research communications

Solvothermal synthesis and crystal structures of two new cadmium coordination polymers containing polynitrile ligands

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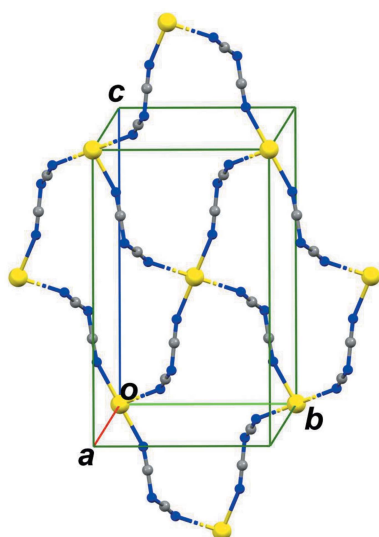
Two new coordination polymers of cadmium-containing polynitrile ligands have been synthesized using sovothermal methods. In both poly[$trans,trans,trans$-bis(μ-dicyanamido-κ^2N^1:N^3)bis(2-methylbenzimidazole-κN)cadmium(II)], [Cd(C$_2$N$_3$)$_2$(C$_8$H$_8$N$_2$)$_2$]$_n$, (I), and poly[$trans,trans,trans$-bis(2-methylbenzimidazole-κN)bis(μ-tricyanomethanido-κ^2N:N')cadmium(II)], [Cd(C$_4$N$_3$)$_2$(C$_8$H$_8$N$_2$)$_2$]$_n$, (II), the Cd atom lies on a centre of inversion, in space groups $P2_1/n$ and $P2_1/c$, respectively. In each polymer, each anionic ligand acts as a bridge between two metal centres, forming sheets of 24-membered rings, and in each structure a single N—H$\cdots$N hydrogen bond links the polymer sheets to form a three-dimensional framework structure. Comparisons are made with the structures of some related complexes.

1. Chemical context

The d^{10} metal complexes of zinc(II) and cadmium(II) with a variety of ligands have attracted considerable attention in recent years because of their luminescence properties (Merabet $et\ al.$, 2017; Wang $et\ al.$, 2017). Polynitrile compounds derived from transition-metal ions are of great interest from the perspective of their magnetic and luminescence properties, rich molecular architectures and for their topologies (Atmani $et\ al.$, 2008; Benmansour $et\ al.$, 2008, 2010, 2012; Setifi $et\ al.$, 2009; Yuste $et\ al.$, 2009; Setifi, Lehchili $et\ al.$, 2014; Setifi, Setifi, El Ammari $et\ al.$, 2014; Addala $et\ al.$, 2015; Dmitrienko $et\ al.$, 2020; Merabet $et\ al.$, 2022).
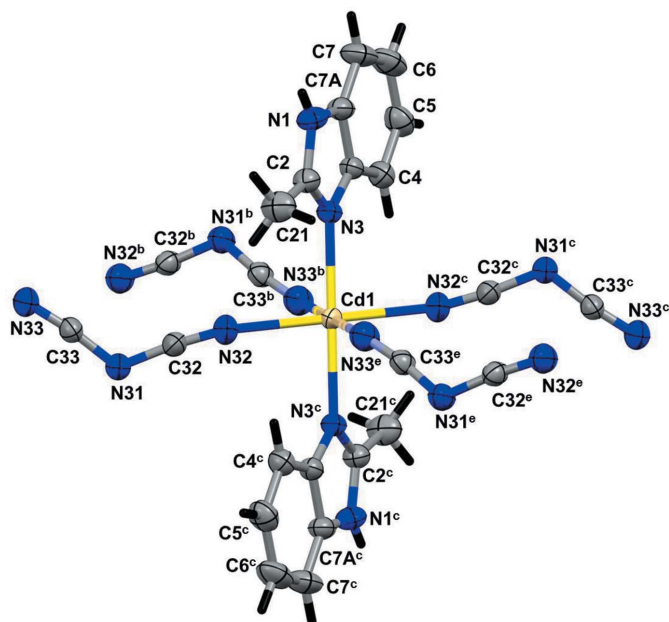
Two of these small bridging polynitrile ligands that have received a lot of attention in the past decade are the dicyanamide, [N(CN)$_2$]$^-$ (dca), and tricyanomethanide [C(CN)$_3$]$^-$ (tcm), ions. This is partly due to their ability to produce a wide variety of coordination compounds with different nuclearity ranging from simple mononuclear to polynuclear species with complex structures (Batten & Murray, 2003; Setifi, Setifi, Saadi $et\ al.$, 2014; Świtlicka-Olszewska $et\ al.$, 2016). Different bonding modes are observed in the polynuclear complexes bridged by the dca and tcm ligands, which results in the formation of polymeric assemblies in one, two or three dimensions (Batten & Murray 2003).

As a part of our continuing study of the structural and luminescence properties of Cd^{II} complexes containing both polynitrile and polypyridyl units (Merabet $et\ al.$, 2017; Addala
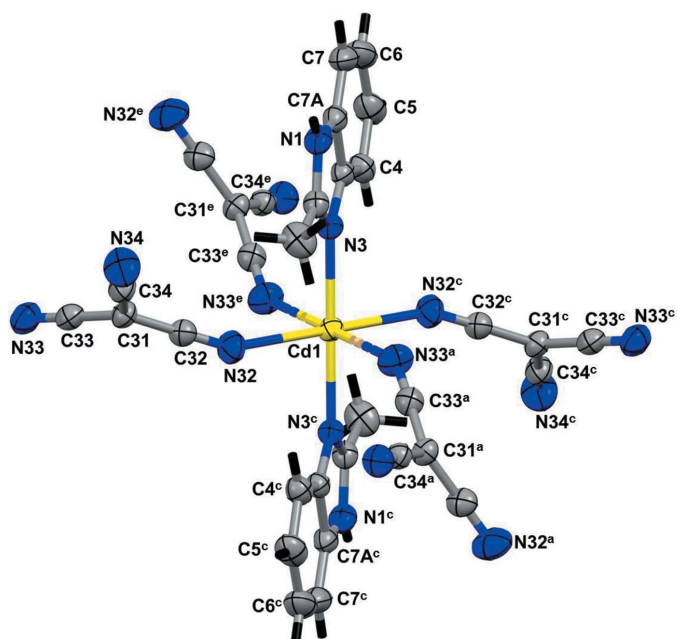
Table 1
Selected bond distances (Å).

Parameter	(I)	(II)
Cd1—N3	2.3094 (11)	2.2813 (14)
Cd1—N32	2.3574 (14)	2.3845 (17)
Cd1—N33^i	2.3729 (14)	2.4265 (17)
N31—C32	1.3081 (19)	
N31—C33	1.3056 (18)	
C31—C32		1.401 (2)
C31—C33		1.396 (2)
C31—C34		1.407 (2)
C32—N32	1.1455 (19)	1.144 (2)
C33—N33	1.1501 (18)	1.151 (2)
C34—N34		1.141 (3)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ for (I) and $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ for (II).

Figure 1
The coordination polyhedron in compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and the atoms marked 'b', 'c' and 'e' are at the symmetry positions ($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$), ($1 - x, 1 - y, 1 - z$) and ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$), respectively.

et al., 2019), we report here the synthesis, and the crystal and molecular structure of two two-dimensional coordination polymers of cadmium containing either dicyanamide (dca⁻) or tricyanomethanide (tcm⁻) anions with 2-methyl-1*H*-benz-

imidazole (2-MeBzlm) as co-ligand, namely poly[*trans,-trans,trans*-bis(*μ*-dicyanamido-$\kappa^2 N^1$:N^3)bis(2-methylbenz-imidazole-κN)cadmium(II)] (I) (Fig. 1) and poly[*trans,-trans,trans*-bis(2-methylbenzimidazole-κN)bis(*μ*-tricyano-methanido-$\kappa^2 N$:N')cadmium(II)] (II) (Fig. 2).

(I) X = N
(II) X = C-CN

2. Structural commentary

Despite the close similarity in their chemical constitutions (Figs. 1 and 2) and the fact that both crystallize in space group No. 14 (Table 3), they are not isomorphous, as the cell dimensions *b* clearly show. In each compound, the octahedral Cd^{II} centre lies on a centre of inversion, coordinated by a pair of neutral 2-methylbenzimidazole ligands, coordinated *via* atom N3 (Figs. 1 and 2) and by cyano N atoms from four anionic ligands of type [X(CN)$_2$]⁻, where X represents N in (I) and C—CN in (II). Each anionic ligand coordinates to two Cd centres, generating sheets of 24-membered rings, lying parallel to (10$\bar{1}$) in (I) and to (100) in (II) (Figs. 3 and 4).

In each compound, the Cd—N distance for the neutral 2-methylbenzimidazole ligand is significantly less than the distances for the anionic ligands (Table 1). In both compounds,
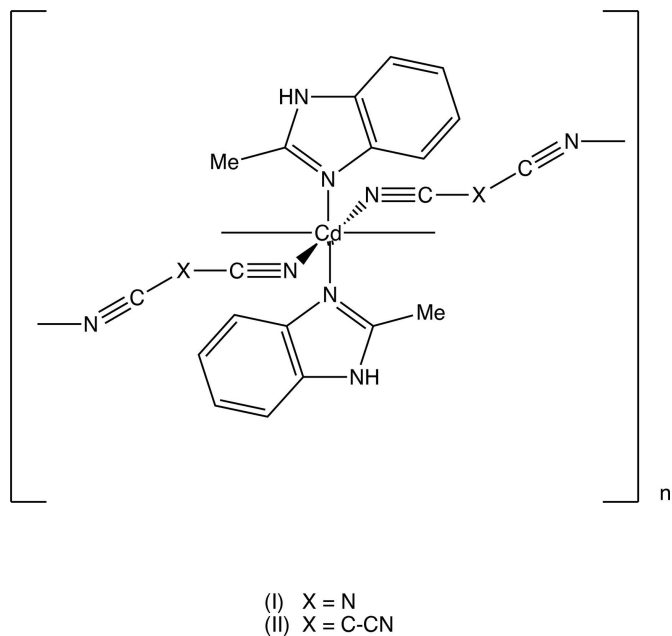

Figure 2
The coordination polyhedron in compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and the atoms marked 'a', 'c' and 'e' are at the symmetry positions ($1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$), ($1 - x, 1 - y, 1 - z$) and ($x, 1.5 - y, \frac{1}{2} + z$), respectively.

Table 2
Hydrogen-bond parameters (Å, °).

Compound	D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
(I)	N1—H1$\cdots$N31[ii]	0.79 (2)	2.327 (19)	3.0447 (19)	151.3 (17)
(II)	N1—H1$\cdots$N34[iii]	0.80 (2)	2.12 (2)	2.906 (3)	171 (3)

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

the C≡N bonds within the anionic ligands are somewhat long for their type [mean value (Allen *et al.*, 1987) = 1.136 Å; upper quartile value = 1.142 Å] while the C—C bonds in the anionic ligand in (II) are somewhat short for their type (mean value 1.431 Å; lower quartile value 1.425 Å). These values are consistent, in each case, with the delocalization of the negative charge over the entire anionic ligand which, in the case of compound (II), is also reflected in the planarity of the anionic ligand, where the maximum deviation from the mean plane through the ligand atoms is only 0.054 (2) Å, for atom C31. Although only two of the three independent cyano groups in (II) are coordinated to the metal centre, there are no significant differences between the C—C and C≡N distances in the uncoordinated group and the two coordinated groups (Table 1).

3. Supramolecular features

The central unit X of the anionic ligand plays no role in the coordination in either compound, but it is involved in hydrogen bonding in both (Table 2). In each structure, the
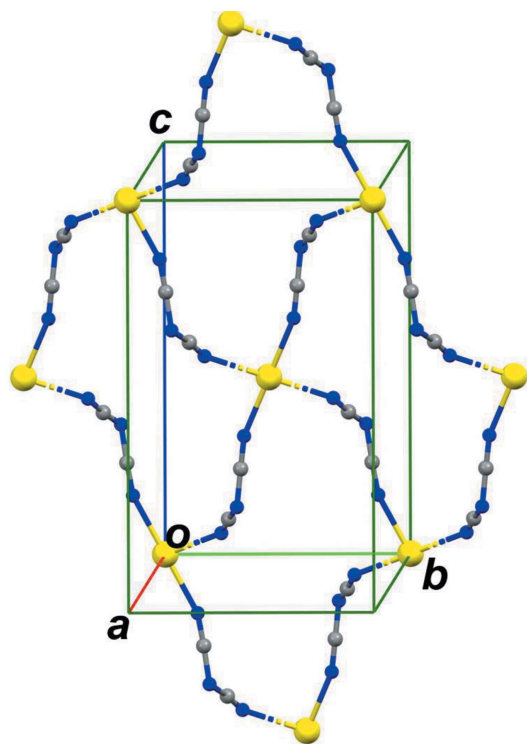
coordination polymer sheets are linked into a three-dimensional array by a single N—H$\cdots$N hydrogen bond, in which the acceptor for (I) is the central N atom of the dicyanamido ligand, while in (II) the acceptor is the N atom of the uncoordinated cyano group in the tricyanomethanido ligand (Table 2). In (I), the action of the hydrogen bond links the complexes into a hydrogen-bonded sheet of $R_2^2(20)$ (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995) rings lying parallel to (101) (Fig. 5). The combination of the polymer sheets parallel to (10$\bar{1}$) and the hydrogen-bonded sheets parallel to (101) generates a three-dimensional structure. By contrast, in (II), the hydrogen bonding generates a chain of spiro-fused $R_2^2(20)$ rings running parallel to [101] (Fig. 6), which again links the coordination polymer sheets into a three-dimensional structure. For both structures, C—H$\cdots\pi$(arene), anion–π(arene) and aromatic π–π stacking interactions are absent.

4. Database survey

Coordination compounds containing either dicyanamide (dca) or tricyanomethanide (tcm) ligands were the subject, some years ago, of a comprehensive review that covered a wide range of both metal centres and co-ligands (Batten & Murray,

Figure 3
Part of the crystal structure of compound (I) showing the formation of a coordination polymer sheet lying parallel to (10$\bar{1}$). For the sake of clarity, the 2-methylbenzimidazole ligands have been omitted.
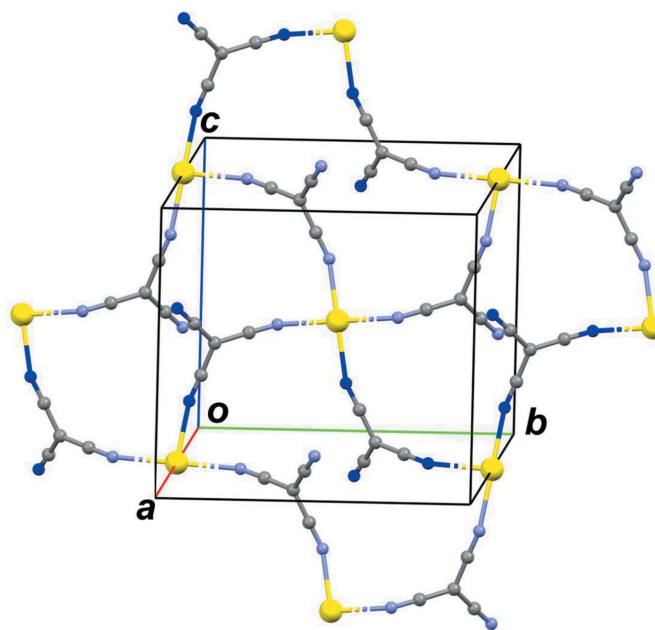

Figure 4
Part of the crystal structure of compound (II) showing the formation of a coordination polymer sheet lying parallel to (100). For the sake of clarity, the 2-methylbenzimidazole ligands have been omitted.

2003), and here we focus on just a few examples that are most closely related to the compounds (I) and (II) reported here.

Structures have been reported for $(2,2'\text{-bipy})_2\text{Cd(dca)}_2$ (Mal *et al.*, 2012) and for cadmium complexes of both dac and tcm containing 4-amino-3,5-bis(pyridine-2-yl)-1,2,4-triazole as the neutral co-ligand (Setifi *et al.*, 2017), but these compounds all comprise monomeric complexes in which the octahedral units are linked only by hydrogen bonds and $\pi-\pi$ stacking interactions. Although the two triazole complexes both crystallize in space group $P\bar{1}$, they are not isomorphous: this behaviour mirrors that of compounds (I) and (II) reported here.

However, $[\text{Cd}(1,10\text{-phen})(\text{dca})_2]$ forms a two-dimensional coordination polymer in which each dca bridges two metal centres but where some of the Cd···Cd links involve just one dca ligand and some involve two, forming a sheet containing both 12-membered and 36-membered rings (Luo *et al.*, 2002), in contrast to the 24-membered rings found in compounds (I) and (II). The compound $[\text{Cd(dipm)(dca)}_2]$, where (dipm) represents bis(pyrimidin-2-yl)amine, forms a three-dimensional coordination polymer framework in which each dca ligand bridges two cadmium centres such that each Cd atom is directly linked to four others (van Albada *et al.*, 2009).

5. Synthesis and crystallization

All chemical reagents and solvents are commercially available and were used as received, without further purification. For the synthesis of compounds (I) and (II), a mixture of 2-methyl-$1H$-benzimidazole (26 mg, 0.2 mmol), cadmium acetate dihydrate (27 mg, 0.1 mmol). and 0.2 mmol of either Na(dca) [for

Figure 5
Part of the crystal structure of compound (I) showing the formation of a hydrogen-bonded sheet of $R_2^2(20)$ rings lying parallel to (101). Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms have been omitted.

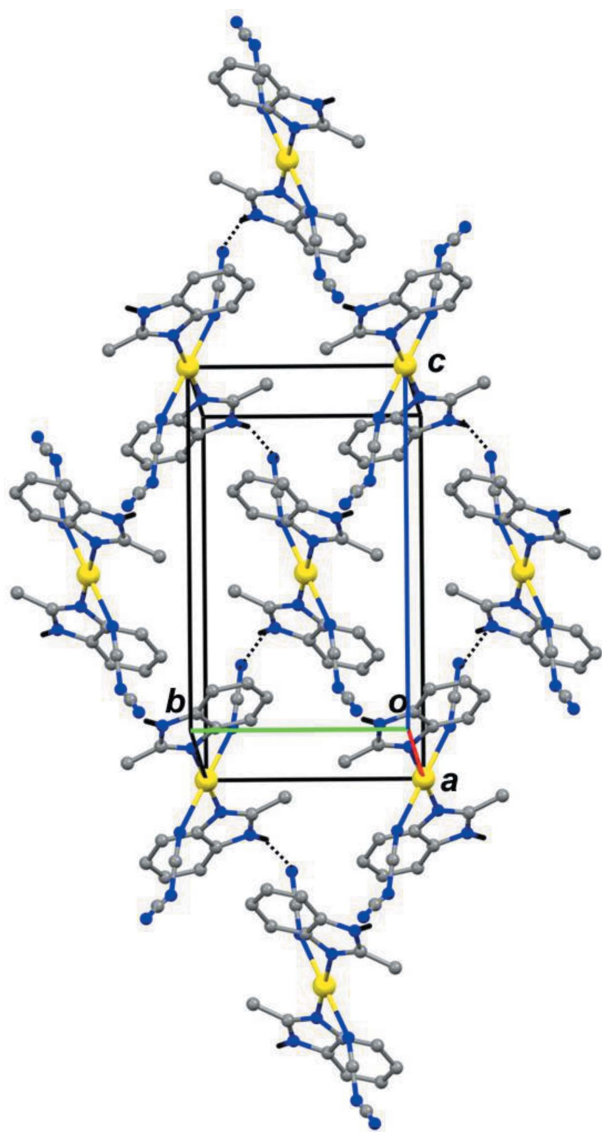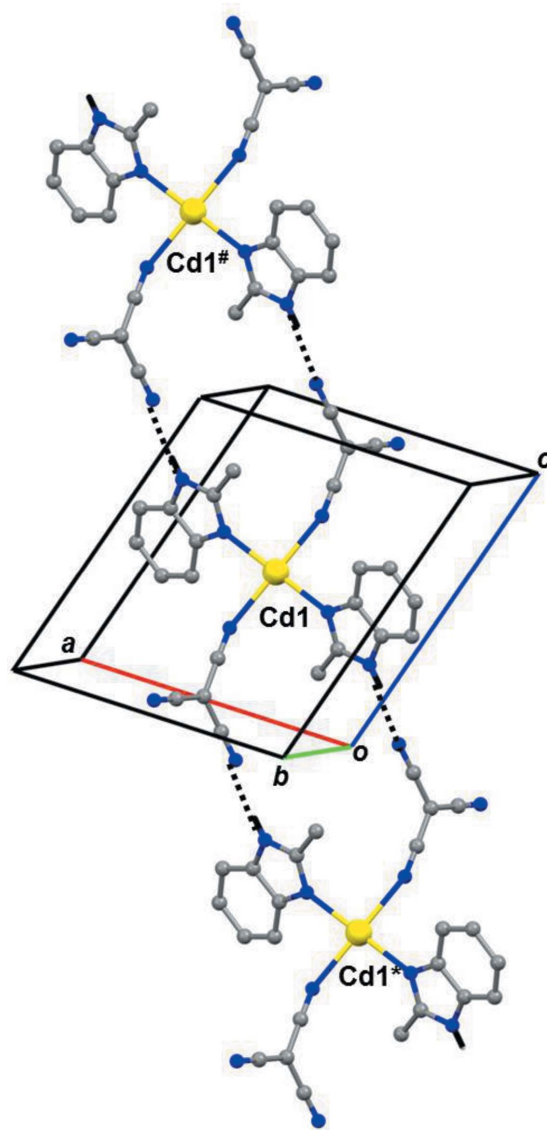**Figure 6**
Part of the crystal structure of compound (II) showing the formation of a chain of $R_2^2(20)$ rings running parallel to [101]. Hydrogen bonds are drawn as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms have been omitted. The Cd atoms marked with an asterisk (*) or a hash (#) are at $(-1/2, 1/2, -1/2)$ and $(3/2, 1/2, 3/2)$, respectively.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$[Cd(C_2N_3)_2(C_8H_8N_2)_2]$	$[Cd(C_4N_3)_2(C_8H_8N_2)_2]$
M_r	508.84	556.88
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
Temperature (K)	297	300
a, b, c (Å)	9.3472 (2), 8.2386 (2), 13.7448 (4)	9.4395 (4), 12.1219 (5), 10.9675 (5)
β (°)	101.908 (1)	107.342 (2)
V (Å³)	1035.68 (5)	1197.91 (9)
Z	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.09	0.95
Crystal size (mm)	$0.50 \times 0.34 \times 0.21$	$0.48 \times 0.36 \times 0.22$
Data collection		
Diffractometer	Rigaku Oxford Diffraction Xcalibur, Eos, Gemini	Rigaku Oxford Diffraction Xcalibur, Eos, Gemini
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.613, 0.796	0.627, 0.812
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	47562, 3954, 3176	41742, 3664, 2869
R_{int}	0.057	0.050
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.770	0.715
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.060, 1.10	0.023, 0.060, 1.15
No. of reflections	3954	3664
No. of parameters	147	165
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.37, −0.39	0.36, −0.32

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXS86* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2020).

(I)] or K(tcm) [for (II)] in a mixture of water and ethanol (3:1 v/v, 20 ml) was sealed in a Teflon-lined autoclave and heated at 438 K for 2 days. After cooling to room temperature at a rate of 10 K h^{-1}, yellow crystals were collected by filtration. Compound (I): yield 40%; analysis, found C 47.1, H 3.3, N 27.4%; $C_{20}H_{16}CdN_{10}$ requires C 47.2, H 3.2, N 27.5%. Compound (II): yield 45%; analysis, found C 51.5, H 3.1, N 24.9%; $C_{24}H_{16}CdN_{10}$ requires C 51.8, H 2.9, N 25.2%.

6. Refinement

Crystal data, data collection and refinement details are summarized in Table 3. All H atoms were located in difference maps. The H atoms bonded to C atoms were then treated as riding atoms in geometrically idealized positions with C—H distances of 0.93 Å (aromatic) or 0.96 Å (methyl), and with $U_{iso}(H) = kU_{eq}(C)$, where $k = 1.5$ for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for the other H atoms bonded to C atoms. For the H atoms bonded to N atoms, the atomic coordinates were refined with $U_{iso}(H) = 1.2U_{eq}(N)$, giving N—H distances of 0.79 (2) Å in (I) and 0.80 (3) Å in (II).

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supporting information

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Computing details

For both structures, data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2020); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2020).

Poly[*trans*,*trans*,*trans*-bis(μ-dicyanamido-$\kappa^2 N^1:N^3$)bis(2-methylbenzimidazole-κN)cadmium(II)] (I)

Crystal data

$[Cd(C_2N_3)_2(C_8H_8N_2)_2]$	$F(000) = 508$
$M_r = 508.84$	$D_x = 1.632$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.3472$ (2) Å	Cell parameters from 3954 reflections
$b = 8.2386$ (2) Å	$\theta = 2.4$–33.4°
$c = 13.7448$ (4) Å	$\mu = 1.09$ mm^{-1}
$\beta = 101.908$ (1)°	$T = 297$ K
$V = 1035.68$ (5) Å^3	Block, yellow
$Z = 2$	$0.50 \times 0.34 \times 0.21$ mm

Data collection

Rigaku Oxford Diffraction Xcalibur, Eos, Gemini diffractometer	47562 measured reflections
	3954 independent reflections
	3176 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed X-raytube	$R_{int} = 0.057$
Graphite monochromator	$\theta_{max} = 33.2°$, $\theta_{min} = 2.4°$
ω scans	$h = -14 \rightarrow 13$
Absorption correction: multi-scan	$k = -12 \rightarrow 12$
(CrysAlis PRO; Rigaku OD, 2015)	$l = -21 \rightarrow 21$
$T_{min} = 0.613$, $T_{max} = 0.796$	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Primary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.021$	
$wR(F^2) = 0.060$	Hydrogen site location: mixed
$S = 1.10$	H atoms treated by a mixture of independent and constrained refinement
3954 reflections	
147 parameters	

$w = 1/[\sigma^2(F_o^2) + (0.0235P)^2 + 0.3418P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}

$\Delta\rho_{min} = -0.39$ e Å^{-3}
Extinction correction: SHELXL,
  $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0321 (14)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.5000	0.5000	0.5000	0.02892 (5)
N1	0.09686 (13)	0.32891 (17)	0.59585 (11)	0.0397 (3)
H1	0.042 (2)	0.258 (2)	0.6014 (15)	0.048*
C2	0.21647 (14)	0.31228 (17)	0.55561 (11)	0.0341 (3)
N3	0.29030 (12)	0.44940 (16)	0.55912 (9)	0.0309 (2)
C3A	0.21417 (14)	0.56257 (18)	0.60516 (10)	0.0305 (2)
C4	0.24340 (16)	0.72464 (19)	0.63016 (11)	0.0381 (3)
H4	0.3243	0.7773	0.6153	0.046*
C5	0.1469 (2)	0.8046 (2)	0.67824 (13)	0.0471 (4)
H5	0.1636	0.9130	0.6957	0.056*
C6	0.0256 (2)	0.7261 (2)	0.70091 (15)	0.0557 (5)
H6	−0.0362	0.7834	0.7335	0.067*
C7	−0.00496 (19)	0.5667 (3)	0.67648 (15)	0.0518 (4)
H7	−0.0863	0.5148	0.6912	0.062*
C7A	0.09181 (16)	0.48644 (17)	0.62846 (12)	0.0358 (3)
C21	0.2554 (2)	0.1554 (2)	0.51506 (15)	0.0495 (4)
H21A	0.3303	0.1031	0.5631	0.074*
H21B	0.2906	0.1745	0.4552	0.074*
H21C	0.1705	0.0870	0.5006	0.074*
N31	0.34628 (14)	0.34457 (19)	0.16293 (10)	0.0433 (3)
C32	0.37029 (14)	0.36394 (18)	0.25940 (11)	0.0348 (3)
N32	0.40344 (15)	0.3836 (2)	0.34355 (11)	0.0520 (4)
C33	0.21918 (15)	0.29123 (17)	0.11597 (10)	0.0331 (3)
N33	0.11198 (15)	0.24538 (19)	0.06690 (10)	0.0462 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.02177 (6)	0.04283 (9)	0.02187 (7)	0.00136 (5)	0.00381 (4)	0.00049 (5)
N1	0.0306 (5)	0.0428 (7)	0.0481 (7)	−0.0057 (5)	0.0140 (5)	0.0036 (6)
C2	0.0299 (6)	0.0372 (6)	0.0360 (7)	−0.0018 (5)	0.0089 (5)	0.0005 (5)
N3	0.0273 (5)	0.0350 (5)	0.0322 (5)	−0.0006 (4)	0.0101 (4)	−0.0019 (4)
C3A	0.0271 (5)	0.0375 (6)	0.0278 (5)	0.0024 (5)	0.0080 (4)	0.0002 (5)
C4	0.0374 (7)	0.0412 (7)	0.0367 (7)	−0.0002 (6)	0.0102 (5)	−0.0035 (6)
C5	0.0542 (9)	0.0460 (8)	0.0430 (8)	0.0081 (7)	0.0146 (7)	−0.0079 (7)

C6	0.0549 (10)	0.0642 (11)	0.0558 (10)	0.0162 (8)	0.0294 (9)	−0.0033 (9)
C7	0.0416 (8)	0.0623 (11)	0.0598 (11)	0.0081 (8)	0.0295 (8)	0.0043 (9)
C7A	0.0278 (6)	0.0457 (8)	0.0360 (7)	0.0020 (5)	0.0114 (5)	0.0036 (5)
C21	0.0499 (9)	0.0379 (8)	0.0634 (11)	−0.0046 (7)	0.0182 (8)	−0.0075 (7)
N31	0.0344 (6)	0.0633 (8)	0.0321 (6)	−0.0085 (6)	0.0069 (5)	−0.0073 (6)
C32	0.0269 (5)	0.0421 (7)	0.0347 (7)	−0.0012 (5)	0.0049 (5)	−0.0068 (5)
N32	0.0392 (7)	0.0806 (11)	0.0346 (7)	−0.0079 (7)	0.0037 (5)	−0.0142 (7)
C33	0.0358 (6)	0.0366 (6)	0.0279 (6)	−0.0022 (5)	0.0088 (5)	−0.0043 (5)
N33	0.0417 (6)	0.0580 (8)	0.0385 (7)	−0.0116 (6)	0.0075 (5)	−0.0127 (6)

Geometric parameters (Å, º)

Cd1—N3	2.3094 (11)	C4—H4	0.9300
Cd1—N3^i	2.3094 (11)	C5—C6	1.395 (3)
Cd1—N32	2.3574 (14)	C5—H5	0.9300
Cd1—N32^i	2.3574 (14)	C6—C7	1.371 (3)
Cd1—N33^{ii}	2.3729 (14)	C6—H6	0.9300
Cd1—N33^{iii}	2.3729 (14)	C7—C7A	1.392 (2)
N1—C2	1.3528 (18)	C7—H7	0.9300
N1—C7A	1.377 (2)	C21—H21A	0.9600
N1—H1	0.79 (2)	C21—H21B	0.9600
C2—N3	1.3194 (18)	C21—H21C	0.9600
C2—C21	1.482 (2)	N31—C33	1.3056 (18)
N3—C3A	1.4008 (18)	N31—C32	1.3081 (19)
C3A—C4	1.392 (2)	C32—N32	1.1455 (19)
C3A—C7A	1.3983 (19)	C33—N33	1.1501 (18)
C4—C5	1.389 (2)	N33—Cd1^{iv}	2.3729 (14)
N3—Cd1—N3^i	180.0	C5—C4—C3A	117.30 (14)
N3—Cd1—N32	93.12 (5)	C5—C4—H4	121.3
N3^i—Cd1—N32	86.88 (5)	C3A—C4—H4	121.3
N3—Cd1—N32^i	86.88 (5)	C4—C5—C6	121.57 (16)
N3^i—Cd1—N32^i	93.12 (5)	C4—C5—H5	119.2
N32—Cd1—N32^i	180.00 (4)	C6—C5—H5	119.2
N3—Cd1—N33^{ii}	92.78 (5)	C7—C6—C5	121.85 (15)
N3^i—Cd1—N33^{ii}	87.22 (5)	C7—C6—H6	119.1
N32—Cd1—N33^{ii}	93.56 (6)	C5—C6—H6	119.1
N32^i—Cd1—N33^{ii}	86.44 (6)	C6—C7—C7A	116.61 (16)
N3—Cd1—N33^{iii}	87.22 (5)	C6—C7—H7	121.7
N3^i—Cd1—N33^{iii}	92.78 (5)	C7A—C7—H7	121.7
N32—Cd1—N33^{iii}	86.44 (6)	N1—C7A—C7	132.17 (15)
N32^i—Cd1—N33^{iii}	93.56 (6)	N1—C7A—C3A	105.29 (12)
N33^{ii}—Cd1—N33^{iii}	180.0	C7—C7A—C3A	122.53 (15)
C2—N1—C7A	108.37 (12)	C2—C21—H21A	109.5
C2—N1—H1	124.9 (14)	C2—C21—H21B	109.5
C7A—N1—H1	126.7 (14)	H21A—C21—H21B	109.5
N3—C2—N1	111.63 (13)	C2—C21—H21C	109.5
N3—C2—C21	126.37 (13)	H21A—C21—H21C	109.5

N1—C2—C21	121.99 (13)	H21B—C21—H21C	109.5
C2—N3—C3A	106.01 (11)	C33—N31—C32	119.37 (13)
C2—N3—Cd1	128.11 (9)	N32—C32—N31	174.18 (15)
C3A—N3—Cd1	125.87 (9)	C32—N32—Cd1	162.06 (15)
C4—C3A—C7A	120.14 (13)	N33—C33—N31	173.85 (15)
C4—C3A—N3	131.15 (13)	C33—N33—Cd1^{iv}	140.21 (14)
C7A—C3A—N3	108.70 (13)		
C7A—N1—C2—N3	−0.36 (18)	C3A—C4—C5—C6	0.1 (3)
C7A—N1—C2—C21	178.79 (15)	C4—C5—C6—C7	−0.4 (3)
N1—C2—N3—C3A	0.33 (17)	C5—C6—C7—C7A	0.5 (3)
C21—C2—N3—C3A	−178.78 (15)	C2—N1—C7A—C7	−178.60 (19)
N1—C2—N3—Cd1	−178.65 (10)	C2—N1—C7A—C3A	0.23 (17)
C21—C2—N3—Cd1	2.2 (2)	C6—C7—C7A—N1	178.30 (19)
C2—N3—C3A—C4	178.46 (15)	C6—C7—C7A—C3A	−0.4 (3)
Cd1—N3—C3A—C4	−2.5 (2)	C4—C3A—C7A—N1	−178.84 (13)
C2—N3—C3A—C7A	−0.17 (16)	N3—C3A—C7A—N1	−0.03 (17)
Cd1—N3—C3A—C7A	178.83 (10)	C4—C3A—C7A—C7	0.1 (2)
C7A—C3A—C4—C5	0.0 (2)	N3—C3A—C7A—C7	178.93 (16)
N3—C3A—C4—C5	−178.51 (15)		

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

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N31^{v}	0.79 (2)	2.327 (19)	3.0447 (19)	151.3 (17)

Symmetry code: (v) x−1/2, −y+1/2, z+1/2.

Poly[*trans*,*trans*,*trans*-bis(2-methylbenzimidazole-κN)bis(μ-tricyanomethanido-$\kappa^2 N$:*N′*)cadmium(II)] (II)

Crystal data

[Cd(C₄N₃)₂(C₈H₈N₂)₂]

$[Cd(C_4N_3)_2(C_8H_8N_2)_2]$
$M_r = 556.88$
Monoclinic, $P2_1/c$
$a = 9.4395\ (4)$ Å
$b = 12.1219\ (5)$ Å
$c = 10.9675\ (5)$ Å
$\beta = 107.342\ (2)°$
$V = 1197.91\ (9)$ Å³
$Z = 2$

$F(000) = 556$
$D_x = 1.544$ Mg m⁻³
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3664 reflections
$\theta = 2.3–30.6°$
$\mu = 0.95$ mm⁻¹
$T = 300$ K
Block, yellow
$0.48 \times 0.36 \times 0.22$ mm

Data collection

Rigaku Oxford Diffraction Xcalibur, Eos, Gemini
    diffractometer
Radiation source: fine-focus sealed X-raytube
Graphite monochromator
ω scans
Absorption correction: multi-scan
    (CrysAlis PRO; Rigaku OD, 2015)
$T_{min} = 0.627$, $T_{max} = 0.812$

41742 measured reflections
3664 independent reflections
2869 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 30.6°$, $\theta_{min} = 2.3°$
$h = −13 \rightarrow 13$
$k = −17 \rightarrow 17$
$l = −15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.060$
$S = 1.15$
3664 reflections
165 parameters
0 restraints
Primary atom site location: difference Fourier map
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0175P)^2 + 0.6078P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0182 (9)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.5000	0.5000	0.5000	0.02855 (6)
N1	0.01561 (17)	0.54588 (14)	0.31770 (16)	0.0392 (3)
H1	−0.057 (3)	0.5291 (19)	0.262 (2)	0.047*
C2	0.15085 (19)	0.50291 (14)	0.32869 (16)	0.0329 (3)
N3	0.25220 (15)	0.53853 (12)	0.43361 (13)	0.0307 (3)
C3A	0.17551 (17)	0.60782 (13)	0.49471 (16)	0.0306 (3)
C4	0.2229 (2)	0.66514 (14)	0.60956 (18)	0.0377 (4)
H4	0.3207	0.6604	0.6614	0.045*
C5	0.1199 (3)	0.72950 (16)	0.6442 (2)	0.0492 (5)
H5	0.1497	0.7695	0.7199	0.059*
C6	−0.0273 (3)	0.73568 (18)	0.5684 (3)	0.0544 (5)
H6	−0.0931	0.7807	0.5939	0.065*
C7	−0.0774 (2)	0.67687 (17)	0.4569 (2)	0.0495 (5)
H7	−0.1763	0.6794	0.4074	0.059*
C7A	0.02632 (19)	0.61325 (14)	0.42113 (18)	0.0359 (4)
C21	0.1739 (2)	0.42717 (19)	0.2308 (2)	0.0498 (5)
H21A	0.2681	0.3910	0.2635	0.075*
H21B	0.1723	0.4683	0.1557	0.075*
H21C	0.0962	0.3730	0.2097	0.075*
C31	0.43763 (19)	0.62012 (14)	0.06929 (16)	0.0331 (3)
C32	0.48307 (19)	0.57340 (14)	0.19170 (17)	0.0335 (3)
N32	0.5172 (2)	0.53331 (16)	0.29060 (16)	0.0463 (4)
C33	0.49794 (19)	0.72007 (15)	0.04552 (18)	0.0366 (4)
N33	0.5467 (2)	0.80337 (14)	0.02750 (18)	0.0493 (4)
C34	0.3206 (2)	0.57001 (16)	−0.02502 (18)	0.0399 (4)
N34	0.2261 (2)	0.5271 (2)	−0.09988 (19)	0.0639 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.02870 (9)	0.02952 (9)	0.02575 (9)	0.00129 (6)	0.00556 (6)	−0.00031 (6)
N1	0.0298 (7)	0.0451 (8)	0.0354 (8)	−0.0072 (6)	−0.0016 (6)	0.0055 (7)
C2	0.0320 (7)	0.0355 (8)	0.0283 (7)	−0.0068 (7)	0.0046 (6)	0.0005 (7)
N3	0.0299 (6)	0.0320 (6)	0.0280 (7)	−0.0027 (5)	0.0053 (5)	−0.0021 (5)
C3A	0.0289 (7)	0.0291 (7)	0.0336 (8)	−0.0025 (6)	0.0088 (6)	0.0029 (6)
C4	0.0397 (9)	0.0358 (8)	0.0393 (10)	−0.0030 (7)	0.0143 (7)	−0.0021 (7)
C5	0.0593 (12)	0.0394 (10)	0.0567 (13)	−0.0013 (9)	0.0295 (10)	−0.0071 (9)
C6	0.0532 (12)	0.0443 (11)	0.0757 (16)	0.0099 (9)	0.0345 (12)	0.0052 (10)
C7	0.0341 (9)	0.0478 (11)	0.0676 (14)	0.0077 (8)	0.0167 (9)	0.0170 (10)
C7A	0.0309 (8)	0.0356 (8)	0.0398 (9)	−0.0030 (6)	0.0085 (7)	0.0083 (7)
C21	0.0488 (11)	0.0607 (12)	0.0369 (10)	−0.0145 (10)	0.0082 (9)	−0.0151 (9)
C31	0.0338 (8)	0.0333 (8)	0.0288 (8)	0.0009 (6)	0.0044 (6)	0.0015 (6)
C32	0.0328 (8)	0.0354 (8)	0.0312 (9)	−0.0003 (6)	0.0077 (6)	−0.0030 (6)
N32	0.0488 (9)	0.0564 (9)	0.0313 (8)	−0.0008 (8)	0.0085 (7)	0.0050 (7)
C33	0.0358 (8)	0.0359 (8)	0.0353 (9)	0.0049 (7)	0.0065 (7)	0.0018 (7)
N33	0.0497 (9)	0.0371 (8)	0.0577 (11)	0.0016 (7)	0.0107 (8)	0.0084 (8)
C34	0.0366 (9)	0.0477 (10)	0.0319 (9)	−0.0004 (8)	0.0050 (7)	0.0055 (7)
N34	0.0508 (11)	0.0863 (15)	0.0426 (11)	−0.0169 (10)	−0.0043 (9)	−0.0005 (10)

Geometric parameters (Å, º)

Cd1—N3	2.2813 (14)	C5—C6	1.392 (3)
Cd1—N3^i	2.2813 (14)	C5—H5	0.9300
Cd1—N32	2.3845 (17)	C6—C7	1.372 (3)
Cd1—N32^i	2.3845 (17)	C6—H6	0.9300
Cd1—N33^{ii}	2.4265 (17)	C7—C7A	1.391 (3)
Cd1—N33^{iii}	2.4265 (17)	C7—H7	0.9300
N1—C2	1.351 (2)	C21—H21A	0.9600
N1—C7A	1.377 (3)	C21—H21B	0.9600
N1—H1	0.80 (3)	C21—H21C	0.9600
C2—N3	1.330 (2)	C31—C33	1.396 (2)
C2—C21	1.477 (3)	C31—C32	1.401 (2)
N3—C3A	1.403 (2)	C31—C34	1.407 (2)
C3A—C4	1.391 (2)	C32—N32	1.144 (2)
C3A—C7A	1.400 (2)	C33—N33	1.151 (2)
C4—C5	1.386 (3)	N33—Cd1^{iv}	2.4264 (17)
C4—H4	0.9300	C34—N34	1.141 (3)
N3—Cd1—N3^i	180.0	C5—C4—H4	121.1
N3—Cd1—N32	90.89 (6)	C3A—C4—H4	121.1
N3^i—Cd1—N32	89.11 (6)	C4—C5—C6	121.6 (2)
N3—Cd1—N32^i	89.11 (6)	C4—C5—H5	119.2
N3^i—Cd1—N32^i	90.89 (6)	C6—C5—H5	119.2
N32—Cd1—N32^i	180.0	C7—C6—C5	121.45 (19)
N3—Cd1—N33^{ii}	88.27 (6)	C7—C6—H6	119.3

N3^i—Cd1—N33^{ii}	91.73 (6)	C5—C6—H6	119.3
N32—Cd1—N33^{ii}	83.76 (6)	C6—C7—C7A	117.05 (19)
N32^i—Cd1—N33^{ii}	96.24 (6)	C6—C7—H7	121.5
N3—Cd1—N33^{iii}	91.73 (6)	C7A—C7—H7	121.5
N3^i—Cd1—N33^{iii}	88.27 (6)	N1—C7A—C7	132.53 (18)
N32—Cd1—N33^{iii}	96.24 (6)	N1—C7A—C3A	105.14 (15)
N32^i—Cd1—N33^{iii}	83.76 (6)	C7—C7A—C3A	122.33 (18)
N33^{ii}—Cd1—N33^{iii}	180.0	C2—C21—H21A	109.5
C2—N1—C7A	108.66 (15)	C2—C21—H21B	109.5
C2—N1—H1	123.1 (17)	H21A—C21—H21B	109.5
C7A—N1—H1	128.1 (17)	C2—C21—H21C	109.5
N3—C2—N1	111.65 (16)	H21A—C21—H21C	109.5
N3—C2—C21	127.35 (17)	H21B—C21—H21C	109.5
N1—C2—C21	121.00 (16)	C33—C31—C32	120.29 (16)
C2—N3—C3A	105.49 (14)	C33—C31—C34	120.81 (16)
C2—N3—Cd1	127.90 (12)	C32—C31—C34	118.62 (16)
C3A—N3—Cd1	126.59 (10)	N32—C32—C31	178.2 (2)
C4—C3A—C7A	119.70 (16)	C32—N32—Cd1	154.77 (16)
C4—C3A—N3	131.24 (15)	N33—C33—C31	178.8 (2)
C7A—C3A—N3	109.05 (15)	C33—N33—Cd1^{iv}	144.66 (16)
C5—C4—C3A	117.83 (18)	N34—C34—C31	178.4 (2)

C7A—N1—C2—N3	−0.5 (2)	C3A—C4—C5—C6	1.1 (3)
C7A—N1—C2—C21	−179.83 (17)	C4—C5—C6—C7	1.1 (3)
N1—C2—N3—C3A	0.92 (19)	C5—C6—C7—C7A	−1.8 (3)
C21—C2—N3—C3A	−179.79 (18)	C2—N1—C7A—C7	179.92 (19)
N1—C2—N3—Cd1	−177.68 (11)	C2—N1—C7A—C3A	−0.17 (19)
C21—C2—N3—Cd1	1.6 (3)	C6—C7—C7A—N1	−179.71 (19)
C2—N3—C3A—C4	177.72 (18)	C6—C7—C7A—C3A	0.4 (3)
Cd1—N3—C3A—C4	−3.7 (3)	C4—C3A—C7A—N1	−178.17 (15)
C2—N3—C3A—C7A	−1.01 (18)	N3—C3A—C7A—N1	0.73 (18)
Cd1—N3—C3A—C7A	177.61 (11)	C4—C3A—C7A—C7	1.7 (3)
C7A—C3A—C4—C5	−2.4 (3)	N3—C3A—C7A—C7	−179.35 (16)
N3—C3A—C4—C5	178.93 (18)		

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

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯N34^v	0.80 (2)	2.12 (2)	2.906 (3)	171 (3)

Symmetry code: (v) −x, −y+1, −z.