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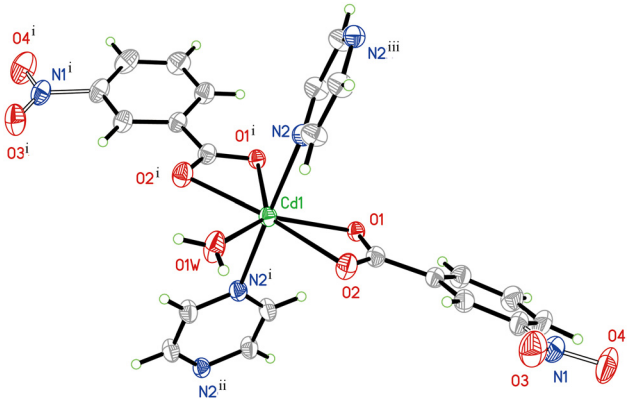
Crystal structure of *catena*-poly [aquabis(3-nitrobenzoato-κ^2*O*:*O*′)-(μ_2-pyrazine-*N*:*N*′)cadmium(II)], $C_{18}H_{14}N_4O_9Cd$



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Abstract

$C_{18}H_{14}N_4O_9Cd$, monoclinic, *C*2/*c* (no. 15), a = 22.390(4) Å, b = 6.2758(13) Å, c = 14.962(3) Å, β = 104.15(3)°, V = 7700.2(10) Å^3, Z = 4, $R_{gt}(F)$ = 0.0238, $wR_{ref}(F^2)$ = 0.0539, T = 293 K.

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A part of the polymeric 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.

Source of material

All reagents used were of commercially available quality and were used as received without further purification. 0.6 mmol 3-nitrobenzoate, 0.3 mmol pyrazine, 0.3 mmol cadmium chloride, 10 ml ethanol and 10 ml water were mixed and placed in a thick-walled Pyrex tube, which was sealed and heated to 413 K for 72 h. The tube was cooled to ambient temperature spontaneously and yellow

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.35 × 0.28 × 0.17 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.13 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9582, 2312, 0.050
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 2164
$N(param)_{refined}$:	174
Programs:	Bruker [1], SHELX [2, 3]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.0000	−0.02250 (3)	0.2500	0.03470 (8)
N1[a]	0.3387 (6)	0.046 (3)	0.4599 (10)	0.059 (2)
N1′[b]	0.3433 (13)	0.074 (4)	0.437 (2)	0.058 (4)
N2	−0.00269 (9)	−0.0108 (2)	0.40654 (11)	0.0415 (4)
O1	0.07316 (6)	0.2605 (2)	0.27490 (9)	0.0511 (3)
O1W	0.0000	−0.3853 (3)	0.2500	0.0629 (6)
H1W	−0.0301	−0.4718	0.2377	0.094*
O2	0.11001 (8)	−0.0598 (2)	0.31042 (11)	0.0530 (4)
O3[a]	0.3277 (5)	−0.1277 (18)	0.4814 (10)	0.083 (2)
O3′[b]	0.3359 (9)	−0.122 (3)	0.446 (3)	0.082 (6)
O4[a]	0.3895 (6)	0.142 (2)	0.4850 (12)	0.098 (3)
O4′[b]	0.3923 (9)	0.115 (4)	0.447 (3)	0.089 (5)
C1	0.28792 (10)	0.1903 (3)	0.40554 (15)	0.0531 (5)
C2	0.29946 (11)	0.3959 (4)	0.38298 (17)	0.0638 (6)
H2A	0.3394	0.4497	0.3977	0.077*
C3	0.25092 (15)	0.5202 (3)	0.3383 (2)	0.0621 (7)
H3A	0.2578	0.6602	0.3232	0.075*
C4	0.19172 (11)	0.4386 (3)	0.31553 (15)	0.0507 (5)
H4A	0.1591	0.5244	0.2856	0.061*
C5	0.18079 (9)	0.2294 (3)	0.33710 (12)	0.0410 (4)
C6	0.22972 (10)	0.1025 (3)	0.38351 (13)	0.0470 (5)
H6A	0.2233	−0.0375	0.3992	0.056*
C7	0.11727 (9)	0.1360 (3)	0.30659 (12)	0.0405 (4)
C8	0.02582 (10)	−0.1599 (3)	0.46501 (12)	0.0491 (5)
H8A	0.0446	−0.2738	0.4428	0.059*
C9	−0.02807 (10)	0.1485 (3)	0.44212 (12)	0.0481 (5)
H9A	−0.0480	0.2559	0.4033	0.058*

[a]Occupancy: 0.67 (4). [b]Occupancy: 0.33 (4).

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prism-shaped crystals of the title compound were obtained. **Elemental analysis**: Calcd. For $C_{18}H_{14}N_4O_9Cd$: C, 39.83%; H, 2.60%; N, 10.33%; Found: C, 39.67%; H, 2.69%; N, 10.40%.

Experimental details

H atoms bound to C atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 (phenyl & pyrazinyl) Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atom of the water molecule was located in a difference Fourier map, then constrained to ride on its parent O atom, with O—H = 0.85 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. The NO_2^- group of the 3-nitrobenzoate ligand (atoms O3, O4 and N1) are disordered over two positions with site occupancies of 0.716(1) and 0.284(1).

Comment

The supramolecular assembly and the crystal engineering of metal-organic coordination frameworks have attracted considerable attention because of their interesting molecular topologies and potential applications as functional materials [4–7]. Pyrazine has been used as a bridging ligand, and has been widely applied in constructing interesting coordination polymers [8, 9]. On the other hand, the aromatic carboxylates have been utilized in constructing interesting supramolecular networks [10–12]. Solvothermal synthesis is an effective method for the construction of new metal-organic coordination polymers because it can provide ideal conditions for crystal growth, owing to the enhanced transport ability of solvents in superheated systems [13]. We focus our attention on the construction of novel coordination polymer with pyrazine and aromatic carboxylate mixed ligands.

The asymmetric unit is comprised of one half of Cd(II), one 3-nitro-benzoate, one half of a pyrazine and one half of a water molecule (see the Figure). The Cd^{2+} ion, the O atom of the water and the pyrazine molecule are located on special positions. The Cd^{II} centre is surrounded by two N atoms (N2 and $N2^i$) from two different bridging pyrazine ligands and five O atoms, *i.e.* one O atom from the water ligand and four O atoms (O1, O2, $O1^i$ and $O2^i$) from two 3-nitrobenzoate anions [symmetry code: (i) $-x, y, 1/2 - z$]. Atoms N2 and $N2^i$ occupy the axial positions. Atoms Cd1, O1, $O1^i$, O2 and $O2^i$ occupy the equatorial sites, and are almost coplanar, the mean deviation from the plane being 0.088 Å. The *cis* bond angles around each Cd1 centre are in the range 84.42(7)—95.93(7)°, giving rise to a slightly distorted pentagonal bipyramidal coordination environment. The Cd—N bond length is 2.3588(17) Å and the Cd—O bond lengths range from 2.2770(19) to 2.4187(18) Å, which are similar to that observed in a previously reported cadmium compound, namely $\{[Cd(3\text{-nphaH})_2(pz)(H_2O)\cdot 2H_2O\}_n$, where 3-nphaH is 3-nitrobenzene-2-carboxylato-1-carboxylic acid and pz is pyrazine [14]. The pyrazine as bridging ligand links the neighboring Cd^{II} centres which results in a chain along the [0 1 0] direction. The structure of title compound is further stabilized by classical intermolecular $O_{water}—H\cdots O_{carboxylate}$ hydrogen bonds connecting the chains into an extensive two-dimensional network.

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