metal-organic compounds

A new chain-like cadmium(II) coordination polymer containing chains of water molecules

Xiue Lin,[a]* Yan-Qin Wang,[a] Rong Cao,[b] Feng Li[b] and Wen-Hua Bi[b]

[a]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou, Fujian 350002, People's Republic of China, and [b]Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China
Correspondence e-mail: linxiue@fjirsm.ac.cn

The title cadmium(II) polymer, catena-poly[[[bis(4-aminopyridine-κN)aquacadmium(II)]-μ-1,4-phenylenediacetato-$\kappa^4 O,O':O'',O'''$] dihydrate], $\{[Cd(C_{10}H_8O_4)(C_5H_6N_2)_2(H_2O)]\cdot 2H_2O\}_n$, comprises one-dimensional wave-like chains, in which the Cd atom is coordinated by 1,4-phenylenediacetate and 4-aminopyridine molecules. The 1,4-phenylenediacetate ligands lie about inversion centres. Extensive hydrogen-bonding interactions between the chains lead to a three-dimensional structure. Free water molecules form chains in the structure.

Comment

Various rigid benzenedicarboxylic acids, such as 1,2-benzenedicarboxylic acid and 1,4-benzenedicarboxylic acid, which have been demonstrated to be excellent candidates for bridging metal centers and metal clusters and which form architectures of various dimensions, have been used in numerous reactions to produce metal-organic frameworks (Li *et al.*, 2004). However, phenylenediacetic acids, for example, 1,4-phenylenediacetic acid (H$_2$PDA), derived from benzenedicarboxylic acid, have more flexible carboxylic acid groups, which do not tend to take part in reactions; hence, there are only a few examples of polymeric compounds containing these acids (Pan *et al.*, 2003). In this context, we introduced a secondary building unit (4-aminopyridine) for the design of metal-organic carboxylate frameworks, to improve the activity of the carboxylate group coordination with transition metal ions. Remarkably and fortunately, a three-dimensional complex was obtained containing the two ligands. The other significant observation is that free water molecules form hydrogen-bonded chains in the structure, a phenomenon that is of current interest (Ghosh & Bharadwaj, 2004).

As shown in Fig. 1, the chain consists of [Cd^{II}(PDA)(4-aminopyridine)(H$_2$O)] building blocks that are linked head-

to-tail by PDA^{2-} ligands through M—O bonds. The Cd atom has a distorted decahedral environment, with the equatorial


(1)
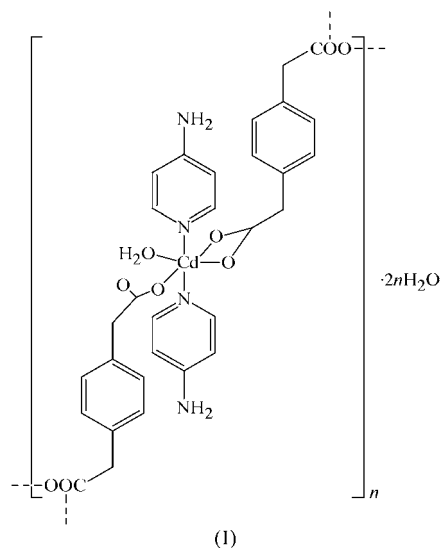
plane occupied by five O atoms, *viz.* four (O1, O2, O3 and O4) from two deprotonated PDA^{2-} molecules and one (O5) from the coordinated water molecule (Table 1). Two N atoms from two 4-aminopyridine molecules occupy the two axial positions, with bond lengths of 2.276 (3) (Cd—N3) and 2.296 (3) Å (Cd—N2). The 4-aminopyridine ligand uses its pyridine ring N atom to coordinate with the metal ion and its amine N atom is uncoordinated. The deprotonated PDA^{2-} ligands both lie about inversion centres and act as bridges, linking three Cd^{II} ions through carboxylate groups. The M—O$_{PDA^{2-}}$ distances range from 2.378 (3) to 2.651 (3) Å, and the M—O$_{water}$ distance is 2.334 (4) Å. Hence, each metal centre connects two PDA^{2-} ligands to form a one-dimensional chain in a step-like arrangement, with metal–metal distances of 11.644 (5) Å.
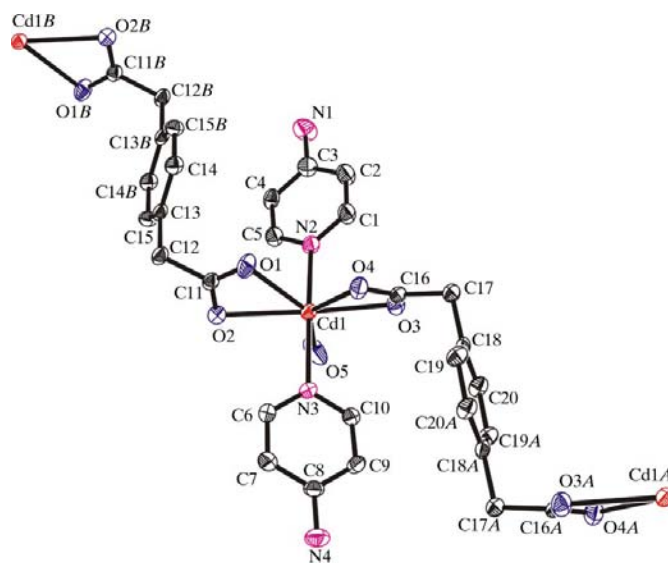
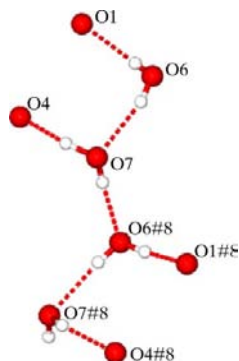**Figure 1**
The local environment of the Cd^{II} ions in (I). H atoms have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (A) $-x$, $2-y$, $1-z$; (B) $1-x$, $2-y$, $-z$.]

In the structure, several different kinds of hydrogen bonds (Table 2) are observed: (i) hydrogen bonds between free water molecules [O6···O7 = 2.825 (6) Å], (ii) hydrogen bonding of free water and carboxyl O atoms [O7···O4 = 2.770 (5) Å], (iii)

(a)

(b)
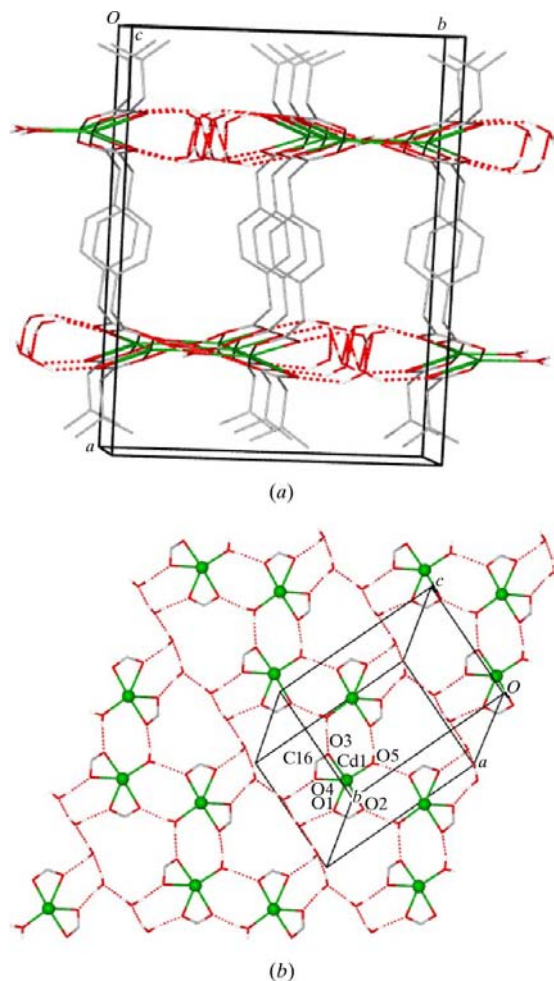
Figure 2
(*a*) The two-dimensional layer in the title compound, showing hydrogen-bonding interactions along the *b* axis. H atoms, except those involved in the interactions shown, and 4-aminopyridine molecules have been omitted. (*b*) The two-dimensional layer of the title compound, showing hydrogen-bond interactions along the *a* axis. Benzene rings and 4-aminopyridine molecules have been omitted.

Figure 3
The chain of water molecules in the title structure. [Symmetry code: (vi) $x, -y + \frac{5}{2}, z + \frac{1}{2}$.]

hydrogen bonding of coordinated water and carboxyl O atoms [O5···O2^{ii} = 2.745 (5) Å and O5···O3^{iii} = 2.782 (5) Å; symmetry codes are as given in Table 2], (iv) hydrogen bonding between the amine N atoms in the 4-aminopyridine molecules and free water molecules [N4···O7^{iv} = 3.168 (6) Å and N1···O6^{v} = 3.015 (7) Å], and (v) hydrogen bonding between the amine N atoms and carboxyl O atoms [N4···O4^{i} = 3.241 (6) Å]. Through these hydrogen-bonding interactions, each Cd^{II} polymer chain links to other chains to form a three-dimensional structure (Fig. 2*a*) in a layer–chain grid construction (for clarity, 4-aminopyridine molecules have been omitted from the plot). These central parts are linked by hydrogen bonds to form two-dimensional layers (Fig. 2*b*). The supramolecular layers are connected by the PDA^{2-} molecules of the step-like chains (Fig. 2*a*) to form the final three-dimensional supramolecular structure. Moreover, the uncoordinated amine N atoms of the 4-aminopyridine molecules are hydrogen bonded to O atoms of water molecules and carboxyl groups to stabilize the conformation.

Free water molecules play an interesting role in the structure, forming infinite chains by supramolecular assembly (Fig. 3). Through hydrogen bonds, these chains further organize the coordination polymer chains to be distributed alternately side by side, thus forming the two-dimensional structure (Fig. 2*b*).

Experimental

The title compound, (I), was produced under hydrothermal conditions. Cadmium nitrate tetrahydrate (0.119 g), 1,4-phenylenediacetic acid (97%, 0.040 g), 4-aminopyridine (98%, 0.020 g) and water (15 ml) were added to a Teflon-lined steel autoclave vessel. The mixture was heated at 438 K for 3 d and then cooled slowly over a period of 2 d to room temperature. The product consisted of white crystals of the title complex in 40% yield.

Crystal data

[Cd(C$_{10}$H$_8$O$_4$)(C$_5$H$_6$N$_2$)$_2$-(H$_2$O)]·2H$_2$O	D_x = 1.624 Mg m^{-3}
M_r = 546.85	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5000
a = 18.1668 (12) Å	reflections
b = 13.6273 (10) Å	θ = 3.1–27.5°
c = 9.2692 (7) Å	μ = 1.02 mm^{-1}
β = 102.998 (3)°	T = 293 (2) K
V = 2235.9 (3) Å^3	Prism, white
Z = 4	0.30 × 0.16 × 0.15 mm

Data collection

Rigaku Mercury 70 diffractometer	5117 independent reflections
φ and ω scans	4579 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan [empirical from equivalent reflections (*XEMP* in *SHELXTL*; Siemens, 1994)]	R_{int} = 0.030
	θ_{max} = 27.5°
	$h = -23 \rightarrow 23$
	$k = -8 \rightarrow 17$
T_{min} = 0.757, T_{max} = 0.857	$l = -12 \rightarrow 12$
16 963 measured reflections	

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)]$ = 0.045	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$wR(F^2)$ = 0.148	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.07	$(\Delta/\sigma)_{max} < 0.001$
5117 reflections	$\Delta\rho_{max}$ = 0.60 e Å^{-3}
393 parameters	$\Delta\rho_{min}$ = -0.51 e Å^{-3}

metal-organic compounds

Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.418 (3)	Cd1—N3	2.276 (3)
Cd1—O2	2.511 (3)	O1—C11	1.250 (5)
Cd1—O3	2.378 (3)	O2—C11	1.243 (5)
Cd1—O4	2.651 (3)	O3—C16	1.250 (5)
Cd1—O5	2.334 (4)	O4—C16	1.244 (5)
Cd1—N2	2.296 (3)		
N3—Cd1—O3	91.49 (12)	O5—Cd1—O2	89.13 (12)
N2—Cd1—O3	89.47 (12)	O1—Cd1—O2	52.27 (9)
O5—Cd1—O3	95.40 (12)	O3—Cd1—O4	51.23 (9)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N4—H9$\cdots$O4[i]	0.82 (6)	2.44 (6)	3.241 (6)	170 (5)
O5—H21$\cdots$O2[ii]	0.90 (6)	1.86 (5)	2.745 (5)	166 (5)
O5—H22$\cdots$O3[iii]	0.71 (5)	2.07 (5)	2.782 (5)	172 (6)
N4—H10$\cdots$O7[iv]	0.96 (6)	2.25 (6)	3.168 (6)	161 (5)
N1—H4$\cdots$O6[v]	0.78 (6)	2.23 (6)	3.015 (7)	178 (6)
O6—H26$\cdots$O1	0.82 (1)	1.94 (3)	2.703 (5)	156 (8)
O6—H25$\cdots$O7	0.81 (1)	2.03 (2)	2.825 (6)	166 (5)
O7—H23$\cdots$O4	0.94 (6)	1.92 (6)	2.770 (5)	149 (6)
O7—H24$\cdots$O6[vi]	0.82 (1)	2.01 (1)	2.832 (6)	177 (5)

Symmetry codes: (i) $-x, -y + 2, -z$; (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (iv) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $x, -y + \frac{5}{2}, z + \frac{1}{2}$.

H atoms were included in calculated positions and their parameters were refined isotropically [C—H = 0.87 (5)–1.07 (5) Å, O—H = 0.71 (5)–0.94 (6) Å and N—H = 0.78 (6)–0.96 (6) Å].

Data collection: *CrystalClear* (Rigaku/MSC, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXTL*.

References

Ghosh, S. K. & Bharadwaj, P. K. (2004). *Inorg. Chem.* **43**, 5180–5182.
Li, X. J., Cao, R., Sun, D. F. & Yuan, D. Q. (2004). *J. Mol. Struct.* **694**, 205–210.
Pan, L., Adams, K. M., Hernandez, H. E., Wang, X. T., Zheng, C., Hattori, Y. & Kaneko, K. (2003). *J. Am. Chem. Soc.* **125**, 3062–3067.
Rigaku/MSC (2001). *CrystalClear*. Version 1.3. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Siemens (1994). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.