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Poly[di-μ-aqua-μ-1,2-bis(pyridin-4-yl)ethene-κ^2N:N'-tetrakis(4-iodobenzoato-κ^2O,O')dicadmium]

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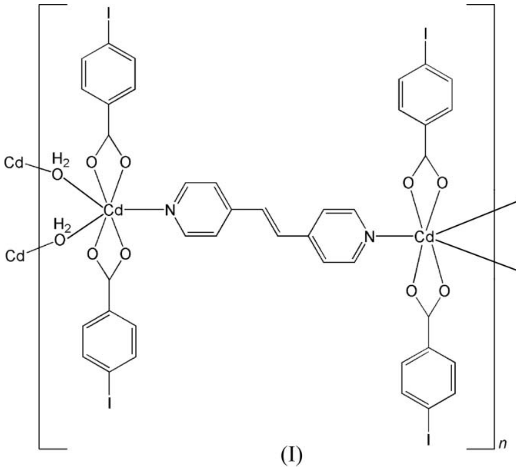
Colourless crystals of the title compound, $[Cd_2(C_7H_4IO_2)_4(C_{12}H_{10}N_2)(H_2O)_2]_n$, were obtained by the self-assembly of $Cd(NO_3)_2\cdot 4H_2O$, 1,2-bis(pyridin-4-yl)ethene (bpe) and 4-iodobenzoic acid (4-IBA). Each Cd^{II} atom is seven-coordinated in a pentagonal–bipyramidal coordination environment by four carboxylate O atoms from two different 4-IBA ligands, two O atoms from two water molecules and one N atom from a bpe ligand. The Cd^{II} centres are bridged by the aqua molecules and bpe ligands, which lie across centres of inversion, to give a two-dimensional net. Topologically, taking the Cd^{II} atoms as nodes and the μ-aqua and μ-bpe ligands as linkers, the two-dimensional structure can be simplified as a (6,3) network.

Comment

In recent years, coordination polymers have attracted much attention owing to their enormous variety of interesting framework topologies and their wide range of potential applications in adsorption, separation, catalysis, magnetism and luminescence (Chen *et al.*, 2006; Fang *et al.*, 2007; Yuan *et al.*, 2010; Zhao *et al.*, 2009). A comprehensive review of coordination polymers with O- or N-containing ligands showed that this field of research has witnessed tremendous growth (Batten & Robson, 1998). Previously, coordination polymers were usually constructed by metal ions and one type of ligand. However, the number of such coordination polymers is limited since the types of ligands are limited. Compared with complexes assembled by one type of ligand, the co-ligand assembly system, consisting of more linkers which are capable of providing more variability to build complicated and interesting structures, has been widely adopted for the generation of new compounds (Kitagawa *et al.*, 2004). As a result, a large number of co-ligand achitectures have been reported, most of which use multi-pyridinyl ligands in metal–carboxylate systems (Blatov *et al.*, 2004). The application of bis(pyridin-4-yl)-type ligands is an effective method of forming meaningful coordination networks because they can satisfy and even mediate the coordination needs of the metal centres.

To date, a large number of coordination polymers assembled from carboxylates and bis(pyridin-4-yl)-type ligands, as well as their derivatives, have been extensively investigated (Li *et al.*, 2009). These complexes exhibit extraordinary structural diversity and provide facile accessibility to functionalized new materials. If water is employed as the solvent to synthesize the aforementioned complexes, the water molecules usually function as bridges to link the metal centres to form new subunits (Liu *et al.*, 2010). We report herein the synthesis and structure of the title complex, (I), which was constructed from the mixed ligands of 4-iodobenzoate (IBA), 1,2-bis(pyridin-4-yl)ethene (bpe) and H_2O.



(I)

A segment of the polymeric structure of (I) lies acoss an inversion centre located at the centre of the bridging bpe ligand, so that the asymmetric unit is composed of one Cd^{II} atom, one μ-aqua ligand, two 4-IBA ligands and half of a μ-bpe ligand. As shown in Fig. 1, the symmetry-unique Cd^{II} atom is located in a pentagonal–bipyramidal environment, coordinated by four carboxylate O atoms from two different 4-IBA ligands, two O atoms from two water molecules and one N atom from a bpe ligand. Overall, each Cd^{II} atom is completely coordinated by one N atom and six O atoms. Such a coordination mode is different from those of the Cd atoms in $[Cd(CBA)_2(bpe)]_n$ (CBA is 4-chlorobenzoate; Liu *et al.*, 2011) and $[Cd(bpe)(CH_3COO)_2(H_2O)]_n$ (Nagarathinam & Vittal, 2008), which are coordinated by two N and five O atoms. The average Cd—O distance [2.374 (3) Å] is shorter than those in $[Cd(CBA)_2(bpe)]_n$ [2.410 (19) Å; Liu *et al.*, 2011] and $[Cd(CH_3COO)_2(bpe)(H_2O)]_n$ [2.423 (4) Å; Nagarathinam & Vittal, 2008]. The Cd—N distance [2.320 (3) Å] is also somewhat shorter than those of 2.321 (19) and 2.397 (4) Å, respectively, in the same two compounds. The N1—Cd1—O5 angle [174.63 (10)°] is close to 180°, and the other N—Cd—O and O—Cd—O angles are in the range 55.87 (9)–160.55 (11)°, consistent with a pentagonal–bipyramidal coordination environment about the Cd^{II} centre.

In (I), each Cd^{II} atom is interlinked by μ-aqua molecules to form a one-dimensional $[Cd(\mu\text{-aqua})]_n$ chain extending along the *b* axis (Fig. 2). Each Cd^{II} atom is then chelated by two

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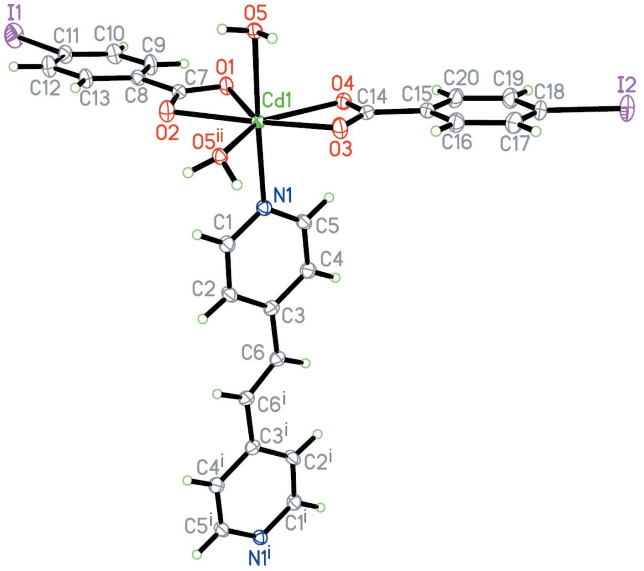

Figure 1
The coordination environment of the Cd atom in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.]

ligands in the one-dimensional chain (Fig. 3). The chain is stabilized by intermolecular hydrogen-bonding interactions ($O5-H1W\cdots O4^{ii}$ and $O5-H2W\cdots O1^{ii}$) between aqua and carboxylate groups (see Table 1 for symmetry code). The unsaturated coordinated Cd^{II} atoms are further linked to neighbouring atoms by bridging bpe ligands to produce a two-dimensional net which lies parallel to the $(\overline{1}01)$ plane (Fig. 4). From a topological point of view, this two-dimensional net can be simplified as a (6,3) network by treating the Cd^{II} centres as nodes and the aqua and bpe ligands as linkers (Fig. 5).

Some Cd^{II} coordination polymers with bpe and monocarboxylate ligands have been reported in recent years. For example, the Cd complex $[Cd(CBA)_2(bpe)]_n$ was isolated from the reaction between $Cd(NO_3)_2$, bpe and 4-chlorobenzoic acid under hydrothermal conditions. In $[Cd(CBA)_2(bpe)]_n$, the carboxylate groups of the CBA ligands adopt both chelating and tridentate modes, coordinating the Cd atoms to form dinuclear $[Cd_2(CBA)_4]$ units. The dinuclear $[Cd_2(CBA)_4]$ units are then linked by pairs of bpe ligands to form a one-dimensional ladder-like structure (Liu *et al.*, 2011). In (I), the carboxylate groups of the IBA ligands adopt only chelating coordination modes. As a result, each pair of IBA ligands can supply only four coordination sites for each Cd^{II} centre. In order to complete its coordination environment, the Cd^{II} atom must be coordinated by more atoms. Thus, the aqua ligands could function as bridges to connect the Cd^{II} atoms to form a polymeric structure.

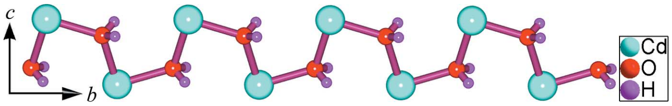

Figure 2
A view of the one-dimensional $[Cd(\mu\text{-aqua})]_n$ chain extending along the *b* axis.

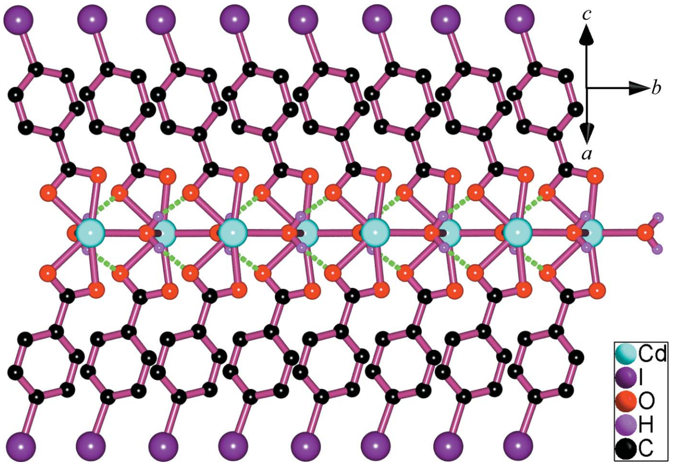

Figure 3
A view of the one-dimensional $[Cd(4\text{-IBA})_2(\mu\text{-aqua})]_n$ chain extending along the *b* axis.

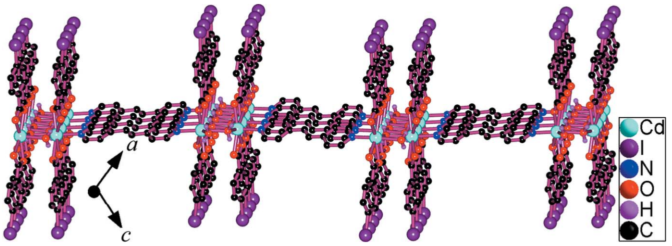

Figure 4
A view of the two-dimensional network of (I).

If $Cd(CH_3COO)_2$ and bpe are employed as the starting materials, the complex $[Cd(CH_3COO)_2(bpe)(H_2O)]_n$ is obtained by the slow evaporation of a solution containing the starting materials in an ethanol and water mixture (Nagarathinam & Vittal, 2008). It is noted that the solvent water molecules function as ligands in the product. The main structure of $[Cd(CH_3COO)_2(bpe)(H_2O)]_n$ is still a one-dimensional chain, since the water molecules are only terminal ligands. The H atoms of the coordinated water molecules in one chain form complementary hydrogen bonds to the O atoms of the chelating acetate ions in an adjacent chain. As a result, these one-dimensional chains are interconnected to form a two-dimensional supramolecular sheet *via* hydrogen-

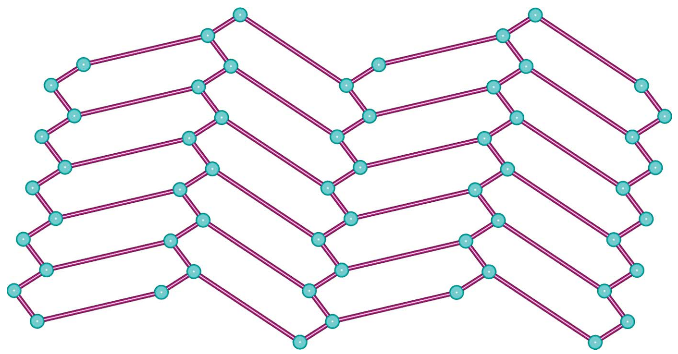

Figure 5
A view of the topological net of (I).

bonding interactions. However, in (I), the aqua ligands function as linkers, so they can only connect adjacent Cd^{II} atoms into a one-dimensional polymeric chain. These one-dimensional chains are further linked by bpe ligands to form a two-dimensional coordination network which is completely different from those of the two previously reported complexes.

In summary, we have demonstrated the formation of a coordination polymer, (I), from the hydrothermal reaction of Cd(NO$_3$)$_2$ with 4-IBA, bpe and H$_2$O. The results indicate that the bridging aqua ligands can increase the dimensionality of the final structure. It is expected that other systems containing carboxylate, dipyridinyl and aqua ligands can produce other multidimensional coordination polymers with new topological structures.

Experimental

Into a 25 ml Teflon-lined stainless steel autoclave were loaded Cd(NO$_3$)$_2$·4H$_2$O (154 mg, 0.5 mmol), 1,2-bis(pyridin-4-yl)ethene (91 mg, 0.5 mmol) and 4-iodobenzoic acid (248 mg, 1 mmol). The tube was sealed and heated in an oven to 443 K for 3 d, and then cooled to ambient temperature at a rate of 5 K h^{-1} to form colourless crystals of (I), which were washed with water/ethanol (1:1 *v*/*v*) and dried in air (yield: 297 mg, 83% yield based on Cd). Analysis calculated for C$_{20}$H$_{15}$CdI$_2$NO$_5$: C 33.57, H 2.11, N 1.96%; found: C 33.82, H 2.01, N 1.63%. IR (KBr, ν, cm^{-1}): 3440 (*m*), 3029 (*m*), 1616 (*s*), 1560 (*s*), 1431 (*m*), 1385 (*s*), 1224 (*w*), 1204 (*m*), 1086 (*m*), 1028 (*m*), 959 (*m*), 833 (*s*), 757 (*s*), 716 (*s*), 618 (*m*), 555 (*s*), 436 (*m*).

Crystal data

[Cd$_2$(C$_7$H$_4$IO$_2$)$_4$(C$_{12}$H$_{10}$N$_2$)(H$_2$O)$_2$]
M_r = 715.54
Monoclinic, $C2/c$
a = 29.236 (6) Å
b = 5.7289 (11) Å
c = 28.417 (6) Å
β = 112.82 (3)°
V = 4387.0 (18) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 3.84 mm^{-1}
T = 223 K
0.45 × 0.30 × 0.30 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
Absorption correction: multi-scan (*REQAB*; Jacobson, 1998)
$T_{\rm min}$ = 0.277, $T_{\rm max}$ = 0.392
20159 measured reflections
5018 independent reflections
3615 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.089
S = 0.91
5018 reflections
265 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 1.16 e Å^{-3}
$\Delta\rho_{\rm min}$ = −1.76 e Å^{-3}

The H atoms of the coordinated water molecules were located in a Fourier map. All other H atoms were placed in geometrically idealized positions, with C—H = 0.95 Å for phenyl, pyridinyl and vinyl groups, and constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The minimum and maximum residual electron densities are located 0.30 and 0.80 Å, respectively, from atom I2. The location of the maximum residual electron-density peak does not fit the geometry of any potential disorder or impurity.

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H1W···O4^{ii}	0.85	1.83	2.672 (4)	170
O5—H2W···O1^{ii}	0.85	1.90	2.701 (4)	157

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

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DT3009). Services for accessing these data are described at the back of the journal.

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