Xiao Wei, Dong Aiqin, Bao Guang-Ming, Peng Xiong-Xin, Sun Ting-Ting, Hu Chun-Yan and Yuan Hou-Qun*

Crystal structure of poly[dodekakis(μ_2 -2,6-difluorobenzoato- $\kappa^2 O:O'$)-bis($(\mu_3$ -hexamethylenetetramine- $\kappa^3 N:N':N'')$)hexacopper(II)],

$C_{48}H_{30}N_4O_{12}F_{12}Cu_3$

Abstract

$C_{48}H_{30}N_4O_{12}F_{12}Cu_3$, monoclinic, $P2_1/n$ (no. 14), $a = 12.9112(5)$ Å, $b = 28.1127(6)$ Å, $c = 14.2324(5)$ Å, $\beta = 110.665(4)^\circ$, $V = 4833.5(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0489$, $wR_{ref}(F^2) = 0.1108$, $T = 173(10)$ K.

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

Table 1: Data collection and handling.

Crystal:	Green block
Size:	$0.2 \times 0.1 \times 0.08$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.42 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ω -scans
$\theta_{\max}$, completeness:	27° , >98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	27059, 10405, 0.054
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 7283
$N(\text{param})_{\text{refined}}$:	709
Programs:	CrysAlis ^{PRO} [1], SHELX [2]

Source of material

All reagents and solvents were purchased from commercial sources and used as received. An aqueous solution (15 mL) of 2,6-difluorobenzoic acid (470 mg, 3.0 mmol), NaHCO_3 (240 mg, 3.0 mmol), and hexamethylenetetramine (70 mg, 0.5 mmol) was mixed with a DMF/MeOH solution (15 mL) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (450 mg, 3.3 mmol). The light blue solution was allowed to stand at room temperature to give green plate crystals within two weeks (yield 220 mg, 18%).

Experimental details

H atoms bound to C atoms were placed in calculated positions and refined as riding on their parent atoms, with $\text{C-H} = 0.93$ Å (aromatic), $\text{C-H} = 0.96$ Å (methylene), $\text{C-H} = 0.97$ Å (ethylene), and with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ for

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*Corresponding author: Yuan Hou-Qun, Institute of Functional Materials and Agricultural Applied Chemistry, Jiangxi Agricultural University, Nanchang 330045, P.R. China, e-mail: hqyuan2014@126.com

Xiao Wei, Dong Aiqin, Peng Xiong-Xin, Sun Ting-Ting and Hu Chun-Yan: Institute of Functional Materials and Agricultural Applied Chemistry, Jiangxi Agricultural University, Nanchang 330045, P.R. China

Bao Guang-Ming: Institute of Veterinary Drug, Jiangxi Agricultural University/Jiangxi, Provincial Key Laboratory for Animal Health, Nanchang 330045, P.R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.94722(4)	0.27774(2)	0.19889(3)	0.01874(11)
Cu2	0.83750(3)	0.21729(2)	0.05955(3)	0.01827(11)
O1	0.9699(2)	0.20854(9)	0.0237(2)	0.0301(6)
C1	1.0556(3)	0.23172(12)	0.0729(3)	0.0202(8)
O2	1.0651(2)	0.25941(8)	0.14419(19)	0.0250(6)
C2	1.1551(3)	0.22618(12)	0.0418(3)	0.0219(8)
C3	1.1911(3)	0.18307(14)	0.0186(3)	0.0333(10)
F1	1.1326(2)	0.14376(8)	0.0240(2)	0.0531(8)
C4	1.2825(4)	0.17730(16)	−0.0079(4)	0.0464(12)
H1	1.304524	0.147256	−0.020755	0.056*
C5	1.3409(4)	0.21749(18)	−0.0149(4)	0.0534(14)
H2	1.402430	0.214659	−0.034087	0.064*
C6	1.3089(4)	0.26156(16)	0.0062(4)	0.0491(13)
H3	1.347726	0.288695	0.001002	0.059*
C7	1.2185(4)	0.26473(14)	0.0352(3)	0.0373(11)
F2	1.1879(2)	0.30870(8)	0.0541(2)	0.0636(9)
O3	0.9879(2)	0.22272(9)	0.2878(2)	0.0325(7)
C8	0.9536(3)	0.18162(13)	0.2578(3)	0.0229(8)
O4	0.8946(2)	0.17082(8)	0.17000(19)	0.0290(6)
C9	0.9854(3)	0.14263(13)	0.3354(3)	0.0257(9)
C10	1.0243(3)	0.15065(13)	0.4381(3)	0.0284(9)
F3	1.0359(2)	0.19562(8)	0.47232(17)	0.0418(6)
C11	1.0511(4)	0.11529(16)	0.5087(4)	0.0531(14)
H4	1.076331	0.122714	0.576712	0.064*
C12	1.0404(6)	0.06916(19)	0.4781(4)	0.087(2)
H5	1.059937	0.044857	0.525418	0.104*
C13	1.0008(6)	0.05827(17)	0.3773(4)	0.085(2)
H6	0.990828	0.026754	0.356194	0.102*
C14	0.9760(5)	0.09465(15)	0.3084(3)	0.0517(14)
F4	0.9428(3)	0.08212(9)	0.2109(2)	0.0716(10)
O5	0.8026(2)	0.27557(9)	−0.0258(2)	0.0335(7)
C15	0.8339(3)	0.31664(13)	0.0070(3)	0.0237(8)
O6	0.8940(2)	0.32632(8)	0.0960(2)	0.0305(6)
C16	0.8002(3)	0.35767(14)	−0.0641(3)	0.0313(9)
C17	0.7602(3)	0.35284(15)	−0.1684(3)	0.0355(10)
F5	0.7502(2)	0.30925(9)	−0.20839(18)	0.0508(7)
C18	0.7307(5)	0.39014(18)	−0.2341(4)	0.0604(15)
H7	0.705758	0.384812	−0.302982	0.072*
C19	0.7384(6)	0.4351(2)	−0.1974(4)	0.090(2)
H8	0.733610	0.460872	−0.239623	0.108*
C20A ^a	0.7542(9)	0.4431(4)	−0.0907(8)	0.050(3)*
H9A ^a	0.731687	0.470275	−0.065862	0.060*
C20B ^a	0.7988(9)	0.4428(4)	−0.1008(8)	0.048(3)*
H9B ^a	0.833648	0.471846	−0.079109	0.058*
C21	0.8073(5)	0.40451(16)	−0.0322(4)	0.0707(18)
F6A ^a	0.8148(5)	0.41333(18)	0.0713(4)	0.0471(14)*
F6B ^a	0.8679(5)	0.41503(18)	0.0632(4)	0.0460(14)*
O7	0.7163(2)	0.23194(9)	0.10723(19)	0.0267(6)
C22	0.7263(3)	0.25756(12)	0.1819(3)	0.0222(8)
O8	0.8099(2)	0.28187(9)	0.2301(2)	0.0341(7)
C23	0.6297(3)	0.25879(13)	0.2170(3)	0.0257(9)
C24	0.5947(3)	0.29936(14)	0.2514(3)	0.0313(9)
F7	0.6480(2)	0.34066(8)	0.2494(2)	0.0497(7)
C25	0.5076(4)	0.30069(16)	0.2856(3)	0.0424(11)
H10	0.486186	0.329125	0.306759	0.051*
C26	0.4527(4)	0.25878(16)	0.2879(3)	0.0444(12)

Table 2 (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
H11	0.394310	0.258768	0.311843	0.053*
C27	0.4838(4)	0.21722(16)	0.2550(4)	0.0498(13)
H12	0.446858	0.188936	0.256127	0.060*
C28	0.5706(4)	0.21815(14)	0.2203(4)	0.0409(11)
F8	0.6002(3)	0.17640(9)	0.1902(3)	0.0760(11)
N1	0.7281(2)	0.16800(9)	−0.0511(2)	0.0144(6)
C29	0.7870(3)	0.14397(11)	−0.1111(3)	0.0176(7)
H19	0.820956	0.167842	−0.140110	0.021*
H20	0.845422	0.124085	−0.067129	0.021*
N2	0.7124(2)	0.11478(9)	−0.1913(2)	0.0164(6)
C30	0.6250(3)	0.14523(12)	−0.2572(3)	0.0190(8)
H21	0.575040	0.126122	−0.310851	0.023*
H22	0.657863	0.169067	−0.287316	0.023*
N3	0.5607(2)	0.16949(9)	−0.2016(2)	0.0139(6)
C31	0.5117(3)	0.13256(11)	−0.1567(3)	0.0163(7)
H23	0.460356	0.113585	−0.209709	0.020*
H24	0.470519	0.147643	−0.119545	0.020*
N4	0.5977(2)	0.10110(9)	−0.0883(2)	0.0147(6)
C32	0.6767(3)	0.13076(11)	−0.0079(3)	0.0167(7)
H25	0.637798	0.145702	0.031442	0.020*
H26	0.734123	0.110577	0.036530	0.020*
C33	0.6605(3)	0.07901(11)	−0.1473(3)	0.0185(8)
H27	0.717277	0.058282	−0.103687	0.022*
H28	0.610506	0.059678	−0.200504	0.022*
C34	0.6396(3)	0.19779(11)	−0.1200(2)	0.0152(7)
H29	0.599930	0.213633	−0.082427	0.018*
H30	0.672539	0.222072	−0.149017	0.018*
Cu3	0.52604(3)	0.04192(2)	−0.02942(3)	0.01926(11)
O9	0.3697(2)	0.06138(8)	−0.0691(2)	0.0262(6)
C35	0.3034(3)	0.03038(12)	−0.0613(3)	0.0218(8)
O10	0.3271(2)	−0.01021(8)	−0.0226(2)	0.0273(6)
C36	0.1821(3)	0.04197(12)	−0.1025(3)	0.0217(8)
C37	0.1171(3)	0.04125(13)	−0.0426(3)	0.0282(9)
F9	0.1685(2)	0.03229(9)	0.05662(19)	0.0441(6)
C38	0.0053(3)	0.05003(14)	−0.0790(4)	0.0374(11)
H13	−0.035105	0.049576	−0.036340	0.045*
C39	−0.0459(4)	0.05952(14)	−0.1797(4)	0.0425(12)
H14	−0.121771	0.065108	−0.205495	0.051*
C40	0.0144(3)	0.06082(14)	−0.2429(4)	0.0395(11)
H15	−0.019939	0.067351	−0.310974	0.047*
C41	0.1266(3)	0.05222(13)	−0.2029(3)	0.0297(9)
F10	0.1851(2)	0.05218(9)	−0.26494(18)	0.0491(7)
O11	0.5520(2)	0.06365(9)	0.1073(2)	0.0306(6)
C42	0.5496(3)	0.03463(13)	0.1736(3)	0.0264(9)
O12	0.5173(2)	−0.00798(9)	0.1589(2)	0.0293(6)
C43	0.5901(4)	0.05191(14)	0.2806(3)	0.0341(10)
C44	0.5435(5)	0.03883(17)	0.3500(4)	0.0623(16)
F11A ^a	0.4341(5)	0.0167(2)	0.3072(5)	0.0561(17)*
F11B ^a	0.4741(5)	0.00145(19)	0.3319(4)	0.0415(14)*
C45	0.5785(6)	0.0550(2)	0.4477(4)	0.079(2)
H16	0.542325	0.045810	0.490870	0.095*
C46	0.6678(6)	0.08476(19)	0.4795(4)	0.078(2)
H17	0.693570	0.095932	0.545271	0.093*
C47	0.7191(5)	0.0981(2)	0.4148(4)	0.0771(19)
H18	0.780123	0.118190	0.436028	0.093*
C48	0.6796(5)	0.08140(17)	0.3175(4)	0.0545(14)
F12	0.7341(3)	0.09399(12)	0.2564(2)	0.0808(10)

^aOccupancy: 0.5.

methyl H atoms and $1.2 U_{eq}(C)$ for all other H atoms. The atoms of C20, F6, and F11 were disordered and the components of disordered atoms were refined isotropically.

Discussion

In the past decades, design and construction of transition metal complexes have received much attention owing to their structures as well as their potential applications [3–5]. The selection and utilization of different organic ligands is considered to be a key point for rational designing and building targeted structures. A number of multicarboxylates and neutral *N*-containing heterocyclic molecules are usually employed to obtain novel structures. Compared with the using of complicated organic ligands, the very simple benzoic acid/derivatives and simple heterocyclic compound hexamethylenetetramine (hmt), have been explored to a less extent. However, there are some polynuclear clusters with fascinating structures and properties constructed by benzoic derivatives have been reported [6, 7]. On the other hand, hexamethylenetetramine having four coordinating N atoms in a diamandoid-like geometry, is a versatile ligand, because it is capable of various coordination modes that span from terminal monodentate to μ_2 -, μ_3 -, or μ_4 -bridging mode [8]. Recently, we have reported some one-dimensional structures which were built by hmt and monocarboxylates. In the course of our study on construction new structures based on *M*-hmt-monocarboxylate system [9–11]. Herein, we report a new two-dimensional structure $[Cu_2(dfba)_4]_3(hmt)_2$ (*dfba* = 2,6-difluorobenzoate).

X-ray crystal structural analysis revealed that the asymmetric unit of the title complex is composed of three Cu^{2+} ions, six *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 four *dfba*[−] ligands using four carboxylate groups link two Cu^{2+} ions with distances of 2.6164(6) Å for $Cu1 \cdots Cu2$, and 2.6659(8) Å for $Cu3 \cdots Cu3^i$ (Symmetry code: $i - x + 1, -y, -z$), respectively, to form $[Cu_2(COO)_4]$ paddle wheel building blocks. Each hexamethylenetetramine ligands links the vertices of $[Cu_2(COO)_4]$ paddlewheel units through three N atoms using μ_3 -bridging mode ($Cu2-N1 = 2.196(3)$, $Cu3-N4 = 2.207(3)$, and $Cu1-N3^{ii} = 2.211(3)$ Å, Symmetry code: $ii x + 1/2, -y + 1/2,$

$z + 1/2$). Therefore, a 2-D honeycomb structure is formed in the title complex.

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