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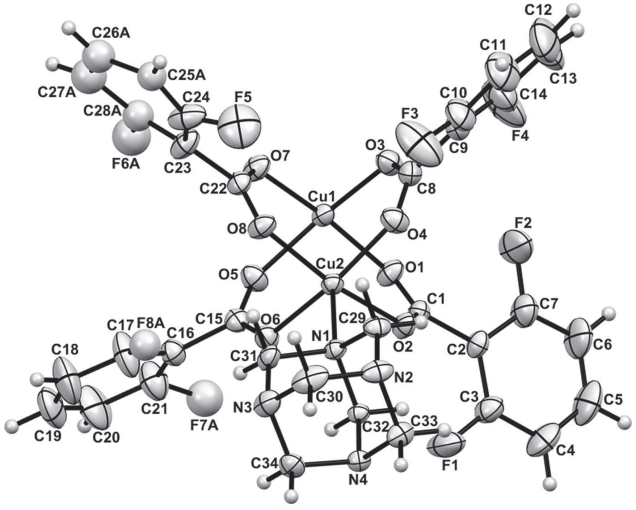
Crystal structure of *catena*-poly[(μ_2-hexamethylenetetramine-κ^2N:N')-tetrakis(μ_2-2,6-difluorobenzoato-κ^2O:O')dicopper(II)], $C_{34}H_{24}Cu_2F_8N_4O_8$



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Abstract

$C_{34}H_{24}Cu_2F_8N_4O_8$, monoclinic, $P2_1/n$ (no. 14), $a = 13.074(3)$ Å, $b = 20.229(4)$ Å, $c = 14.419(3)$ Å, $\beta = 108.889(2)°$, $V = 3608.2(12)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0512$, $wR_{ref}(F^2) = 0.1465$, $T = 296(2)$ K.

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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.

Table 1: Data collection and handling.

Crystal:	Green needle
Size:	0.15 × 0.10 × 0.08 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	12.8 cm^{-1}
Diffractometer, scan mode:	Bruker CCD, φ and ω
$2\theta_{max}$, completeness:	56.8°, 98.7%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	33606, 8923, 0.050
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5323
$N(param)_{refined}$:	498
Programs:	Bruker programs [1], SHELX [2]

Source of materials

An aqueous solution (10 mL) of 2,6-difluorobenzoic acid (dfbaH) (315 mg, 2.0 mmol), $NaHCO_3$ (160 mg, 2.0 mmol), and hexamethylenetetramine (70 mg, 0.5 mmol) was mixed with DMF/MeOH solution (10 mL) dissolving $Cu(NO_3)_2{\cdot}3H_2O$ (300 mg, 2.2 mmol). The light blue solution was allowed to stand at room temperature to give green needle-like crystals within two weeks (yield 350 mg, 39% based on copper nitrate trihydrate).

Experimental details

Hydrogen atoms were placed in calculated positions and refined as riding on their parent atoms, with C—H = 0.93 Å (aromatic), C—H = 0.96 Å (methylene), and $U_{iso}(H) = 1.2\ U_{eq}(C)$.

Comment

Coordination polymers are of special interest because of their fascinating topological structures as well as their potential applications in many fields [3–7]. The self-assembly of organic molecules and metal ions construct a broad range of coordination polymers. The selection of organic ligands is a key point for rational design of targeted structures. A number of aromatic acids, especially aromatic multicarboxylates, have

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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}
Cu1	0.81154(4)	0.28704(2)	0.16716(3)	0.03845(13)
Cu2	0.69321(4)	0.20461(2)	0.03194(3)	0.03659(13)
O1	0.7756(2)	0.35179(12)	0.06081(19)	0.0505(7)
C1	0.7297(3)	0.33562(18)	−0.0262(3)	0.0407(8)
O2	0.6882(2)	0.28056(12)	−0.05585(18)	0.0474(6)
C2	0.7254(3)	0.38642(18)	−0.1026(3)	0.0474(9)
C3	0.6329(4)	0.3987(2)	−0.1803(3)	0.0642(12)
F1	0.5449(2)	0.36447(17)	−0.1859(2)	0.1021(11)
C4	0.6287(6)	0.4457(3)	−0.2517(4)	0.0920(18)
H1	0.5649	0.4535	−0.3026	0.110*
C5	0.7202(7)	0.4799(3)	−0.2451(5)	0.107(2)
H2	0.7189	0.5109	−0.2931	0.128*
C6	0.8137(6)	0.4698(3)	−0.1698(5)	0.101(2)
H3	0.8758	0.4935	−0.1662	0.121*
C7	0.8144(5)	0.4249(3)	−0.1008(4)	0.0750(14)
F2	0.9072(3)	0.4140(2)	−0.0273(3)	0.1231(14)
O3	0.9271(2)	0.24890(14)	0.1207(2)	0.0538(7)
C8	0.9145(3)	0.2049(2)	0.0571(3)	0.0495(10)
O4	0.8266(2)	0.17840(14)	0.0092(2)	0.0558(7)
C9	1.0117(4)	0.1800(3)	0.0346(3)	0.0601(12)
C10	1.0200(5)	0.1152(3)	0.0054(4)	0.0797(15)
F3	0.9405(3)	0.07354(18)	−0.0003(4)	0.1351(16)
C11	1.1086(6)	0.0909(4)	−0.0136(5)	0.109(2)
H4	1.1111	0.0468	−0.0311	0.131*
C12	1.1924(7)	0.1317(5)	−0.0068(6)	0.135(3)
H5	1.2532	0.1152	−0.0191	0.162*
C13	1.1896(6)	0.1960(5)	0.0177(7)	0.131(3)
H6	1.2463	0.2244	0.0197	0.157*
C14	1.0989(5)	0.2188(3)	0.0401(6)	0.100(2)
F4	1.0965(3)	0.2831(2)	0.0639(4)	0.1477(19)
O5	0.6739(2)	0.30572(14)	0.1941(2)	0.0536(7)
C15	0.5907(3)	0.27400(18)	0.1509(3)	0.0436(9)
O6	0.5755(2)	0.23955(13)	0.07484(18)	0.0469(6)
C16	0.5007(3)	0.2741(2)	0.1938(3)	0.0504(10)
C17	0.4573(5)	0.2165(3)	0.2149(5)	0.097(2)
C18	0.3792(6)	0.2139(3)	0.2576(6)	0.116(3)
H7	0.3540	0.1732	0.2713	0.139*
C19	0.3383(5)	0.2700(4)	0.2801(5)	0.103(2)
H8	0.2836	0.2686	0.3082	0.124*
C20	0.3765(6)	0.3277(4)	0.2621(5)	0.110(2)
H9	0.3493	0.3669	0.2784	0.132*
C21	0.4554(5)	0.3292(3)	0.2198(5)	0.0838(16)
O7	0.8285(2)	0.21164(12)	0.2549(2)	0.0529(7)
C22	0.7839(3)	0.15707(18)	0.2271(3)	0.0447(9)
O8	0.7267(2)	0.14165(13)	0.14296(19)	0.0513(7)
C23	0.8007(4)	0.1055(2)	0.3051(3)	0.0611(12)
C24	0.8319(4)	0.0419(2)	0.2940(4)	0.0741(15)
F5	0.8464(3)	0.02582(16)	0.2104(3)	0.1195(13)
C25A[a]	0.8639(9)	−0.0091(5)	0.3512(8)	0.065(3)*
H11[a]	0.8827	−0.0500	0.3322	0.078*
C25B[a]	0.8407(9)	−0.0018(6)	0.3825(9)	0.067(3)*
H12[a]	0.8713	−0.0436	0.3863	0.080*
C26A[a]	0.8654(11)	0.0081(6)	0.4482(10)	0.083(3)*
H13[a]	0.8845	−0.0246	0.4960	0.100*
C26B[a]	0.8069(12)	0.0181(7)	0.4515(10)	0.097(4)*
H14[a]	0.8135	−0.0120	0.5019	0.116*
C27A[a]	0.8407(12)	0.0695(7)	0.4753(10)	0.097(4)*
H15[a]	0.8384	0.0785	0.5379	0.116*
C27B[a]	0.7629(13)	0.0770(7)	0.4610(11)	0.111(4)*
H16[a]	0.7397	0.0871	0.5139	0.134*
C28A[a]	0.8189(10)	0.1179(6)	0.4009(8)	0.074(3)*
C28B[a]	0.7551(10)	0.1213(6)	0.3851(8)	0.076(3)*
F6A[a]	0.7947(7)	0.1803(4)	0.4238(6)	0.114(2)*
F6B[a]	0.7119(7)	0.1802(4)	0.3880(6)	0.106(2)*
N1	0.5802(2)	0.14315(13)	−0.07898(19)	0.0342(6)
C29	0.6332(3)	0.09934(18)	−0.1318(3)	0.0456(9)
H17	0.6732	0.1261	−0.1641	0.055*
H18	0.6844	0.0710	−0.0849	0.055*
N2	0.5554(3)	0.05837(15)	−0.2046(2)	0.0520(9)
C30	0.4938(4)	0.01888(19)	−0.1549(3)	0.0654(13)
H19	0.4415	−0.0082	−0.2029	0.079*
H20	0.5430	−0.0105	−0.1080	0.079*
N3	0.4376(3)	0.06010(16)	−0.1040(2)	0.0540(9)
C31	0.5179(3)	0.10028(19)	−0.0323(3)	0.0463(9)
H21	0.5675	0.0715	0.0151	0.056*
H22	0.4818	0.1279	0.0026	0.056*
C32	0.5036(3)	0.18553(16)	−0.1516(2)	0.0329(7)
H23	0.5430	0.2131	−0.1834	0.039*
H24	0.4673	0.2143	−0.1185	0.039*
N4	0.4219(2)	0.14643(13)	−0.22678(19)	0.0344(6)
C33	0.4799(3)	0.10225(18)	−0.2754(3)	0.0472(9)
H25	0.4278	0.0758	−0.3246	0.057*
H26	0.5195	0.1289	−0.3082	0.057*
C34	0.3644(3)	0.10398(19)	−0.1754(3)	0.0494(10)
H27	0.3268	0.1319	−0.1422	0.059*
H28	0.3106	0.0777	−0.2234	0.059*
F7A[a]	0.4713(7)	0.3874(4)	0.1734(6)	0.103(2)*
F7B[a]	0.5128(5)	0.3870(3)	0.2247(5)	0.0749(16)*
F8A[a]	0.4726(5)	0.1590(3)	0.1682(5)	0.0746(16)*
F8B[a]	0.5227(6)	0.1598(3)	0.2194(5)	0.0883(19)*

[a]Occupancy: 0.50.

been used as bridging ligands. That is because the multicarboxylates not only have versatile coordination modes but also act as hydrogen bonding acceptors and donors [8]. Compared with the aromatic multicarboxylates, benzoic acid or its substituted derivatives possess a limited scope for the construction of coordination polymers [9]. However, polynuclear clusters with fascinating structures and properties which are constructed by benzoic acids have been reported [10, 11]. Meanwhile, the coordination polymers based on fluorine substituted organic molecules are found to be more stable to oxidation and show enhanced thermal stability [12].

On the other hand, the neutral *N*-containing heterocyclic molecules are ubquitously used as linker to construct coordination polymers. Lots of coordination polymers built from bipyridines and pyrazines are reported, while hexamethylenetetramine (hmt) was explored to a less extent [13].

However, hexamethylenetetramine has four coordinating N atoms which may link with different metal ions through various coordination modes that span from terminal monodentate to μ_2-, μ_3-, or μ_4-bridging modes, which lead to one- (1D), two- (2D) and three-dimensional (3D) coordination polymers [14, 15].

X-ray crystal structural analysis revealed that the asymmetric unit of the title complex is composed of two Cu^{2+} ions, four $dfba^-$ ligands and one hmt ligand. Each Cu^{2+} ion is coordinated in a square-pyramidal geometry with four oxygen atoms from four $dfba^-$ ligands and one nitrogen atom from a hmt ligand. The four oxygen atoms are located in the equatorial positions and the coordinated nitrogen atom is located at the axial position. The Cu^{2+} ions are deviated by 0.2179(14) Å for Cu1 and 0.2055(14) Å for Cu2 from the equatorial plane (defined by the four coordinated oxygen atoms) towards the axial N atoms, respectively. The four $dfba^-$ ligands using four carboxylate groups link two Cu^{2+} ions with distances of 2.6500(7) Å for Cu1$\cdots$Cu2 to form the typical $[Cu_2(COO)_4]$ paddlewheel building block. Hexamethylenetetramine ligands link the vertices of $[Cu_2(COO)_4]$ paddlewheel units in a μ_2-bridging mode. Therefore, a 1-D zigzag chain structure is formed in the structure of the title complex.

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