C4—C5—N1—Cd1	-179.2 (4)
C3—C4—C5—C6	-175.4 (5)	C6—C5—N1—Cd1	-2.3 (6)
N1—C5—C6—N2	-0.6 (7)	C5—C6—N2—N3	-176.9 (4)
C4—C5—C6—N2	176.2 (5)	C5—C6—N2—Cd1	3.4 (6)
O1—C7—C8—N4	174.9 (4)	O1—C7—N3—N2	0.2 (6)



N3—C7—C8—N4	-4.3 (6)	C8—C7—N3—N2	179.3 (4)
O1—C7—C8—C9	-5.0 (7)	C6—N2—N3—C7	179.5 (4)
N3—C7—C8—C9	175.9 (4)	Cd1—N2—N3—C7	-0.8 (5)
N4—C8—C9—C10	-1.7 (7)	C11—C12—N4—C8	-1.6 (7)
C7—C8—C9—C10	178.1 (4)	C9—C8—N4—C12	2.7 (7)
C8—C9—C10—C11	-0.5 (7)	C7—C8—N4—C12	-177.1 (4)
C9—C10—C11—C12	1.5 (7)	N3—C7—O1—Cd1	0.5 (6)
C10—C11—C12—N4	-0.5 (8)	C8—C7—O1—Cd1	-178.6 (3)
C2—C1—N1—C5	-2.7 (10)		

## Hydrogen-bond geometry (Å, °)

<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>
N3—H3N...O2 <sup>i</sup>	0.88	1.96	2.803 (5)	161
O2—H2A...Br1 <sup>ii</sup>	0.84	2.70	3.456 (4)	150
C2—H2...Br2 <sup>iii</sup>	0.95	2.90	3.734 (6)	147
C4—H4...Br2 <sup>iv</sup>	0.95	2.91	3.826 (5)	162
C10—H10...Br1 <sup>v</sup>	0.95	2.85	3.703 (5)	149

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

(II) Diiodido{*N*-[(pyridin-2-yl- $\kappa$ N)methylidene]picolinohydrazide- $\kappa^2$ N',O}cadmium

## Crystal data

[CdI<sub>2</sub>(C<sub>12</sub>H<sub>10</sub>N<sub>4</sub>O)] $M_r = 592.44$ Monoclinic,  $P2_1/n$  $a = 7.5264$  (7) Å $b = 13.1325$  (12) Å $c = 16.5718$  (15) Å $\beta = 94.384$  (1)° $V = 1633.2$  (3) Å<sup>3</sup> $Z = 4$  $F(000) = 1088$  $D_x = 2.409$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 6468 reflections

 $\theta = 2.5$ – $28.0$ ° $\mu = 5.12$  mm<sup>-1</sup> $T = 296$  K

Plate, light yellow

 $0.48 \times 0.20 \times 0.02$  mm

## Data collection

Bruker D8 Venture

diffractometer with Photon 100 CMOS detector

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3 pixels mm<sup>-1</sup>Sets of exposures each taken over  $0.5^\circ \omega$ 

rotation scans

Absorption correction: multi-scan

(SADABS; Bruker, 2016)

 $T_{\min} = 0.616, T_{\max} = 0.903$ 

3946 measured reflections

3946 independent reflections

3193 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.023$  $\theta_{\max} = 28.2^\circ, \theta_{\min} = 2.0^\circ$  $h = -9 \rightarrow 10$  $k = -17 \rightarrow 17$  $l = -21 \rightarrow 21$ 

## Refinement

Refinement on  $F^2$ 

Least-squares matrix: full

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

3946 reflections

204 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 0.6207P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.65 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$$

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.5553 (5)	0.3164 (3)	0.9481 (2)	0.0622 (9)	
H1	0.5027	0.2525	0.9506	0.075*	
C2	0.6695 (5)	0.3481 (3)	1.0130 (2)	0.0691 (10)	
H2	0.6933	0.3064	1.0578	0.083*	
C3	0.7462 (5)	0.4426 (3)	1.0092 (2)	0.0662 (9)	
H3	0.8220	0.4664	1.0520	0.079*	
C4	0.7095 (4)	0.5017 (3)	0.9414 (2)	0.0591 (8)	
H4	0.7609	0.5657	0.9376	0.071*	
C5	0.5948 (4)	0.4646 (2)	0.87896 (18)	0.0481 (7)	
C6	0.5559 (4)	0.5222 (2)	0.80398 (18)	0.0503 (7)	
H6	0.5999	0.5879	0.7986	0.060*	
C7	0.3276 (4)	0.4766 (2)	0.61592 (18)	0.0488 (7)	
C8	0.2989 (4)	0.5342 (2)	0.53845 (18)	0.0498 (7)	
C9	0.2074 (5)	0.4925 (3)	0.4719 (2)	0.0635 (9)	
H9	0.1609	0.4269	0.4732	0.076*	
C10	0.1865 (5)	0.5520 (3)	0.4020 (2)	0.0695 (10)	
H10	0.1230	0.5271	0.3558	0.083*	
C11	0.2590 (5)	0.6460 (3)	0.4019 (2)	0.0692 (10)	
H11	0.2461	0.6865	0.3558	0.083*	
C12	0.3516 (6)	0.6809 (3)	0.4704 (2)	0.0727 (11)	
H12	0.4031	0.7453	0.4695	0.101 (15)*	
N1	0.5174 (3)	0.3727 (2)	0.88258 (15)	0.0496 (6)	
N2	0.4609 (3)	0.48064 (19)	0.74667 (15)	0.0473 (6)	
N3	0.4243 (4)	0.5284 (2)	0.67483 (16)	0.0508 (6)	
H3N	0.461 (5)	0.590 (3)	0.668 (2)	0.061*	
N4	0.3717 (5)	0.6265 (2)	0.53900 (18)	0.0659 (8)	
O1	0.2696 (3)	0.39087 (18)	0.62576 (14)	0.0592 (6)	
Cd1	0.32992 (3)	0.32196 (2)	0.76532 (2)	0.05080 (8)	
I1A	0.4779 (3)	0.1408 (2)	0.7239 (2)	0.0549 (3)	0.75 (2)
I2A	-0.0093 (3)	0.31832 (13)	0.81000 (15)	0.0555 (4)	0.75 (2)
I1B	0.4749 (10)	0.1451 (7)	0.7364 (9)	0.0654 (16)	0.25 (2)
I2B	0.0012 (11)	0.3249 (6)	0.8180 (7)	0.0787 (18)	0.25 (2)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.071 (2)	0.060 (2)	0.055 (2)	0.0027 (17)	0.0032 (17)	0.0053 (16)
C2	0.073 (2)	0.081 (3)	0.053 (2)	0.018 (2)	-0.0004 (17)	0.0083 (18)
C3	0.058 (2)	0.088 (3)	0.0519 (19)	0.0085 (19)	-0.0055 (15)	-0.0109 (18)
C4	0.0529 (18)	0.065 (2)	0.0587 (19)	-0.0021 (16)	0.0016 (15)	-0.0105 (16)
C5	0.0423 (15)	0.0520 (18)	0.0500 (16)	0.0055 (13)	0.0039 (12)	-0.0044 (13)
C6	0.0490 (17)	0.0468 (18)	0.0551 (18)	-0.0015 (13)	0.0048 (13)	-0.0003 (14)
C7	0.0480 (16)	0.0503 (18)	0.0485 (16)	0.0069 (13)	0.0062 (13)	-0.0016 (13)
C8	0.0491 (17)	0.0503 (17)	0.0502 (17)	0.0049 (13)	0.0059 (13)	0.0020 (13)
C9	0.067 (2)	0.065 (2)	0.058 (2)	-0.0120 (17)	0.0011 (16)	-0.0026 (17)
C10	0.071 (2)	0.088 (3)	0.0490 (19)	-0.004 (2)	-0.0041 (16)	0.0038 (18)
C11	0.075 (2)	0.077 (3)	0.055 (2)	0.006 (2)	0.0017 (17)	0.0150 (18)
C12	0.096 (3)	0.058 (2)	0.063 (2)	-0.003 (2)	-0.001 (2)	0.0137 (18)
N1	0.0526 (15)	0.0482 (15)	0.0478 (14)	0.0044 (11)	0.0029 (11)	-0.0017 (11)
N2	0.0469 (14)	0.0479 (15)	0.0473 (13)	0.0069 (11)	0.0043 (11)	0.0008 (11)
N3	0.0601 (16)	0.0426 (14)	0.0494 (14)	0.0027 (12)	0.0028 (12)	0.0037 (11)
N4	0.088 (2)	0.0536 (18)	0.0547 (17)	-0.0011 (15)	-0.0024 (15)	0.0027 (13)
O1	0.0695 (15)	0.0508 (13)	0.0565 (13)	-0.0077 (11)	-0.0013 (11)	0.0046 (10)
Cd1	0.05478 (14)	0.04400 (13)	0.05349 (14)	-0.00171 (9)	0.00328 (10)	-0.00142 (9)
I1A	0.0610 (5)	0.0468 (4)	0.0568 (7)	0.0081 (3)	0.0034 (5)	-0.0055 (4)
I2A	0.0516 (5)	0.0512 (7)	0.0641 (5)	0.0071 (3)	0.0069 (4)	0.0103 (3)
I1B	0.0736 (17)	0.0486 (12)	0.077 (4)	0.0009 (11)	0.0232 (18)	-0.0098 (15)
I2B	0.065 (2)	0.097 (3)	0.077 (2)	0.0126 (15)	0.0233 (17)	0.0117 (15)

*Geometric parameters (Å, °)*

C1—N1	1.326 (4)	C9—C10	1.396 (5)
C1—C2	1.389 (5)	C9—H9	0.9300
C1—H1	0.9300	C10—C11	1.350 (6)
C2—C3	1.372 (6)	C10—H10	0.9300
C2—H2	0.9300	C11—C12	1.365 (6)
C3—C4	1.376 (5)	C11—H11	0.9300
C3—H3	0.9300	C12—N4	1.341 (5)
C4—C5	1.384 (5)	C12—H12	0.9300
C4—H4	0.9300	N1—Cd1	2.407 (3)
C5—N1	1.343 (4)	N2—N3	1.355 (4)
C5—C6	1.465 (4)	N2—Cd1	2.336 (3)
C6—N2	1.268 (4)	N3—H3N	0.86 (4)
C6—H6	0.9300	O1—Cd1	2.493 (2)
C7—O1	1.223 (4)	Cd1—I1B	2.626 (10)
C7—N3	1.355 (4)	Cd1—I2B	2.687 (6)
C7—C8	1.492 (4)	Cd1—I2A	2.7128 (19)
C8—N4	1.329 (4)	Cd1—I1A	2.736 (3)
C8—C9	1.370 (5)		
N1—C1—C2	123.2 (4)	C12—C11—H11	120.4

N1—C1—H1	118.4	N4—C12—C11	122.9 (4)
C2—C1—H1	118.4	N4—C12—H12	118.6
C3—C2—C1	118.3 (4)	C11—C12—H12	118.6
C3—C2—H2	120.8	C1—N1—C5	118.1 (3)
C1—C2—H2	120.8	C1—N1—Cd1	125.6 (2)
C2—C3—C4	119.2 (3)	C5—N1—Cd1	116.3 (2)
C2—C3—H3	120.4	C6—N2—N3	121.6 (3)
C4—C3—H3	120.4	C6—N2—Cd1	120.3 (2)
C3—C4—C5	119.1 (4)	N3—N2—Cd1	118.0 (2)
C3—C4—H4	120.5	N2—N3—C7	117.6 (3)
C5—C4—H4	120.5	N2—N3—H3N	120 (2)
N1—C5—C4	122.1 (3)	C7—N3—H3N	122 (2)
N1—C5—C6	116.3 (3)	C8—N4—C12	117.4 (3)
C4—C5—C6	121.6 (3)	C7—O1—Cd1	114.6 (2)
N2—C6—C5	118.5 (3)	N2—Cd1—N1	68.43 (9)
N2—C6—H6	120.7	N2—Cd1—O1	66.56 (8)
C5—C6—H6	120.7	N1—Cd1—O1	134.63 (8)
O1—C7—N3	122.9 (3)	N2—Cd1—I1B	125.4 (2)
O1—C7—C8	123.5 (3)	N1—Cd1—I1B	99.6 (3)
N3—C7—C8	113.6 (3)	O1—Cd1—I1B	101.6 (3)
N4—C8—C9	123.5 (3)	N2—Cd1—I2B	116.02 (18)
N4—C8—C7	115.1 (3)	N1—Cd1—I2B	103.4 (3)
C9—C8—C7	121.4 (3)	O1—Cd1—I2B	100.9 (2)
C8—C9—C10	117.5 (3)	I1B—Cd1—I2B	118.5 (2)
C8—C9—H9	121.3	N2—Cd1—I2A	117.87 (7)
C10—C9—H9	121.3	N1—Cd1—I2A	106.89 (9)
C11—C10—C9	119.5 (4)	O1—Cd1—I2A	98.69 (7)
C11—C10—H10	120.2	N2—Cd1—I1A	123.94 (9)
C9—C10—H10	120.2	N1—Cd1—I1A	102.63 (9)
C10—C11—C12	119.2 (4)	O1—Cd1—I1A	97.56 (9)
C10—C11—H11	120.4	I2A—Cd1—I1A	117.57 (7)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3N $\cdots$ I2A <sup>i</sup>	0.87 (4)	3.04 (4)	3.866 (3)	161 (3)

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