Poly[[aquabis(μ_2-isonicotinato-$\kappa^3 N$:O,O')cadmium(II)] 1,4-di-3-pyridyl-2,3-diaza-1,3-butadiene hemisolvate]

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The title compound, $\{[Cd(C_6H_4NO_2)_2(H_2O)]\cdot 0.5C_{12}H_{10}N_4\}_n$, presents an intricate three-dimensional network with cavities traversing it in three orthogonal directions, where the (disordered) guest molecules lodge. The compound is a member of a series of coordination polymers presenting the same main host framework but with guests of variable size and geometry, to which the flexible skeleton seems to adapt. The disorder in the structure is explained in terms of an apparently well defined specificity in the position/orientation of the guest molecules, as determined by the main framework.

Comment

Isonicotinate is a versatile ligand, taking part in many coordination polymers with interesting structural features. In particular, $\{[Cd(isonicotinate)_2(H_2O)]\cdot X\}_n$ (X = guest molecules) defines an isostructural family presenting a three-dimensional $[Cd(isonicotinate)_2(H_2O)]_n$ porous framework (*Pbca* symmetry), with two interpenetrating diamondoid substructures ($P2_12_12_1$ symmetry) related to each other by an inversion centre. The empty space in the framework is occupied by guest molecules. Previously reported structures in the series correspond to X = dimethylformamide (Liao *et al.*, 2004), (1), pyrazine, (2) (Evans *et al.*, 1999), and biformyl, (3) (Liu *et al.*, 2006). We present here a slightly different assembly with a metal–guest ratio of 1:0.5, the title complex, $\{[Cd(isonicotinate)_2(H_2O)]\cdot 0.5(3pa)\}_n$ (3pa is 1,4-di-3-pyridyl-2,3-diaza-1,3-butadiene), (4), where the porous host network contains the large bipyridyl guest molecule in a disordered fashion (see discussion below, and *Experimental* section for refinement details).

As in the rest of the series, the basic unit of (4) (Fig. 1) is composed of Cd^{II} ions bridged to four nearest neighbours by isonicotinate ligands, each of which uses both carboxylate O

atoms to chelate to one side of the bridge and the pyridyl N atom to bind to the other. Thus, each Cd^{II} ion is seven-coordinated in the form of a pentagonal bipyramid, with four carboxylate O atoms from two isonicotinate ligands and one pyridyl N atom from a third isonicotinate ligand defining the equatorial plane, while the N atom from a fourth isonicotinate ligand and the aqua ligand determine the apical axis (Table 1). This results in the formation of two interpenetrated $P2_12_12_1$ substructures defining the main *Pbca* framework, with large tunnels traversing it in three orthogonal directions (Fig. 2).


(4)
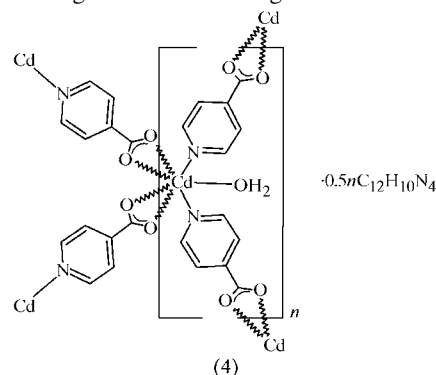
Stabilization of the framework is modestly enhanced by four nonconventional hydrogen bonds involving the four C—H groups of one single ligand (Cj2—Hj2, j = 2, 3, 5 or 6) as donors and the carboxylate O atoms of both ligands as acceptors, as well as by two strong hydrogen bonds formed by the aqua ligand: that involving atom H1WA is directed towards the main framework, while the second, involving atom H1WB, is a diffuse interaction with the disordered 3pa molecule (Table 2).

Although interpenetration reduces the volume of the overall empty space amenable to filling by guest species, it appears that the framework is flexible enough to adapt to the requirements of a diversity of guests. This can be inferred from the variations in cell dimensions displayed by the four known structures in the series, where a direct correlation with the guest size and geometry can be detected (Table 3).

Finally, it is interesting to compare the present structure, (4), with the pyrazine analogue, (2). For convenience, we will describe this latter structure with the aromatic guests disposed along those channels parallel to the *b* axis, with their planar face nearly perpendicular to *a*, and with two rings per cell in each of the four available channels. Fig. 3(*a*) depicts this situation, with the left-hand side showing the column contents and the rightmost part of the figure displaying a view down *a*, with the pyrazine rings highlighted. In (4), the much longer 3pa units dispose along *b* in such a way as to have the orientation of the aromatic rings also perpendicular to *a* [and thus parallel to the pyrazines in (2)]. Surprisingly, if only the rings in the 3pa molecule are considered, disregarding the connecting chains in between, the packing of these disordered guests (with individual site occupancy factors of 0.25) ends up in two conglomerates per column within each cell. These groups are made up of four rings each, nearly parallel to each other and almost overlapping [maximum deviation of the centre of gravity from the centroid = 0.60 (2) Å].

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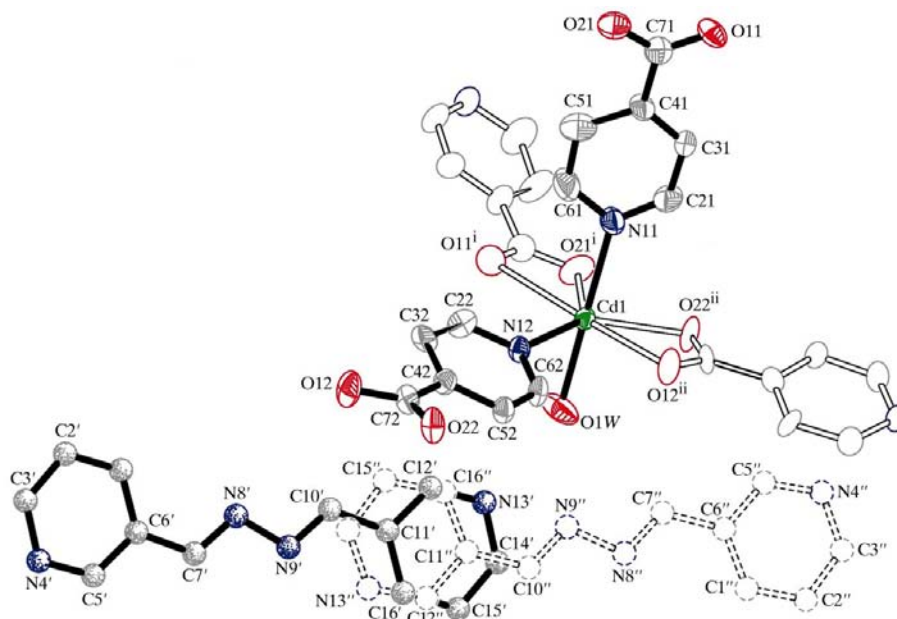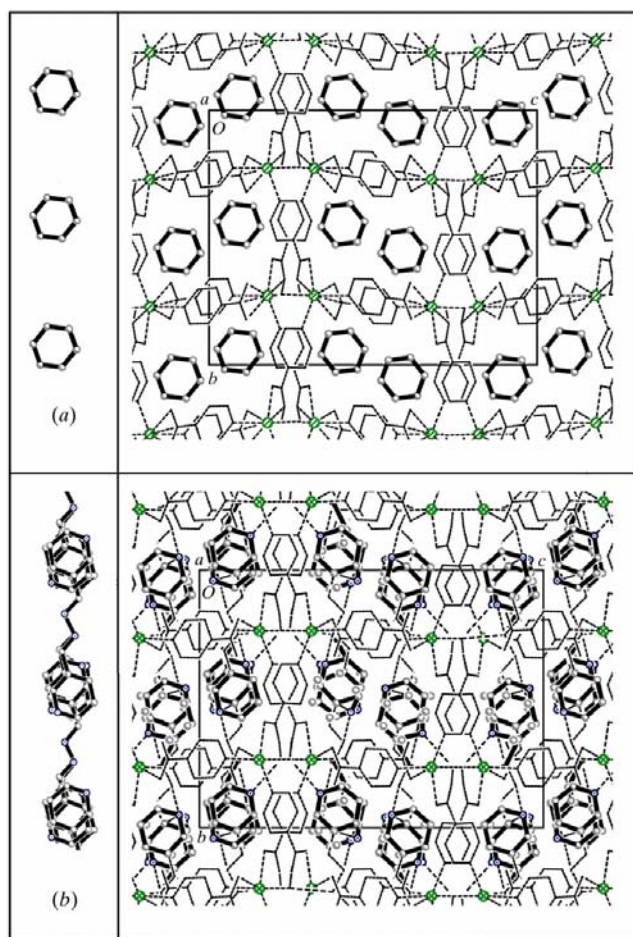
Figure 1
The structure of (4), showing the Cd environment and the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. H atoms have been omitted for clarity. Also shown is the uncoordinated 3pa molecule, which was modelled isotropically due to disorder. Symmetry codes are as in Table 1.
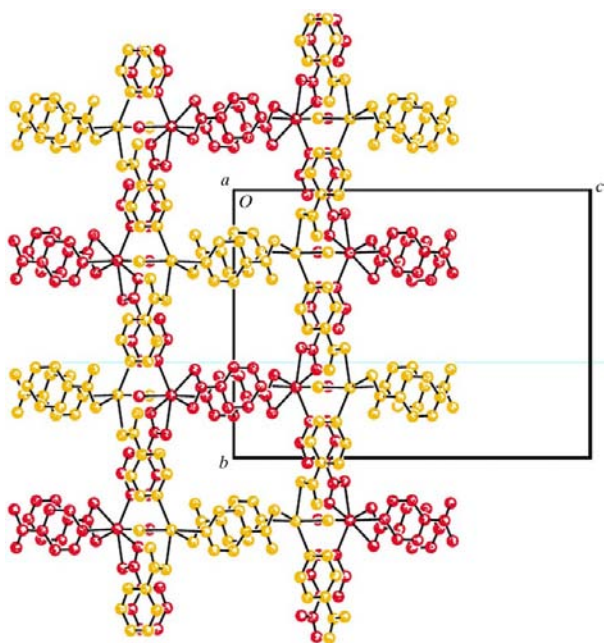
Figure 2
A schematic view of the main framework along the a axis, showing the two interpenetrating networks. The guest molecules (omitted for clarity) are disordered along the b axis (top to bottom).

In addition, the group presents a (global) population of $4 \times 0.25 = 1.00$, the equivalent of a complete ring. The locations in which these groups fall, as measured by their centroids, are almost coincident with those in (2) [differences in fractional coordinates between the centres of gravity of pyrazine and the centroid of 3pa: $\Delta(x)$ 0.03695; $\Delta(y)$ 0.00609; $\Delta(z)$ 0.00348]. Fig. 3(b) illustrates this, in parallel to that shown for (2). Thus, the left-hand side presents the (disor-

Figure 3
A comparison of (a) structure (2) [guest = one full ordered pyrazine per Cd atom] and (b) structure (4) [guest = one half of a disordered 3pa per Cd atom]. See *Comment* for details.

dered) column content, drawn in full so as to visualize the way in which the guests dispose, while the right-hand side exhibits, in turn, the view down a, with only the aromatic rings highlighted in order to emphasize the similarities with the pyrazine case.

In summary, the highly disordered 3pa structure, (4), reproduces, on average but with a surprising spatial match, the ordered pyrazine structure, and the leading factor in this similarity seems to be the planar aromatic rings lodged in the cavities. The conclusion which can be drawn from this is that the guest positions are not weakly defined, but instead appear to be firmly determined by the host environment in combination with the particular guest shape, in this case the planar aromatic ring, irrespective of its being isolated [pyrazine in (2)] or part of a more complex molecule [3pa in (4)].

Experimental

For the synthesis of the title compound, $Cd(NO_3)_2 \cdot 4H_2O$ (0.154 g, 0.5 mmol), isonicotinic acid (0.123 g, 1.0 mmol), 3pa (0.053 g, 0.25 mmol) and 0.1 M NaOH solution (10.0 ml, 1.0 mmol) were placed in a Parr Teflon-lined stainless steel vessel (23 ml). The vessel was sealed and heated to 383 K for 24 h, and then the reactor was cooled slowly to ambient temperature. The resulting yellow block-shaped crystals of (4), which were suitable for X-ray structure analysis, were filtered off and dried (yield: 80%, based on Cd).

Crystal data

$[Cd(C_6H_4NO_2)_2(H_2O)] \cdot$	$V = 3805$ (3) Å^3
$0.5C_{12}H_{10}N_4$	$Z = 2$
$M_r = 1919.00$	Mo $K\alpha$ radiation
Orthorhombic, $Pbca$	$\mu = 1.19$ mm^{-1}
$a = 11.882$ (7) Å	$T = 294$ (2) K
$b = 15.518$ (5) Å	$0.32 \times 0.24 \times 0.20$ mm
$c = 20.637$ (8) Å	

Data collection

Rigaku AFC-6S diffractometer	1889 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan	$R_{int} = 0.064$
(North *et al.*, 1968)	3 standard reflections
$T_{min} = 0.72$, $T_{max} = 0.79$	every 150 reflections
4656 measured reflections	intensity decay: <2%
3735 independent reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$	H atoms treated by a mixture of
$wR(F^2) = 0.186$	independent and constrained
$S = 1.00$	refinement
3735 reflections	$\Delta\rho_{max} = 0.82$ e Å^{-3}
217 parameters	$\Delta\rho_{min} = -1.45$ e Å^{-3}
23 restraints	

Table 1
Selected bond lengths (Å).

Cd1—O1W	2.285 (8)	Cd1—N11	2.370 (8)
Cd1—N12	2.331 (7)	Cd1—O11^{ii}	2.557 (7)
Cd1—O22^i	2.352 (6)	Cd1—O12^i	2.574 (7)
Cd1—O21^{ii}	2.336 (8)		

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

H atoms attached to carbon were placed in geometrically idealized positions, with C—H = 0.93 Å; those in the water molecule were found in a difference map and refined with restrained distances of O—H = 0.85 (3) Å and H···H = 1.35 (4) Å. In all cases, U_{iso}(H) values were set at $1.2U_{eq}$(carrier).

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$WA\cdots$O12^{iii}	0.85 (5)	1.98 (6)	2.739 (12)	148 (11)
O1W—H1$WB\cdots$N4$''^{iv}$	0.84 (2)	2.11 (4)	2.751 (17)	132.7 (18)
O1W—H1$WB\cdots$N8$'^{iii}$	0.84 (2)	1.85 (4)	2.66 (3)	161 (5)
O1W—H1$WB\cdots$N9$''$	0.84 (2)	1.93 (4)	2.741 (17)	161 (4)
O1W—H1$WB\cdots$N13$'$	0.84 (2)	2.27 (4)	2.968 (18)	139.9 (19)
C22—H22$\cdots$O11^{ii}	0.93	2.58	3.258 (11)	130
C32—H32$\cdots$O21^v	0.93	2.49	3.400 (13)	166
C52—H52$\cdots$O11^{vi}	0.93	2.55	3.356 (11)	145
C62—H62$\cdots$O12^i	0.93	2.41	3.087 (11)	129

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

Table 3
Comparison of cell dimensions in the $\{[Cd(isonicotinate)_2(H_2O)] \cdot X\}_n$ family (Å, Å^3).

a	b	c	V	Guest (X)	Reference
12.340 (1)	15.505 (1)	18.944 (1)	3624.4 (3)	DMF	(*a*)
12.181 (9)	15.354 (12)	18.785 (15)	3513 (5)	Biformyl	(*b*)
12.081 (5)	15.323 (5)	19.705 (3)	3647.7 (2)	Pyrazine	(*c*)
11.882 (7)	15.518 (5)	20.637 (8)	3805 (3)	3pa	(*d*)

References: (*a*) Liao *et al.* (2004); (*b*) Liu *et al.* (2006); (*c*) Evans *et al.* (1999); (*d*) this work.

The 3pa molecule appeared to be disordered over two sites, shifted along the crystallographic b direction (Fig. 1) and defining a kind of chain. Due to difficulties in the handling of the guest molecules (both moieties tended to deform on refinement), each of the two independent images was treated as a rigid body to which the coordinates of the free moiety [as taken from Dong *et al.* (2000)] were fitted. Their occupancy factors, when freely refined, converged very nearly to 0.25 and were all fixed at this value in the final stages of refinement. This treatment appears justified by the acceptably low maximum residual electron density found around the guest molecules after convergence ($\sim$0.68 e Å^{-3}).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3116). Services for accessing these data are described at the back of the journal.

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