Ying Zhao* and San-Tai Wang

Crystal structure of *catena*-poly[bis(μ_2 -1,4-bis(triazol-1-ylmethyl)benzene- $\kappa^2N:N'$)-bis(5-*tert*-butyl-isophthalate- κO)copper(II)] tetrahydrate, $C_{36}H_{46}CuN_6O_{12}$

<https://doi.org/10.1515/ncrs-2017-0325>

Received November 16, 2017; accepted March 20, 2018; available online April 12, 2018

Abstract

$C_{36}H_{46}CuN_6O_{12}$, triclinic, $P\bar{1}$ (no. 2), $a = 8.3759(18)$ Å, $b = 10.749(2)$ Å, $c = 11.873(3)$ Å, $\alpha = 63.165(2)^\circ$, $\beta = 82.979(2)^\circ$, $\gamma = 80.932(2)^\circ$, $V = 940.3(3)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0460$, $wR_{ref}(F^2) = 0.1107$, $T = 296(2)$ K.

CCDC no.: 1831146

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.

Source of material

A mixture of $Cu(OAc)_2 \cdot H_2O$ (0.1 mmol, 19.9 mg), 5-*tert*-butyl isophthalic acid (tbipH) (0.1 mmol, 25.5 mg), 1,4-bis(triazol-1-ylmethyl)benzene (btb) (0.1 mmol, 23.0 mg), and 12 mL

Table 1: Data collection and handling.

Crystal:	Block, clear light blue
Size:	$0.36 \times 0.21 \times 0.12$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.65 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
$\theta_{\max}$, completeness:	25.5° , >98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7111, 3463, 0.034
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2608
$N(\text{param})_{\text{refined}}$:	267
Programs:	Bruker programs [1], SHELX [2, 3]

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.0000	1.0000	0.0000	0.03101(18)
O1	0.0614(2)	0.82443(19)	0.14903(18)	0.0350(5)
O2	−0.1050(3)	0.9508(2)	0.2261(2)	0.0449(6)
O3	0.4119(3)	0.4164(2)	0.4332(2)	0.0484(6)
H3	0.4621	0.3388	0.4500	0.073*
O4	0.3551(3)	0.3237(2)	0.6408(2)	0.0538(6)
O5	0.4165(3)	0.8289(2)	0.5155(2)	0.0643(7)
H5A	0.4286	0.8549	0.5714	0.096*
H5B	0.4745	0.8855	0.4564	0.096*
O6	0.6024(3)	0.0302(2)	0.3218(2)	0.0567(6)
H6A	0.6957	0.0011	0.3000	0.085*
H6B	0.5850	0.0677	0.2436	0.085*
N1	0.2010(3)	1.0718(2)	0.0155(2)	0.0338(6)
N2	0.4067(3)	1.1899(2)	−0.0295(2)	0.0335(6)
N3	0.4213(3)	1.0921(3)	0.0920(2)	0.0432(7)
C1	0.0450(4)	0.7440(3)	0.3725(3)	0.0331(7)
C2	0.1642(3)	0.6317(3)	0.3899(3)	0.0341(7)
H2	0.2137	0.6187	0.3208	0.041*
C3	0.2080(3)	0.5399(3)	0.5107(3)	0.0335(7)
C4	0.1326(4)	0.5610(3)	0.6127(3)	0.0373(7)
H4	0.1628	0.4982	0.6937	0.045*
C5	0.0148(4)	0.6715(3)	0.5982(3)	0.0346(7)
C6	−0.0260(4)	0.7625(3)	0.4760(3)	0.0367(7)
H6	−0.1039	0.8389	0.4630	0.044*
C7	−0.0056(4)	0.8457(3)	0.2431(3)	0.0355(7)
C8	0.3309(4)	0.4157(3)	0.5363(3)	0.0378(7)
C9	−0.0624(4)	0.6951(3)	0.7119(3)	0.0439(8)
C10 ^a	−0.0542(12)	0.5563(5)	0.8344(5)	0.082(3)
H10A ^a	−0.1116	0.5722	0.9027	0.123*
H10B ^a	0.0569	0.5224	0.8538	0.123*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H10C ^a	−0.1027	0.4880	0.8229	0.123*
C11 ^a	0.0353(8)	0.7931(9)	0.7275(8)	0.071(2)
H11A ^a	0.0035	0.7958	0.8069	0.107*
H11B ^a	0.0159	0.8857	0.6598	0.107*
H11C ^a	0.1484	0.7599	0.7256	0.107*
C12 ^a	−0.2386(6)	0.7573(10)	0.6947(7)	0.082(3)
H12A ^a	−0.2971	0.6991	0.6767	0.123*
H12B ^a	−0.2450	0.8499	0.6258	0.123*
H12C ^a	−0.2849	0.7624	0.7708	0.123*
C10 ^b	−0.149(3)	0.5696(17)	0.803(2)	0.082(3)
H10D ^b	−0.1918	0.5826	0.8761	0.123*
H10E ^b	−0.0734	0.4859	0.8283	0.123*
H10F ^b	−0.2354	0.5611	0.7618	0.123*
C11 ^b	0.059(2)	0.721(3)	0.783(2)	0.071(2)
H11D ^b	0.0030	0.7369	0.8515	0.107*
H11E ^b	0.1117	0.8013	0.7263	0.107*
H11F ^b	0.1380	0.6400	0.8157	0.107*
C12 ^b	−0.191(2)	0.8257(18)	0.667(2)	0.082(3)
H12D ^b	−0.2677	0.8145	0.6192	0.123*
H12E ^b	−0.1382	0.9079	0.6138	0.123*
H12F ^b	−0.2454	0.8355	0.7384	0.123*
C13	0.2761(4)	1.1762(3)	−0.0732(3)	0.0368(7)
H13	0.2417	1.2319	−0.1545	0.044*
C14	0.2952(4)	1.0240(3)	0.1152(3)	0.0382(7)
H14	0.2724	0.9498	0.1929	0.046*
C15	0.5268(4)	1.2908(3)	−0.0952(3)	0.0421(8)
H15A	0.5100	1.3377	−0.1850	0.051*
H15B	0.6349	1.2405	−0.0837	0.051*
C16	0.5130(4)	1.3991(3)	−0.0452(3)	0.0367(7)
C17	0.4263(4)	1.5278(3)	−0.1066(3)	0.0489(9)
H17	0.3764	1.5486	−0.1798	0.059*
C18	0.4118(4)	1.6277(3)	−0.0611(3)	0.0498(9)
H18	0.3504	1.7137	−0.1032	0.060*

Occupancies: ^a = 0.776(12), ^b = 0.224(12)

deionized water was sealed in a Teflon-lined stainless vessel (25 mL) and heated at 413 K for 72 h, then cooled slowly to room temperature. Blue block crystals were obtained by filtration.

Experimental details

The hydrogen atoms were placed in calculated positions riding on attached atoms with $U_{iso} = 1.2U_{eq}(C)$. The methyl groups were idealized and refined using rigid groups allowed to rotate about the C—C bond (AFIX 137 option of the SHELX program [3]). The U_{iso} values of the hydrogen atoms of methyl groups and oxygen were set to $1.5U_{eq}(C, O)$.

Discussion

Current interest for the crystal engineering of coordination polymers has attracted much attention not only because of

their potential application in many fields, but also for their intriguing structures and topologies [4–7]. Many factors, such as the coordination geometry of the metal ions, solvent systems, and metal-to-ligand ratios, have been found to influence the topology of coordination polymers. The selection of organic bridging ligands plays a crucial role in the synthesis. For example, 5-R-isophthalic acids with special conformation (such as an angle of 120° between two carboxyl groups) and versatile coordination fashions, may provide the potential to construct unpredictable polynuclear clusters [8, 9].

Each Cu(II) center is four-coordinated with a distorted tetrahedral coordination geometry, by two oxygen atoms (Cu1—O1/O1A = 1.9643(19) Å) from two thip anions and two nitrogen atoms (Cu1—N1/N1A = 2.019(2) Å) from two btb ligands. The btb ligand connect the Cu(II) center to form a polymeric chain. Two partially deprotonated thip anions complete the coordination. Each polymeric chain is extended to form a 2D supramolecular layer through C—H···O hydrogen-bonds between triazol groups and carboxylate oxygen atoms.

Acknowledgements: This work was supported financially by key scientific research projects of higher education of He'nan Province (16A150016).

References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2012).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **71** (2015) 3–8.
4. Kuai, H.-W.; Fan, J.; Liu, Q.; Sun, W.-Y.: Structural diversity in imidazole and carboxylate-containing metal complexes dependent on the alkaline reagents. *CrystEngComm* **14** (2012) 3708–3716.
5. Pachfule, P.; Chen, Y.; Sahoo, S. C.; Jiang, J.; Banerjee, R.: Structural isomerism and effect of fluorination on gas adsorption in copper-tetrazolate based metal organic frameworks. *Chem. Mater.* **23** (2011) 2908–2916.
6. Yang, X.; Yan, D.: Long-afterglow metal-organic frameworks: reversible guest-induced phosphorescence tenability. *Chem. Sci.* **7** (2016) 4519–4526.
7. Ma, L.-F.; Shi, Z.-Z.; Li, F.-F.; Zhang, J.; Wang, L.-Y.: Coordination polymers with free Bronsted acid sites for selective catalysis. *New J. Chem.* **39** (2015) 810–812.
8. Li, C.-P.; Yu, Q.; Zhang, Z.-H.; Du, M.: Multifarious ZnII and CdII coordination frameworks constructed by a versatile trans-1-(2-pyridyl)-2-(4-pyridyl)ethylene tecton and various benzenedicarboxyl ligands. *CrystEngComm* **12** (2010) 834–844.
9. Abourahma, H.; Bodwell, G. J.; Lu, J.; Moulton, B.; Pottier, I. R.; Walsh, R. B.; Zaworotko, M. J.: Coordination polymers from calixarene-like [Cu₂(dicarboxylate)₂]₄ building blocks: structural diversity via atropisomerism. *Cryst. Growth Des.* **3** (2003) 513–519.