Synthesis and crystal structure of a novel tartrate copper(II) two-dimensional coordination polymer: {[Cu$_2$(C$_4$H$_4$O$_6$)$_2$(H$_2$O)$_2$]·4H$_2$O}$_\infty$

Fangfang Jian[a]; Pusu Zhao[a]; Qingxiang Wang[a]

[a] New Materials & Function Coordination Chemistry Laboratory, Qingdao University of Science and Technology, Qingdao, 266042, P.R. China

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Synthesis and crystal structure of a novel tartrate copper(II) two-dimensional coordination polymer: $\{[Cu_2(C_4H_4O_6)_2(H_2O)_2]\cdot 4H_2O\}_\infty$

FANGFANG JIAN*, PUSU ZHAO and QINGXIANG WANG

New Materials & Function Coordination Chemistry Laboratory,
Qingdao University of Science and Technology, Qingdao, 266042, P.R. China

A new 2D coordination polymer, $\{[Cu_2(C_4H_4O_6)_2(H_2O)_2]\cdot 4H_2O\}_\infty$ has been synthesized by the hydrothermal method and characterized by X-ray single crystal diffraction. Every copper(II) atom adopts a distorted octahedral geometry and coordinates with six oxygen atoms from one water molecule and three tartrate acid ions. The two tartrate acid ions have different coordination modes, one provides four oxygen atoms to coordinate with Cu(II) and another coordinates with all six oxygen atoms. Such a coordination mode generates a two-dimensional coordination polymer. In the solid state, the title compound forms a 3D network structure through hydrogen bonds.

Keywords: 2D coordination polymer; Tartrate copper(II); Crystal structure; Hydrogen bond

1. Introduction

In recent years, there has been great interest in the study of coordination polymers with network structures due to their possible chemical and physical properties [1–4]. A number of unique networks have been obtained by reactions between transition metal ions and rationally designed organic ligands [1–6]. From these studies, it is known that assembly of coordination networks is not only controlled by the geometry of metal ions but also determined by the nature of ligands (building blocks). So in order to obtain the desired polymers with predictable structure and properties, it is very important to choose appropriate multidentate ligands. Moreover, recently, intense research activities have been directed towards the development of porous frameworks including assembly of coordination complexes and organic molecules into extended motifs held together by strong metal–ligand bonding or by weaker bonding forces [7–10]. We selected tartaric acid as building blocks to construct 1D, 2D and 3D frameworks due to the diversity of binding modes of the carboxyl group and hydroxyl group

---

*Corresponding author. Email: zhaopusu@163.com

in the tartaric acid. As expected, when we reacted fresh $Cu(OH)_2$ with tartaric acid by hydrothermal method, a novel two-dimensional coordinate polymer containing a porous framework was obtained. In this article, we report the crystal structure of the title compound.

2. Experimental

2.1. *Physical measurements*

Elemental analyses were measured with a Perkin-Elmer 1400C analyser.

2.2. *Preparation of $\{[Cu_2(C_4H_4O_6)_2(H_2O)_2]\cdot 4H_2O\}_\infty$*

All chemicals were of analytical grade and were used without further purification. Fresh $Cu(OH)_2$ (0.049 g, 0.5 mmol) and tartaric acid (0.15 g, 1.0 mmol) were mixed in EtOH with stirring, and the mixture was sealed in a 30-mL stainless steel reactor with Teflon liner at 150°C for 12 h, resulting in the formation of light blue crystals of the title complex. Yield: 37%. The C and H content were determined by elemental analysis: Anal. Calcd for $[Cu_2(C_4H_4O_6)_2(H_2O)_2]\cdot 4H_2O$ (%): C, 18.21; H, 3.51. Found: C, 18.08; H, 3.79.

2.3. *Crystallographic data collection and solution of structure*

A summary of the key crystallographic information is given in table 1. The diffraction data were collected on a Rigaku Raxis-IV diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å, $T = 293$ K). The technique used

Table 1. Summary of crystallographic results for the title compound.

Empirical formula	$C_8H_{20}Cu_2O_{18}$
Formula weight	531.32
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P21$
Unit cell dimensions	$a = 8.3878(17)$ Å
	$b = 8.7850(18)$ Å, $\beta = 104.63(3)°$
	$c = 12.197(2)$ Å
Volume	869.6(3) Å^3
Z, Calculated density	2, 2.029 Mg m^{-3}
Absorption coefficient	2.541 mm^{-1}
$F(000)$	540
θ range for data collection	1.73–24.50°
Limiting indices	$-9 \leq h \leq 0$, $-10 \leq k \leq 10$, $-13 \leq l \leq 14$
Reflections collected/unique	2515/2455 [$R_{int} = 0.1296$]
Completeness to $\theta = 24.50$	95.5%
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.021
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0639$, $wR_2 = 0.1505$
R indices (all data)	$R_1 = 0.0738$, $wR_2 = 0.1583$
Absolute structure parameter	0.00
Extinction coefficient	0.004(2)
Largest diff. peak and hole	1.052 and -0.849 e Å^{-3}

was ω-scan with limits 1.73 to 24.50°. Empirical absorption correction was carried out by using the *SADABS* [11] program. The structure of the title compound was solved by direct methods and refined by least squares on F^2 by using the *SHELXTL* [12] software package. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms of water were located by difference synthesis and refined isotropically and other hydrogen atoms were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final conventional $R_1 = 0.0639$ and $wR_2 = 0.1505$ for 2131 reflections with $I > 2\sigma(I)$ using the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.1114P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$ were obtained. The molecular graphics were plotted using *SHELXTL*. Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* [13].

CCDC-252680 for the title compound contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Description of the structure of $\{[Cu_2(C_4H_4O_6)_2(H_2O)_2] \cdot 4H_2O\}_\infty$*

Figure 1 shows a perspective view of the title compound with atomic numbering scheme, and figure 2 shows a perspective view of the crystal packing in the unit cell. Hydrogen bonds forming among the four uncoordinated water molecules are shown in figure 3. Selected bond lengths and angles are presented in table 2.

X-ray crystal structural analysis indicates that the repeat unit of the title compound contains two copper(II) atoms, two tartrate acid ions, two coordinated water molecules and four independent uncoordinated water molecules. Each Cu(II) adopts a
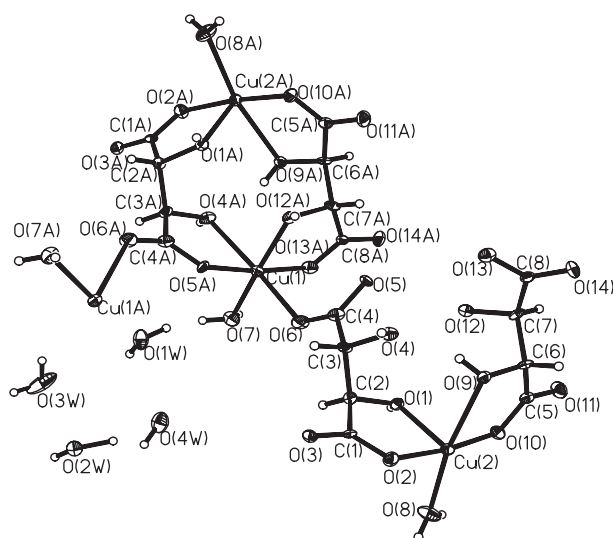

Figure 1. Molecular structure for the title compound with the atomic numbering scheme.
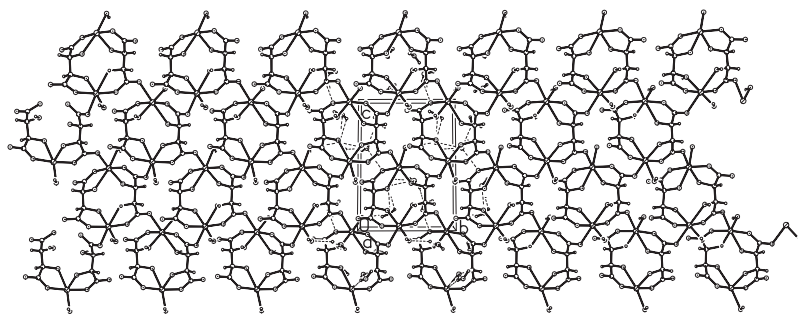
Figure 2.   A view of the crystal packing down the *a* axis for the title compound.
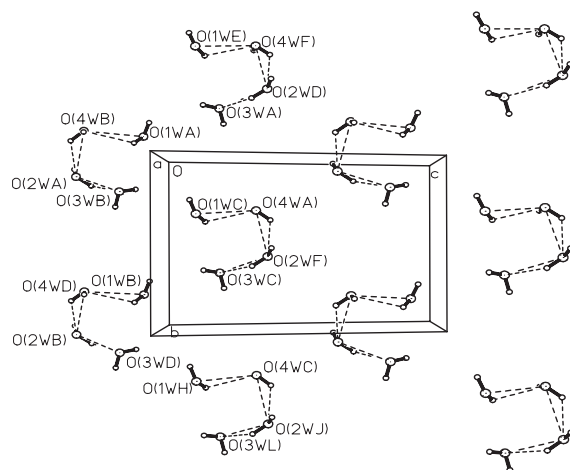

Figure 3.   Hydrogen bonds forming among the four non-coordinated water molecules. For clarity, copper(II) tartrates are not shown.

distorted octahedral geometry and coordinates with six oxygen atoms, which come from one water molecule and three tartrate acid ions, respectively. The two tartrate acid ions have different coordination modes, one only offers two carboxyl oxygen atoms and two hydroxyl oxygen atoms to coordinate Cu(II); the other coordinates all six oxygen atoms to Cu(II) atoms. Such coordination generates a two-dimensional coordination polymer. The bond distances around two copper(II) atoms are all different. For Cu(1), the Cu–O lengths vary from 1.916(7) to 2.454(8) Å, and for Cu(2), the Cu–O lengths fall in the range of 1.938(6) to 2.402(8) Å, comparable with those of similar coordination complexes reported by Deqing Zhang *et al.* [14] and Hugo Núñez *et al.* [15]. Although two Cu(II) centers show Jahn-Teller elongations along one of the axes, there are slight differences between the coordination environments around Cu(II). For Cu(1), O(7) of the water and oxygen atoms O(5), O(12) and O(13) occupy the equatorial plane, while O(4) and O(6) occupy axial positions, with Cu(1)–O(4) 2.454(8) Å, Cu(1)–O(6) 2.363(7) Å and O(6)–Cu(1)–O(4) 169.7(2)°. For Cu(2), O(8) of the water and O(9) occupy axial positions, with bond lengths Cu(2)–O(8) 2.402(8) Å,

Table 2. Selected bond lengths (Å) and angles (°) of the title compound.

Bond lengths		Bond angles	
Cu(1)–O(5)#1	1.916(7)	O(5)#1–Cu(1)–O(13)#1	172.5(3)
Cu(1)–O(13)#1	1.925(7)	O(5)#1–Cu(1)–O(7)	94.8(3)
Cu(1)–O(7)	1.987(7)	O(13)#1–Cu(1)–O(7)	90.3(3)
Cu(1)–O(12)#1	2.018(6)	O(5)#1–Cu(1)–O(12)#1	92.3(3)
Cu(1)–O(6)	2.363(7)	O(13)#1–Cu(1)–O(12)#1	82.2(3)
Cu(1)–O(4)#1	2.454(8)	O(7)–Cu(1)–O(12)#1	171.4(3)
O(1)–C(2)	1.436(11)	O(5)#1–Cu(1)–O(6)	95.4(3)
O(2)–C(1)	1.251(12)	O(13)#1–Cu(1)–O(6)	90.0(3)
O(3)–C(1)	1.267(12)	O(5)#1–Cu(1)–O(4)#1	74.9(3)
O(4)–C(3)	1.422(11)	O(6)–Cu(1)–O(4)#1	169.7(2)
O(5)–C(4)	1.287(12)	O(3)–C(1)–O(2)	123.6(8)
Cu(2)–O(10)	1.938(6)	O(2)–C(1)–C(2)	119.8(8)
Cu(2)–O(2)	1.964(7)	O(10)–Cu(2)–O(2)	172.4(3)
Cu(2)–O(3)#2	1.977(6)	O(10)–Cu(2)–O(3)#2	100.0(3)
Cu(2)–O(1)	2.040(6)	O(2)–Cu(2)–O(3)#2	87.0(3)
Cu(2)–O(8)	2.402(8)	O(10)–Cu(2)–O(1)	91.8(2)
Cu(2)–O(9)	2.413(6)	O(2)–Cu(2)–O(1)	81.1(3)
O(6)–C(4)	1.228(12)	O(3)#2–Cu(2)–O(1)	168.0(3)
O(9)–C(6)	1.457(11)	O(10)–Cu(2)–O(9)	77.2(2)
O(10)–C(5)	1.288(12)	O(2)–Cu(2)–O(8)	95.8(3)
O(11)–C(5)	1.227(11)	O(3)#2–Cu(2)–O(8)	85.5(3)
O(12)–C(7)	1.444(11)	O(8)–Cu(2)–O(9)	164.8(2)
		O(6)–C(4)–O(5)	125.4(8)
		O(11)–C(5)–O(10)	122.8(9)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $y+1/2$, $-z$; #2: $-x+2$, $y-1/2$, $-z+1$.

Cu(2)–O(9) 2.413(6) Å and bond angle O(8)–Cu(2)–O(9) 164.8(2)°. The two Cu(II) atoms are separated by a distance of 5.928(3) Å, indicating no interaction between them. Bond lengths and angles for each tartrate ligand are normal (and do not deviate significantly from other reported tartrate coordination compounds) [16]. The important feature of the title polymer is that, in each repeat unit, apart from four five-membered chelate rings, there exist bigger pores comprised of ten atoms, Cu(1), O(4), C(3), C(2), O(1), Cu(2), O(9), C(6), C(7) and O(12), which forms a 2D channelled framework with the water molecules included in the channels.

The salient feature in the crystal packing of the title compound is that there are some intermolecular, intramolecular hydrogen bonds and potentially weak C–H···O hydrogen bonds [17]. For example, the four non-coordinated water molecules connect through "head-end-head" to form "U-like" intermolecular hydrogen bonding interactions (see figure 3), with donor–acceptor (O···O) separations of 2.8285, 2.7598, 2.7245 and 2.7598 Å, which are all shorter than that of pure water (2.83 Å) [18]. Each uncoordinated water molecule is also hydrogen bonded to one carboxyl group or one hydroxyl group of the tartrate acid ions acting as a bridge to connect adjacent molecules. The two coordinated water molecules form hydrogen bonds not only with free water molecules, but also with the tartrate acid ions, the donor–acceptor distances are 2.7484 Å for O(7)–H(7C)···O(1W) (symmetry code: $1-x$, $1/2+y$, $-z$) and 2.7510 Å for O(7)–H(7A)···O(14) (symmetry code: $2-x$, $1/2+y$, $-z$), respectively. Additionally, the C–H···O intermolecular hydrogen bonds play an important role in sustaining the assembly of the title compound, with the shortest distance of C(7)···O(11) 2.9082 Å. Some selected hydrogen bond lengths and bond angles are

Table 3. Hydrogen bond lengths (Å) and bond angles (°).

D–H$\cdots$A	Symmetry code	D–H	H$\cdots$A	D$\cdots$A	D–H$\cdots$A
O(1W)–H(11W)$\cdots$O(4W)		0.8499	2.3410	2.8285	116.86
O(4W)–H(14W)$\cdots$O(2W)		0.8500	2.1375	2.7598	129.78
O(2W)–H(12W)$\cdots$O(3W)		0.8785	2.4208	2.7245	100.71
O(2W)–H(22W)$\cdots$O(4W)		0.9253	1.9861	2.7598	140.00
O(1W)–H(21W)$\cdots$O(7)	$1-x, -1/2+y, -z$	0.8501	1.9332	2.7475	160.00
O(2W)–H(12W)$\cdots$O(10)	$1-x, 1/2+y, 1-z$	0.8785	2.2586	2.7808	117.95
O(3W)–H(23W)$\cdots$O(13)	$1-x, 1/2+y, -z$	0.8502	2.1128	2.8257	141.15
O(4W)–H(24W)$\cdots$O(9)	$-1+x, y, z$	0.8500	1.8910	2.7228	165.69
O(7)–H(7C)$\cdots$O(1W)	$1-x, 1/2+y, -z$	0.8509	1.9099	2.7484	168.27
O(7)–H(7A)$\cdots$O(14)	$2-x, 1/2+y, -z$	0.8207	1.9885	2.7510	154.26
O(8)–H(8A)$\cdots$O(4W)	$1-x, 1/2+y, 1-z$	0.8500	2.3586	2.8235	114.88
O(8)–H(8B)$\cdots$O(11)	$1-x, 1/2+y, 1-z$	0.8500	1.9251	2.6949	149.99
O(9)–H(9A)$\cdots$O(4)		0.8199	1.9981	2.7528	152.76
O(9)–H(9A)$\cdots$O(12)		0.8199	2.2614	2.7288	116.16
C(6)–H(6A)$\cdots$O(2)	$2-x, -1/2+y, 1-z$	0.9801	2.5889	2.9733	103.42
C(7)–H(7B)$\cdots$O(11)		0.9801	2.5571	2.9082	101.02
C(7)–H(7B)$\cdots$O(5)	$1-x, -1/2+y, -z$	0.9801	2.5227	2.9575	106.72

listed in table 3. In the solid state, all these hydrogen bonds connect the title compound to form a three-dimensional network, stabilizing the crystal structure.

Acknowledgements

References

[1] P.J. Stang, B. Olenyuk. *Acc. Chem. Res.*, **30**, 502 (1997).
[2] C.B. Aaskeroy, K.R. Seddon. *Chem. Soc. Rev.*, **6**, 397 (1993).
[3] M. Munakata, L.P. Wu, T. Kuroda-Sowa. *Adv. Inorg. Chem.*, **46**, 173 (1999).
[4] F. Robinson, M.J. Zaworotko. *J. Chem. Soc., Chem. Commun.*, **23**, 2413 (1995).
[5] M. Fujita, Y.J. Kwon, M. Miyazawa, K. Ogura. *J. Chem. Soc., Chem. Commun.*, **17**, 1977 (1994).
[6] D. Hagrman, C. Zubieta, D.J. Rose, J. Zubita, R.C. Haushalter. *Angew. Chem., Int. Ed. Eng.*, **35**, 873 (1997).
[7] H. Li, A. Laine, M. O'Keefe, O.M. Yaghi. *Science*, **283**, 1145 (1999).
[8] B. Chen, M. Eddaoudi, S.T. Hyde, M. O'Keeffe, O.M. Yaghi. *Science*, **291**, 1021 (2001).
[9] J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K.A. Kim. *Nature*, **404**, 982 (2001).
[10] L.J. Barbour, G.W. Orr, J.L. Atwood. *Nature*, **393**, 671 (1998).
[11] G.M. Sheldrick. *Program for Empirical Absorption Correction of Area Detector Data*, University of Gottingen, Germany (1996).
[12] G.M. Sheldrick. *SHELXTL V5.1 Software Reference Manual*, Bruker AXS, Inc., Madison, Wisconsin, USA (1997).
[13] A.J. Wilson. *International Table for X-ray Crystallography*, Vol. C, Tables 6.1.1.4 (pp. 500–502) and 4.2.6.8 (pp. 219–222), respectively, Kluwer Academic Publishers, Dordrecht (1992).
[14] D.Q. Zhang, W. Liu, W. Xu, X.L. Jin, D.B. Zhu. *Inorg. Chim. Acta*, **318**, 84 (2001).
[15] H.G. Núñez, J.J. Timor, J.S. Carrió, L. Soto, E. Escrivà. *Inorg. Chim. Acta*, **318**, 8 (2001).
[16] L.J. Bostelaar, R.A.G. De Graaff, F.B. Hulsbergen, J. Reedijk, W.M.H. Sachtler. *Inorg. Chem.*, **23**, 2294 (1984).
[17] T. Steiner. *Cryst. Rev.*, **6**, 1 (1996).
[18] R.G. Xiong, C.M. Liu, J.L. Zuo, H.Z. Li, X.Z. You, H.K. Fun, K. Sivakumar. *Polyhedron*, **16**, 2315 (1997).