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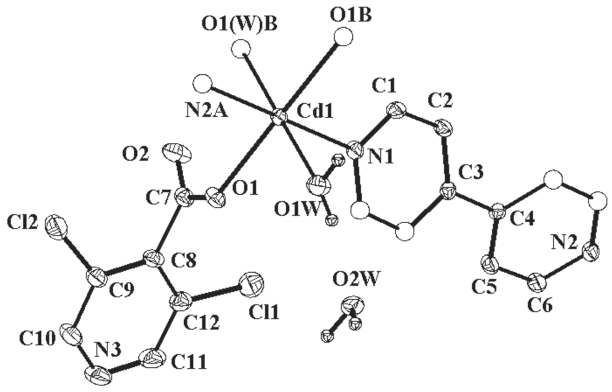
Crystal structure of *catena*-poly[diaqua-(μ_2-bipyridine-κ^2*N*:*N*′)-bis(3,5-dichloroisonicotinato-κ*O*)cadmium(II)] dihydrate, $C_{22}H_{20}CdCl_4N_4O_8$



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Abstract

$C_{22}H_{20}CdCl_4N_4O_8$, monoclinic, *C*2/*c* (no. 15), $a = 14.9908(5)$ Å, $b = 11.6786(3)$ Å, $c = 15.4664(5)$ Å, $\beta = 95.448(3)°$, $V = 2695.50(14)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0226$, $wR_{ref}(F^2) = 0.0516$, $T = 291.5(2)$ K.

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A part of the title structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.31 × 0.29 × 0.24 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.26 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	25.5°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7350, 2483, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2353
$N(param)_{refined}$:	180
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3, 4]

Source of material

All reagents and solvents for synthesis and analysis were commercially available and used as received. The mixture of 3,5-dichloroisonicotinic acid (dcia) (0.1 mmol, 19.2 mg), 4,4′-bipyridine (bpy) (0.1 mmol, 15.6 mg), $Cd(OAC)_2 \cdot 2H_2O$ (0.1 mmol, 26.7 mg) and H_2O (6.0 mL) were placed in a 23 mL Teflon liner stainless steel reactor. The vessel was heated to 393 K for 4 days, then cooled slowly to the room temperature. Colorless crystals were obtained, and further crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield 46% (based on *dcia* ligand).

Experimental details

Using Olex2 [2], the structure was solved with the ShelXT [3] structure solution program and refined with the ShelXL [4] refinement package. All hydrogen atoms were placed in calculated positions and refined isotropically with a riding model except for those bound to water molecules, which were initially located in a difference Fourier map and included in the final refinement with U_{iso}(H) equivalent to 1.5 times of U_{eq}(O).

Comment

The self-assembly of coordination polymers (CPs) using a mixed-ligand strategy continues to attract attention due to their fascinating architectures and topologies, as well as their potential application [5–10]. Among them, isonicotinates own different kinds of coordination donors, that are both pyridyl and carboxylate donor groups which have been used extensively to synthesize CPs [11–15]. With that in mind, we selected the 3,5-dichloroisonicotinic acid (dcia) as the educt, as the architectures of CPs constructed from the *dcia* ligand are rather rare.

The asymmetric unit of complex contains half a cadmium atom, one *dcia* anion, half a *bpy* molecule, one ligated water molecule and one guest water molecule. Each

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Cd1	0.5000	1.03175(2)	0.2500	0.02445(9)
Cl1	0.24664(5)	0.76936(6)	0.35432(5)	0.05245(18)
Cl2	0.21715(5)	1.23093(6)	0.37513(4)	0.05187(18)
O1	0.37754(10)	1.02956(12)	0.33085(10)	0.0322(4)
O1W	0.59373(11)	1.02934(14)	0.38208(10)	0.0436(4)
H1WA	0.5837	0.9770	0.4180	0.065*
H1WB	0.6443	1.0439	0.3639	0.065*
O2	0.26863(12)	1.00620(17)	0.22345(11)	0.0498(5)
N1	0.5000	0.8348(2)	0.2500	0.0268(5)
N2	0.5000	0.22852(19)	0.2500	0.0273(5)
N3	0.11375(16)	0.9752(2)	0.49901(15)	0.0592(7)
C1	0.52998(15)	0.77471(18)	0.18483(14)	0.0298(5)
H1	0.5507	0.8147	0.1388	0.036*
C2	0.53175(14)	0.65701(17)	0.18243(13)	0.0288(5)
H2	0.5540	0.6192	0.1361	0.035*
C3	0.5000	0.5949(2)	0.2500	0.0226(6)
C4	0.5000	0.4681(2)	0.2500	0.0223(6)
C5	0.44032(14)	0.40609(18)	0.29486(14)	0.0310(5)
H5	0.3992	0.4439	0.3261	0.037*
C6	0.44226(14)	0.28851(18)	0.29295(14)	0.0327(5)
H6	0.4013	0.2486	0.3230	0.039*
C7	0.29748(15)	1.01301(18)	0.30013(15)	0.0307(5)
C8	0.23147(14)	0.9998(2)	0.36874(13)	0.0317(5)
C9	0.19390(15)	1.0932(2)	0.40781(14)	0.0378(5)
C10	0.13614(17)	1.0772(3)	0.47149(16)	0.0519(7)
H10	0.1120	1.1415	0.4960	0.062*
C11	0.14801(17)	0.8849(3)	0.46173(17)	0.0522(7)
H11	0.1321	0.8122	0.4795	0.063*
C12	0.20622(15)	0.8934(2)	0.39770(14)	0.0376(5)
O2W	0.55444(16)	0.87438(18)	0.51129(11)	0.0693(6)
H2WA	0.5863	0.9017	0.5549	0.104*
H2WB	0.4987	0.8654	0.5358	0.104*

cadmium atom is six-coordinated by four O donors of two symmetry-related *dcia* anions and two coordinated water molecule in the equatorial plane with two N donors of two symmetry-related *bpy* ligands in the axial positions. The Cd—O bond lengths are 2.3173(14) and 2.3671(16) Å, respectively. The Cd—N bond length are 2.300(2) and 2.298(2) Å, respectively. The $[CdO_4N_2]$ environment are bridged by two N atoms of *bpy* along the *b* direction forming a chain, while each *dcia* carboxylate ligand works as a terminal ligand with uncoordinated pyridine N atoms. The monocoordinated *dcia* ligands decorate the chain. Besides intramolecular O(1W)-H(1WB)$\cdots$O(2) hydrogen bonds, intermolecular H-bonds between ligated H_2O and guest H_2O molecule [O(1W)-H(1WA)$\cdots$O(2W); d(O1W$\cdots$O2W) = 2.800(3) Å; degree (O1W-H1WA$\cdots$O2W) = 171.6°; O(2W)-H(2WB)$\cdots$O(1W); d(O2W$\cdots$O1W) = 3.101(3) Å; degree (O2W-H2WB$\cdots$O1W) = 138.6°] and between guest H_2O molecule and carboxylate O atom of *dcia* ligand [O(2W)-H(2WA)$\cdots$O(1); d(O2W$\cdots$O1) = 2.791(2) Å; degree (O2W-H2WA$\cdots$O1) = 161.9°] further extend the adjacent paralleled chains to result in the 2D layer. The adjacent 2D layers are stacked in a parallel fashion and cohered together by the weak effect of van der Waals force into the entire 3D network. Finally it should not kept unmentioned that the title structure is closely related to a recently reported Co(II) CP [16].

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