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The crystal structure of poly[bis(4-hydroxybenzoato- κO)-(μ_2 -4,4'-bipyridine- $\kappa^2 N:N'$) copper(II)] hydrate, $C_{24}H_{20}N_2O_7Cu$

Table 1: Data collection and handling.

Crystal:	Block, clear light blue
Size:	0.02 × 0.02 × 0.02 mm
Wavelength:	Mo K α radiation (1.54184 Å)
μ :	1.85 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω -scans
2 θ_{max} , completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	3864, 1956, 0.014
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1878
$N(param)_{refined}$:	178
Programs:	CrysAlis ^{PRO} [17], SHELX [18, 19], DIAMOND [20]

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

Atom	x	y	z	U_{iso}^*/U_{eq}
Cu1	0.5000	0.5000	0.5000	0.03017(18)
O1	0.45896(6)	0.66280(12)	0.44833(13)	0.0348(3)
O2	0.30968(8)	1.15535(14)	0.22648(13)	0.0427(4)
H2	0.3394	1.1936	0.1930	0.064*
O3	0.5000	0.4435(2)	0.2500	0.0414(5)
N4	0.59190(7)	0.58428(13)	0.49356(14)	0.0263(3)
O5	0.39786(8)	0.70289(14)	0.60831(13)	0.0423(4)
C1	0.71671(8)	0.71533(16)	0.49822(15)	0.0223(4)
C2	0.70489(9)	0.6261(2)	0.58835(17)	0.0341(4)
H2A	0.7391	0.6081	0.6530	0.041*
C3	0.32181(9)	0.87987(18)	0.43113(16)	0.0295(4)
H3	0.2930	0.8328	0.4773	0.035*
C4	0.41740(9)	0.72956(17)	0.50370(17)	0.0288(4)
C5	0.33841(10)	1.05656(18)	0.29441(16)	0.0315(4)
C6	0.29609(10)	0.98290(18)	0.36094(17)	0.0306(4)
C7	0.60315(9)	0.6680(2)	0.40386(19)	0.0354(4)
C8	0.43265(10)	0.91884(19)	0.3656(2)	0.0377(5)
C9	0.64321(9)	0.56342(19)	0.58369(18)	0.0339(4)
H9	0.6369	0.5039	0.6460	0.041*
C10	0.40751(12)	1.0248(2)	0.2980(2)	0.0403(5)
C11	0.39060(9)	0.84563(17)	0.43351(16)	0.0285(4)
C12	0.66392(9)	0.73433(19)	0.40271(19)	0.0346(4)
H12	0.6695	0.7916	0.3381	0.041*
H10	0.4349(14)	1.071(3)	0.253(2)	0.050(7)*
H6	0.2517(16)	1.004(2)	0.358(2)	0.045(7)*
H7	0.5689(13)	0.681(3)	0.340(2)	0.048(7)*
H8	0.4788(13)	0.897(2)	0.370(2)	0.046(6)*
H3A	0.4685(12)	0.394(3)	0.220(2)	0.048(7)*

<https://doi.org/10.1515/ncrs-2017-0377>

Received January 30, 2018; accepted May 3, 2018; available online May 22, 2018

Abstract

$C_{24}H_{20}N_2O_7Cu$, monoclinic, $C2/c$, $a = 19.6241(4)$ Å, $b = 10.4639(2)$ Å, $c = 10.7024(2)$ Å, $\beta = 96.163(2)^\circ$, $V = 2184.99(8)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0312$, $wR_{ref}(F^2) = 0.0863$, $T = 293$ K.

CCDC no.: 1588361

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

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Source of materials

The title compound was synthesized by hydrothermal reaction of Cu(NO₃)₂·3H₂O (20 mg, 0.08 mmol), 4,4'-bipyridine (5 mg, 0.03 mmol) and 4-hydroxybenzoic acid (10 mg, 0.07 mmol) in 5 mL water. The reaction system was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 80 °C for 72 hours, and blue block crystals yielded after cooling slowly to 30 °C at a rate of 1 °C min⁻¹.

Experimental details

H atoms were included in calculated positions and treated as riding atoms: C—H = 0.93 Å with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (parent C atom). A free rotating group O—H = 0.84 Å with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}$ for the water H atoms, and rotating group O—H = 0.82 Å with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}$ for the hydroxyl group H atoms as idealised tetrahedral OH.

Discussion

The research in supramolecular complexes has been rapidly developing due to their novel motifs [1–4] and potential applications in catalysis [5], proton conductivity [6, 7], fluorescence [8], magnetic property [9]. The supramolecular frameworks display fascinating topologies through diverse coordination modes and covalent or supramolecular contacts, such as hydrogen bonding, π - π packing, C—H... π interactions [3, 10, 11]. The infinite one-dimensional polymer including chain, ladder, helicates, tube and other uncommon frameworks, have been produced by *N*-donor or/and *O*-donor ligands [12, 13]. Regarding the entries of the Cambridge Structural Database [14], only two compounds generated by copper, 4,4'-bipyridine and 4-hydroxybenzoate anions have been reported until now [15, 16].

The asymmetric unit of the title structure consists of one half of a copper cation, one half of a 4,4'-bipyridine, one 4-hydroxybenzoate anion and one half of a water molecule. Each copper(II) cation is four-coordinated adopting square planar geometry, (shown in the figure with 50% probability level), being coordinated by two N atoms from two different 4,4'-bipyridine ligands and two O atoms from two 4-hydroxybenzoate ligands, respectively. The bipyridine is linked with two copper cations in a μ_2 -manner. The structure produces a straight chain due to the interaction between Cu and N. Only carboxylate in ligand 4-hydroxybenzoic acid is deprotonated and coordinated to copper. Therefore, this compound displays a one-dimensional coordination polymer. Adjacent chains are linked by water molecules with the weak Cu—O interactions. The copper atom presents weak interactions to O atoms of free water molecules at axial positions with a distance of 2.7401(5) Å as a result of Jahn-Teller effect different to the ladder compound [15]. The 4-hydroxybenzoate is coordinated to copper by one of its oxygen atoms. This

ladder structure can be considered as the combination of two of the title compounds connected with each other, by 4,4'-bipyridine rings part instead of one 4-hydroxybenzoate.

Acknowledgements: This work was supported by the Natural Science Fund of Jiangsu Province (Grant No. BK20160857), the Fundamental Research Funds for the Central Universities (Grant No. 2015B01414) and the Jiangsu Doctor Program (Grant No. B15065). Dr. H. H. gratefully appreciates the help of Prof. Wen Chen.

References

1. Cook, T. R.; Zheng, Y.-R.; Stang, P. J.: Metal-organic frameworks and self-assembled supramolecular coordination complexes: Comparing and contrasting the design, synthesis, and functionality of metal-organic materials. *Chem. Rev.* **113** (2013) 734–777.
2. Aakeroy, C. B.; Champness, N. R.; Janiak, C.: Recent advances in crystal engineering. *CrystEngComm* **12** (2010) 22–43.
3. Zhong, Y.; Yang, Y.; Shen, Y.; Xu, W.; Wang, Q.; Connor, A. L.; Zhou, X.; He, L.; Zeng, X. C.; Shao, Z.; Lu, Z.-L.; Gong, B.: Enforced tubular assembly of electronically different hexakis(m-phenylene ethynylene) macrocycles: persistent columnar stacking driven by multiple hydrogen-bonding interactions. *J. Am. Chem. Soc.* **139** (2017) 15950–15957.
4. Batten, S. R.; Robson, R.: *Catenane and rotaxane motifs in interpenetrating and self-penetrating coordination polymers*. Wiley, Weinheim, Germany (1999).
5. Elgrishi, N.; Chambers, M. B.; Wang, X.; Fontecave, M.: Molecular polypyridine-based metal complexes as catalysts for the reduction of CO₂. *Chem. Soc. Rev.* **46** (2017) 761–796.
6. Ando, S.; Fukushima, T.; Yamaguchi, T.: Discrete self-assembly and functionality of guest molecules in an organic framework. *Chem. Mater.* **28** (2016) 5847–5854.
7. Borowski, M.; Wolf, I.; Gies, H.: Investigation of proton dynamics within the hydrogen-bond network of the layer silicate Na-RUB-18. *Chem. Mater.* **14** (2002) 38–43.
8. Jin, J.; Chen, C.; Gao, Y.; Zhao, R.; Wang, X.; Lü, C.; Chi, Y.; Niu, S.: Synthesis, structure, and luminescence property of a series of Ag—Ln coordination polymers with the *N*-heterocyclic carboxylate ligand. *J. Solid State Chem.* **235** (2016) 193–201.
9. Knoepfel, D. W.; Shore, S. G.: Unusual one-dimensional ladder structures containing divalent europium and the tetracyanometalates Ni(CN)₄²⁻ and Pt(CN)₄²⁻. *Inorg. Chem.* **35** (1996) 5328–5334.
10. Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J.: Supramolecular coordination: Self-assembly of finite two- and three-dimensional ensembles. *Chem. Rev.* **111** (2011) 6810–6918.
11. Luo, D.; Zhou, X.-P.; Li, D.: Beyond molecules: mesoporous supramolecular frameworks self-assembled from coordination cages and inorganic anions. *Angew. Chem. Int. Ed.* **54** (2015) 6190–6195.
12. Batten, S. R.; Robson, R.: Interpenetrating nets: ordered, periodic entanglement. *Angew. Chem. Int. Ed.* **37** (1998) 1460–1494.
13. Xiao, D.; Yuan, R.; Sun, D.; Zhang, G.; Chen, H.; He, J.; Wang, E.: A novel self-penetrating metal-organic open

- framework containing unusual triple-stranded molecular braid and septuple helices. *J. Mol. Struct.* **936** (2009) 264–269.
14. Allen, F. The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Crystallogr.* **B58** (2002) 380–388.
 15. Tong, M.-L.; Chen, H.-J.; Chen, X.-M.: Molecular ladders with multiple interpenetration of the lateral arms into the squares of adjacent ladders observed for $[\mu_2-(4,4'\text{-bpy})_3(H_2O)_2(phba)_2](NO_3)_2 \cdot 4H_2O$ ($M = Cu^{2+}$ or Co^{2+} ; 4,4'-bpy = 4,4'-Bipyridine; phba = 4-Hydroxybenzoate). *Inorg. Chem.* **39** (2000) 2235–2238.
 16. Sarma, R.; Boudalis, A. K.; Baruah, J. B.: Aromatic *N*-oxide bridged copper(II) coordination polymers: synthesis, characterization and magnetic properties. *Inorg. Chim. Acta* **363** (2010) 2279–2286.
 17. Oxford Diffraction Ltd. CrysAlisPRO, Abingdon, Oxfordshire, England (2006).
 18. Sheldrick, G. M.: SHELXT-Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
 19. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
 20. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Ver. 4.0. Crystal Impact, Bonn, Germany (2015).