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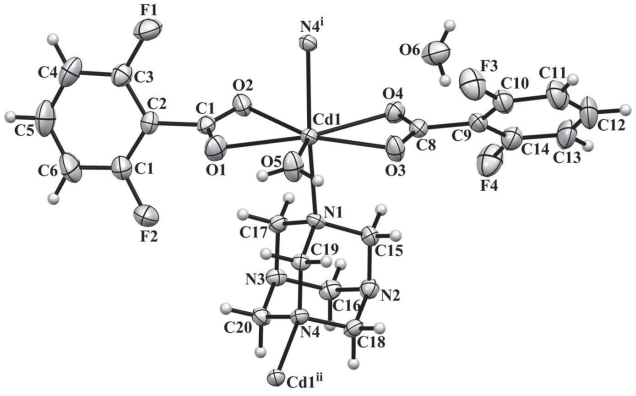
Crystal structure of *catena*-poly[aqua-(μ_2-hexamethylenetetramine-κ^2N:N')-bis(2,6-difluorobenzoato-κ^2 O:O')cadmium(II)] monohydrate, $C_{20}H_{22}CdF_4N_4O_6$



DOI 10.1515/ncrs-2017-0053
Received February 21, 2017; accepted July 13, 2017; available online July 29, 2017

Abstract

$C_{20}H_{22}CdF_4N_4O_6$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 7.475(3)$ Å, $b = 12.246(5)$ Å, $c = 24.615(11)$ Å, $V = 2253.0(17)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0245$, $wR_{ref}(F^2) = 0.0706$, $T = 296(2)$ K.

CCDC no.: 1009373

A part of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.28 × 0.24 × 0.19 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	10.5 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	56.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13694, 5379, 0.029
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5272
$N(param)_{refined}$:	332
Programs:	Bruker programs [1], SHELX [2]

Source of materials

An aqueous solution (10 mL) of 2,6-difluorobenzoic acid (110 mg, 0.70 mmol), $NaHCO_3$ (60 mg, 0.70 mmol), and hexamethylenetetramine (50 mg, 0.36 mmol) was mixed with an ethanolic solution (10 mL) of $Cd(NO_3)_2{\cdot}6H_2O$ (250 mg, 0.81 mmol). The resulting colorless solution was allowed to stand at room temperature to give colorless needle crystals within two weeks (yield 66 mg, 31%).

Experimental details

H atoms bound to C atoms were places in calculated positions and refined as riding on their parent atoms, with C—H = 0.93 Å (aromatic), C—H = 0.96 Å (methylene), C—H = 0.97 Å (ethylene), with $U_{iso}(H) = 1.2\ U_{eq}(C)$ for all H atoms. H atoms bound to water molecules were found from the Fourier difference map.

Comment

Coordination polymers have received much attention in recent years because of their potential applications such as catalysis, separation, gas storage, luminescence, and magnetism [3–5]. The traditional strategy of construction of coordination polymers is the self-assembly of organic molecules and metal ions. Bi- or polytopic molecules such as anionic aromatic acids and neutral *N*-containing heterocyclic

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cd1	−0.05369(2)	0.280356(14)	0.244183(7)	0.02140(6)
O1	0.0575(3)	0.23144(18)	0.15766(9)	0.0383(5)
C1	0.1827(4)	0.3007(2)	0.15616(10)	0.0253(5)
O2	0.2120(3)	0.36609(17)	0.19342(8)	0.0343(5)
C2	0.3018(4)	0.3003(2)	0.10697(10)	0.0264(6)
C3	0.3096(4)	0.3877(3)	0.07116(12)	0.0317(6)
F1	0.2027(3)	0.47473(16)	0.08168(9)	0.0505(5)
C4	0.4179(5)	0.3903(3)	0.02646(14)	0.0485(9)
H7	0.4172	0.4497	0.0030	0.058*
C5	0.5275(6)	0.3026(4)	0.01732(16)	0.0635(11)
H8	0.6041	0.3035	−0.0125	0.076*
C6	0.5270(6)	0.2127(4)	0.05133(15)	0.0583(10)
H9	0.6025	0.1536	0.0451	0.070*
C7	0.4113(4)	0.2140(3)	0.09450(11)	0.0367(6)
F2	0.4067(3)	0.12527(16)	0.12726(9)	0.0527(6)
O3	−0.2439(3)	0.26013(17)	0.31871(8)	0.0367(5)
C8	−0.1676(4)	0.3296(2)	0.34744(10)	0.0259(5)
O4	−0.0276(3)	0.37923(16)	0.33295(8)	0.0311(4)
C9	−0.2492(4)	0.3550(2)	0.40176(11)	0.0290(6)
C10	−0.4301(5)	0.3750(3)	0.40820(12)	0.0366(7)
F3	−0.5341(3)	0.37500(19)	0.36333(9)	0.0528(5)
C11	−0.5098(6)	0.3999(3)	0.45711(16)	0.0533(10)
H10	−0.6312	0.4157	0.4594	0.064*
C12	−0.4026(6)	0.4003(4)	0.50239(15)	0.0593(11)
H11	−0.4538	0.4143	0.5361	0.071*
C13	−0.2207(6)	0.3803(3)	0.49929(13)	0.0523(10)
H12	−0.1493	0.3816	0.5302	0.063*
C14	−0.1490(5)	0.3586(3)	0.44894(12)	0.0380(7)
F4	0.0286(3)	0.3376(2)	0.44587(8)	0.0550(5)
N1	0.1461(3)	0.14677(17)	0.28256(8)	0.0208(4)
C15	0.1637(4)	0.1461(2)	0.34344(10)	0.0258(5)
H13	0.2103	0.2159	0.3555	0.031*
H14	0.0465	0.1362	0.3596	0.031*
N2	0.2827(3)	0.05890(19)	0.36178(9)	0.0272(5)
C16	0.4609(4)	0.0729(2)	0.33745(10)	0.0281(5)
H15	0.5393	0.0149	0.3499	0.034*
H16	0.5114	0.1420	0.3491	0.034*
N3	0.4503(3)	0.07057(16)	0.27768(9)	0.0241(4)
C17	0.3298(3)	0.1587(2)	0.26042(10)	0.0240(5)
H17	0.3239	0.1597	0.2211	0.029*
H18	0.3788	0.2281	0.2722	0.029*
C18	0.2091(4)	−0.0461(2)	0.34448(11)	0.0256(5)
H19	0.0924	−0.0563	0.3610	0.031*
H20	0.2866	−0.1044	0.3570	0.031*
C19	0.0753(3)	0.03885(19)	0.26643(10)	0.0210(5)
H21	0.0631	0.0366	0.2272	0.025*
H22	−0.0428	0.0294	0.2821	0.025*
N4	0.1915(3)	−0.05240(17)	0.28418(9)	0.0212(4)
C20	0.3738(3)	−0.0350(2)	0.26082(11)	0.0243(5)
H23	0.4521	−0.0935	0.2726	0.029*
H24	0.3667	−0.0374	0.2215	0.029*
O5	−0.2730(3)	0.1654(2)	0.21132(10)	0.0402(5)
H5A	−0.250(7)	0.135(4)	0.1824(12)	0.09(2)*
H5B	−0.339(6)	0.135(4)	0.2336(15)	0.092(18)*
O6	0.1471(4)	0.5586(2)	0.38381(11)	0.0479(6)
H6A	0.109(10)	0.498(3)	0.394(4)	0.22(5)*
H6B	0.075(5)	0.609(3)	0.3872(19)	0.071(16)*

molecules are usually used as organic ligands for extending the structures. Among various aromatic acids, the "parent" acid, namely, benzoic acid or its substituted derivatives, have been utilized rather rarely in literature because it has only one carboxyl group, although some polynuclear clusters have been reported so far [6–8]. The fluorine substituted molecules are good candidates for construction of functional coordination polymers, because they are more stable to oxidation and show enhanced thermal stability [9]. Usage of pentafluorobenzoate as ligand has been reported in some studies, while only few complexes with 2,6-difluorobenzoate (dfba) as ligand have been reported [10, 11]. On the other hand, for the *N*-heterocyclic ligands, hexamethylenetetramine (hmt), which has four coordinating N atoms, is a good neutral bridging ligand, not only because it has various coordination modes that span from terminal monodentate to μ_2-, μ_3-, or μ_4-bridging mode; but also because it can act as hydrogen bonding acceptor to generate supramolecular networks [12, 13].

The asymmetric unit of the title complex contains one Cd^{2+} ion, two $dfba^-$ ligands, one hmt ligand, one coordinated and one not coordinated water molecule. The Cd^{2+} ion is seven coordinated in a distorted pentagonal bipyramidal geometry with four oxygen atoms from two $dfba^-$ ligands, two nitrogen atoms from two hmt molecules, and one water molecule. N1 and N4^i are located at the axial positions, and O1, O2, O3, O4, and O5 are in the equatorial plane. It is obviously that the distances of Cd1—O2 (2.571(2) Å) and Cd1—O4 (2.506(2) Å) are longer than those of Cd1—O1, Cd1—O3, and Cd1—O5 (av. 2.307(2) Å). The carboxyl groups of two $dfba^-$ ligands adopt chelating coordination modes. Each hmt ligand bridges two Cd^{2+} ions through N1 and N4 atoms with the Cd···Cd distance of 6.182 Å to form a chain along *b*. The uncoordinated water molecule is hydrogen bonded with the water ligand (O5—H5A···O6 = 2.842(4) Å), and two oxygen atoms of different carboxylate groups (O6—H6B···O1 = 2.803(4), O6—H6A···O4 = 2.845(4) Å). The neighboring chains along *a* are hydrogen bonded with each other through the coordinated water molecules and the nitrogen atoms of hmt ligands (O5—H5B···N3 = 2.881(3) Å) to form a 2D network.

Acknowledgements: This work was supported by the National Nature Foundation of China [No. 21461011 and 31560712], the Natural Science Foundation of Jiangxi Province [No. 20112BBF60024, 20151BAB204014].

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