ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2018, Vol. 44, No. 11, pp. 693–700. © Pleiades Publishing, Ltd., 2018.

Magnetism and Structure of a 3D Uncommon Pentanuclearcopper(II) Coordination Polymer[1]

J. C. Jin[a, *], H. R. Zhong[b], A. Q. Ma[b, **], Y. J. Huang[b], S. W. Qiu[c], J. Q. Liu[b], M. M. Luo[b], J. W. Xu[b], Y. Y. Wang[d, *], and H. S. Sakiyama[e]**

[a]*Anhui Provincial Laboratory of Biomimetic Sensor and Detecting Technology, West Anhui University, Anhui, 23701 P.R. China*

[b]*Key Laboratory of Research and Development of New Medical Materials of Guangdong Medical University, Dongguan Key Laboratory of Drug Design and Formulation Technology and School of Pharmacy, Guangdong Medical University, Dongguan, 523808 P.R. China*

[c]*School of Inspection Science, Guangdong Medical University, Dongguan, 523808 P.R. China*

[d]*Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry & Materials Science, Northwest University, Xi'an, 710069 P.R. China*

[e]*Department of Science, Faculty of Science, Yamagata University, Kojirakawa, Yamagata 990-8560, Japan*

**e-mail: jcjgd2017@126.com*

***e-mail: maqandght@126.com*

****e-mail: wyaoyuxb@126.com*

Received November 20, 2017

Abstract—A 3D coordination polymer, $[Na_3KCu_5(Tar)_2(HTar)_2(H_2O)_7]$ (**I**) (H_2Tar = tartaric acid), was synthesized by the reaction of potassium sodium tartrate and $Cu(NO_3)_2$ and characterized by X-ray single crystal diffraction (CIF file CCDC no. 1575976). Complex **I** is built up in a shell-like manner based on inner two symmetry-related pentanuclear copper cores, the cores are surrounded by coordinated synchronously Na and K atoms, which shapes into 3D nanoporous architecture. Additionally, **I** exhibits antiferromagnetic behavior.

Keywords: tartaric acid, heteronuclear metal, magnetism

DOI: 10.1134/S1070328418110039

INTRODUCTION

The current interest in crystal engineering of metalorganic frameworks (MOFs) stems not only from their potential applications but also from their intriguing variety of architectures and topologies [1–5]. It is well known that flexible and widened aliphatic acids have often been employed as bridging ligands to construct MOFs, because this kind of ligand can act as a multi-connected node, and the synthesized compounds have numerous applications [6–10]. For this intention choosing a good ligand is very important. Tartaric acid ($TarH_2$) is a colorless, diprotic organicacid that occurs naturally in many plants, particularly grapes, bananas, and tamarinds, and is one of the main acids found in wine [11, 12]. Potassium sodium tartrate as carboxylate derivative has drawn extensive attention in coordination chemistry. This ligand has been used as building blocks to construct 1D, 2D and 3D frameworks due to the diversity of binding modes of the carboxyl group and hydroxyl group in the tartaric acid [13–16].

To obtain more insight and to extend this research with this tartrate ligand, we intended to isolate single crystals from reactions of Cu(II) salt with potassium sodium tartrate. In this study a new compound $[Na_3KCu_5(Tar)_2(HTar)_2(H_2O)_7]$ (**I**) has been synthesized and characterized. Complex **I** is built up in a shell-like manner based on inner two symmetry-related pentanuclear copper cores, the cores are surrounded by coordinated synchronously Na and K atoms, which shapes into 3D nanoporous architecture. Additionally, **I** exhibits antiferromagnetic behavior.

EXPERIMENTAL

Materials and physical measurements. All the reagents were purchased from commercial sources and used as received. The magnetic measurements for **I** was carried out on crystalline samples with a MagLab System 2000 magnetometer in a magnetic field up to 1 KOe.

Synthesis I. A water-methanol solution (20 mL, v : v = 1 : 5) of $Cu(NO_3)_2 \cdot 8H_2O$ (0.25 mmol) and

---

[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for **I**

Parameter	Value
Formula weight	1138.12
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions:	
a, Å	16.851(3)
b, Å	19.645(4)
c, Å	20.591(4)
Volume, Å^3; Z	6816(2); 8
F(000)	4520
θ Range for data collection, deg	1.872–25.26
Limiting indices	$-20 \le h \le 20$, $-23 \le k \le 23$, $-24 \le l \le 24$
Reflections collected	40841
Independent reflections (R_{int})	6350 (0.1221)
Numder of refinement	3487
Goodness-of-fit on F^2	1.011
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0583$, $wR_2 = 0.1506$
R indices (all data)	$R_1 = 0.1110$, $wR_2 = 0.1689$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.579/–1.279

potassium sodium tartrate (0.25 mmol) were sealed in a 25mL Telfon-lined stainless steel container, which was heated to 150°C for 96 h. After the sample was cooled to room temperature at a rate of 2°C h^{-1}, the blue crystals were obtained in ~22% yield based on Cu.

For $C_{16}H_{24}O_{31}KNa_3Cu_5$

Anal. calcd., %	C, 16.88	H, 2.18
Found, %	C, 16.81	H, 2.20

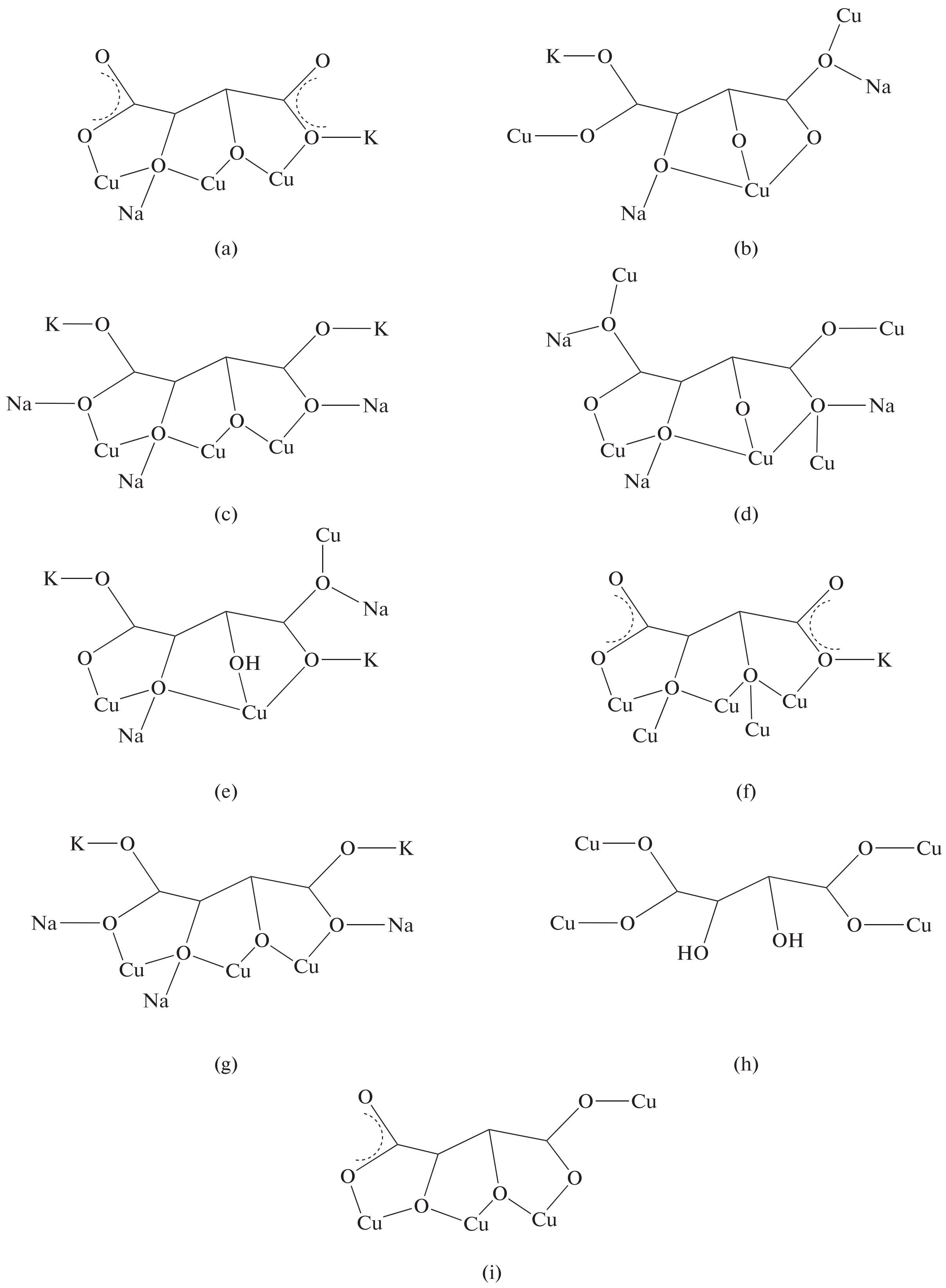
FT-IR (KBr; ν, cm^{-1}): 3568 v.s, 3268 m, 2929 m, 1575 s, 1448 m, 1409 s, 1359 m, 1252 w, 1059 m, 896 m.

X-ray structure determination. X-ray diffraction data were collected on a BRUKER SMART APEX CCD diffractometer with MoK_α radiation (λ = 0.71073 Å) at 298(2) K. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXL-97 program package [17]. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically, some of the hydrogen atoms of the water molecules were located from different Fourier maps. The crystallographic data for **I** was listed in Table 1, selected bond lengths and angles are presented in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1575976; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The 3D polymeric structure of **I** was revealed by X-ray single-crystal determination, in which contains five independent copper(II) atoms, two Tar, two HTar ligands and seven coordinated water molecules. As shown in Fig. 1, in **I**, tartrate ligand adopts some types of coordinated modes when it bonds to Cu, K and Na atoms. It is very rarer for a bridging ligand exhibiting so much coordinated modes in a compound:



(a) (b) (c) (d) (e) (f) (g) (h) (i)

Scheme 1.

Table 2. Selected bond lengths (Å) and angles (deg) for **I**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O (14)	1.948(5)	Cu(1)–O(21)	1.960(5)
Cu(1)–O(15)	1.975(5)	Cu(1)–O(24)	2.028(5)
Cu(1)–O(4*w*)	2.306(6)	Cu(2)–O(10)	1.932(5)
Cu(2)–O(17)	1.933(5)	Cu(2)–O(12)	1.937(5)
Cu(2)–O(16)	1.940(5)	Cu(3)–O(15)	1.925(5)
Cu(3)–O(3)	1.952(5)	Cu(3)–O(4)	1.954(5)
Cu(3)–O(16)	1.944(4)	Cu(4)–O(6)	1.940(5)
Cu(4)–O(10)	1.944(4)	Cu(4)–O(4)	1.948(5)
Cu(4)–O(12)	2.613(6)	Cu(4)–O(8)	2.695(5)
K(1)–O(19)	2.681(6)	K(1)–O(14)	2.714(5)
K(1)–O(5)	2.328(6)	K(1)–O(24)	2.423(8)
Na(1)–O(4*w*)	2.430(12)	Na(1)–O(1*w*)	2.433(6)
Na(1)–O(2*w*)	2.212(9)	Na(1)–O(21)	2.316(6)
Na(2)–O(5*w*)	2.324(6)	Na(2)–O(23)	2.444(5)
Na(2)–O(6)	2.579(6)	Na(2)–O(8)	2.584(6)
Na(2)–O(16)	2.696(11)	Na(2)–O(10)	2.751(11)
Na(3)–O(3*w*)	2.820(7)	Na(3)–O(7*w*)	2.838(6)
Na(3)–O(1*w*)	1.917(5)	Na(3)–O(1)	1.931(5)
Cu(5)–O(20)	1.938(5)	Cu(5)–O(3)	1.940(5)
Cu(5)–O(21)		Cu(5)–O(1)	
Angle	ω, deg	Angle	ω, deg
O(14)Cu(1)O(21)	174.2(2)	O(21)Cu(1)O(15)	92.87(19)
O(15)Cu(1)O(24)	172.5(2)	O(10)Cu(2)O(17)	175.7(2)
O(12)Cu(2)O(16)	178.8(2)	O(15)Cu(3)O(4)	162.6(2)
O(3)Cu(3)O(16)	170.0(2)	O(6)Cu(4)O(10)	175.8(2)
O(10)Cu(4)O(4)	95.26(19)	O(6)Cu(4)Na(2)	131.23(17)
O(21)Cu(5)O(1)	173.5(2)	O(21)Cu(5)Na(1)	123.93(19)
		O(6)Cu(4)Na(2)	

The Cu(1), Cu(4) and Cu(5) atoms are coordinated by six oxygen atoms in distorted octahedral geometries, while Cu(3) and Cu(2) are in an equivalent pentacoordinated environment describing as square pyramid geometries whose apical positions are occupied by the bridging carboxylic O(7) and O(23), respectively. The square planes are defined by O(10), O(16), O(12) and O(17) for Cu(2) and O(3), O(16), O(4) and O(15) for Cu(3) with a mean deviation from the least-squares plane of 0.032 and 0.038 Å, respectively. The bond lengths in basal planes range from 1.932(5) to 1.966(5) Å, and the apical Cu–O distances are the longest (Cu(2)–O(23) 2.472(5), Cu(3)–O(7) 2.444(5) Å) (Table 2). The molecular asymmetrical cluster results from the association of dinuclear units (Cu(1), Cu(5) and Cu(2), Cu(4)), which are linked by two tartrate and the third copper atom (Cu(3)). Five copper atoms in the cluster are arranged as overlap

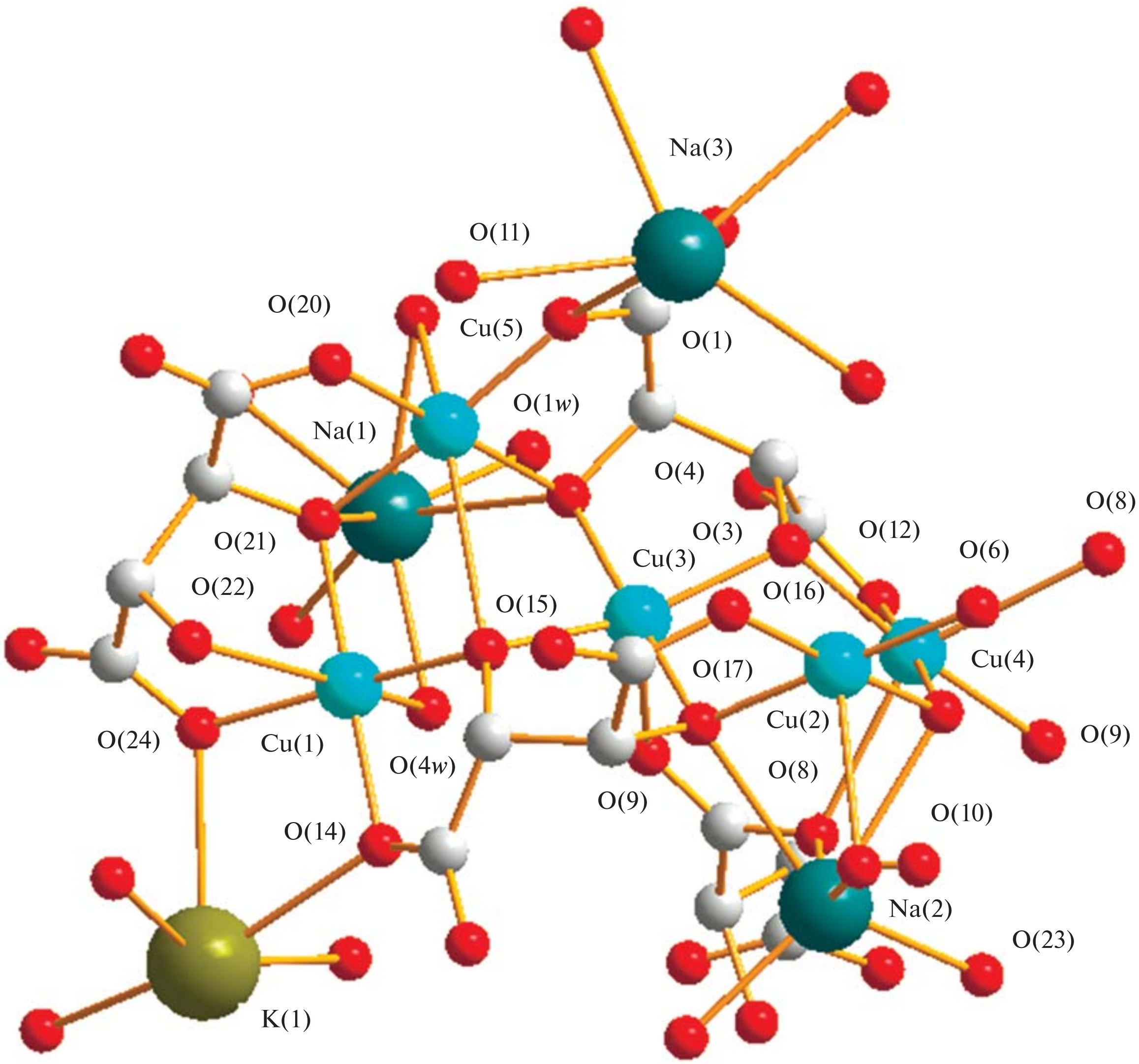


Fig. 1. The coordination environments of the Cu, Na, and K atoms in **I**. All hydrogen atoms have been omitted for clarity.

angle based core with Cu(3) at the middle of the cycle. The distance from middle copper Cu(3) to the four others average is 3.27 Å. This distance is to compared with the one observed, 3.46 Å, in the complex described by Latour et al., where the 3,6-bis((4-methylpiperazino)methyl)pyrocatechols bridges five copper atoms [18]. The pentanuclear copper cluster further binds to adjacent four pentanuclear clusters (Fig. 2a), the $\{Cu_5\}$ core linked alternatively neighboring $\{Cu_5\}$ cores to form a nanosized $\{Cu_{10}\}$ core that appears as hexagonal rim with an empty center along *b* direction in a staggered fashion. Two pairs of $\{Cu_{10}\}$ cores share Cu ions and were joined by four O(COO$^-$) atoms, forming a highly-ordered layered cluster network with honeycomb arrays (Figs. 2b, 2c).

In **I**, two kinds of alkaline earth ions exist, they are coordinated by carboxylic oxygen atoms, hydroxyl atoms and water molecules and share oxygen atoms with five independent Cu centers. Interestingly, sodium atom exhibits three kinds of coordination modes: Na(1), Na(2), and Na(3) are seven-, six- and fivecoordinate, respectively. Four Na atoms (two Na(1), one Na(2), and one Na(3)) are linked by oxo and hydroxo bridges to give one macrocycle (Fig. 3a). Additionally, a claw of crab is constructed by four Na(1), two Na(2), and two Na(3) along *bc* plane, which is extended by tartrate ligands into a layer (Fig. 3b). While potassium ion only adopts five-coordinate and has square pyramidal environment. Adjacent K ions are connected by two tartrate ligands,

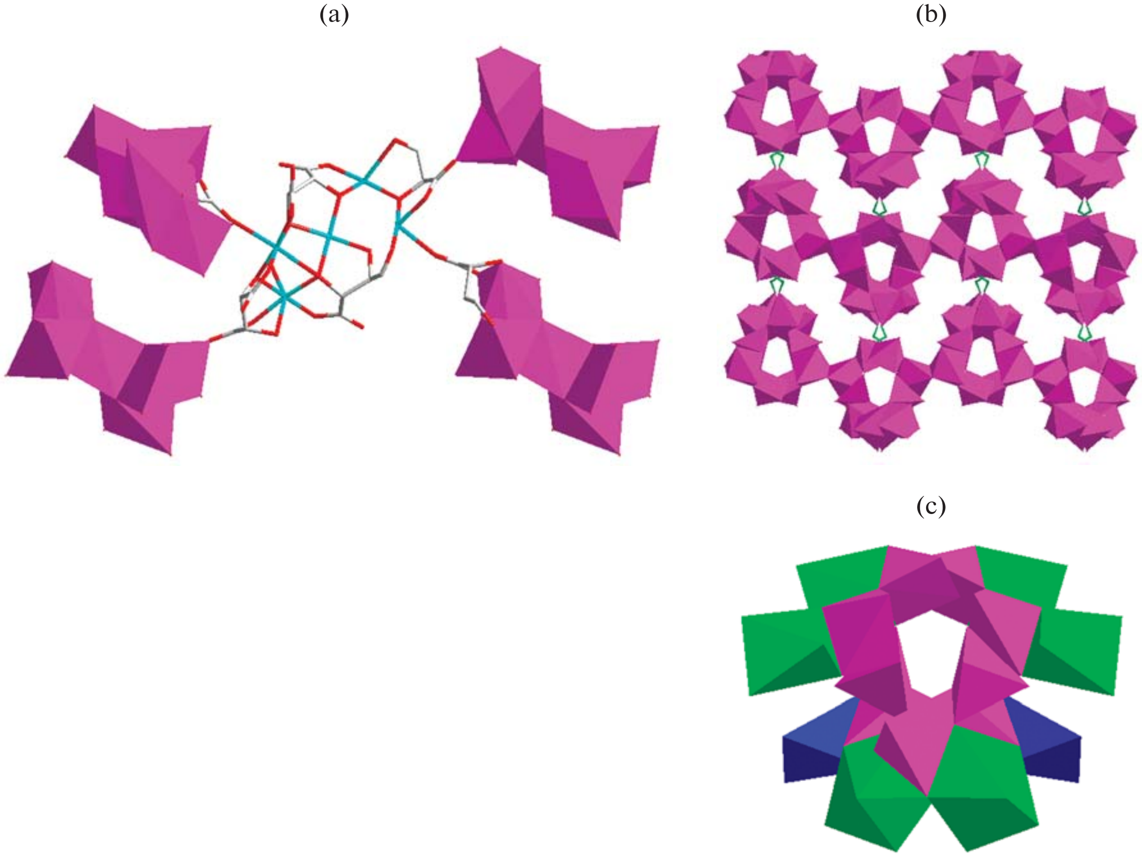


Fig. 2. Schematic view of a pentanuclear copper cluster and its adjacent four copper clusters (a); a perspective viewing of (4,4) cluster layer (b); viewing of a shell-like cap (c).

extending 1D chain with loop. Each $\{Cu_{10}\}$ core is capped by six sodium atoms and two potassium atoms (Fig. 3b). Remarkably, the overall structure of **I** consists of 3D framework. Unlike the $[Cu(H_2Tar)_2KNa]$ polymer [19], the K of eight coordination and Na of six coordination only connect with dicopper atoms via two tartrate ligands, which form a complicated structure with small channel, while in $K_5Na(\mu\text{-}CO_3)(Me\text{-}Hxta)]_2 \cdot 4H_2O$ (H_2Hxta = *N*,*N*'-(2-hydroxy-1,3-xylylene-bis-(*N*-carboxymethylglycine) [20], the potassium and sodium are linked by bridging water ligands to form irregular $\{K_5Na(OH_2)_{10}\}_n$ sheet. The dinuclear copper centers are attached alternatively above and below the $\{K_5Na(OH_2)_{10}\}_n$ sheets, thus, leads to a 2D sandwich architecture. The $\{Cu_{10}\}/\{Na_6\}/\{K_2\}$ serrated-cluster networks formed in **I** due to the synergistic coordination between the tartrate ligands. To the best of our knowledge, compound **I** is the first example of high-nuclear transition metal MOF intercalating two alkaline earth atoms. The framework of **I** can be described as the generation under the synergistic coordination among one bridging linkage and two inorganic light metal ions.

Magnetization fitting was conducted by MagSaki software (ver. BW 0.6.0) [21], and simultaneous fitting of susceptibility and magnetization was conducted by PHI software (ver. 3.1.0) [22]. The χ_mT value was 1.33 cm^3 K mol^{-1} at 300 K (Fig. 4), and this is much larger than the spin only value (0.375 cm^3 K mol^{-1}) for the $S = 1/2$ state. When decreasing the temperature, the χ_mT value decreases monotonously to 1.33 cm^3 K mol^{-1} at 6 K. Below 6 K, the value further decreased to 0.43 cm^3 K mol^{-1} at 2 K, but is still larger than the spin only value. At first, in the in the ground-state search by the brute-force method, the magnetization per Cu_5 unit was successfully simulated by the Brillouin function with $g = 2.1$ for the $S = 3/2$ state. Then, the simultaneous fitting of the magnetic susceptibility and the magnetization data were analyzed by the centrosymmetric Cu_{10} model $[H = -J_1(S_1S_2 + S_9S_{10}) - J_2(S_1S_3 + S_8S_{10}) - J_3(S_2S_3 + S_8S_9) - J_4(S_3S_4 + S_7S_8) - J_5(S_3S_5 + S_6S_8) - J_6(S_4S_5 + S_6S_7) - J_7\ S_5S_6]$ (Fig. 5), fixing the g value to 2.1. Judging from the crystal structure, the interactions between the Cu_{10} units seem to be weaker than the interactions in the Cu_{10} unit. The best-fitting parameters were obtained as $g = 2.1$, $J_1 = 67.9$ cm^{-1},

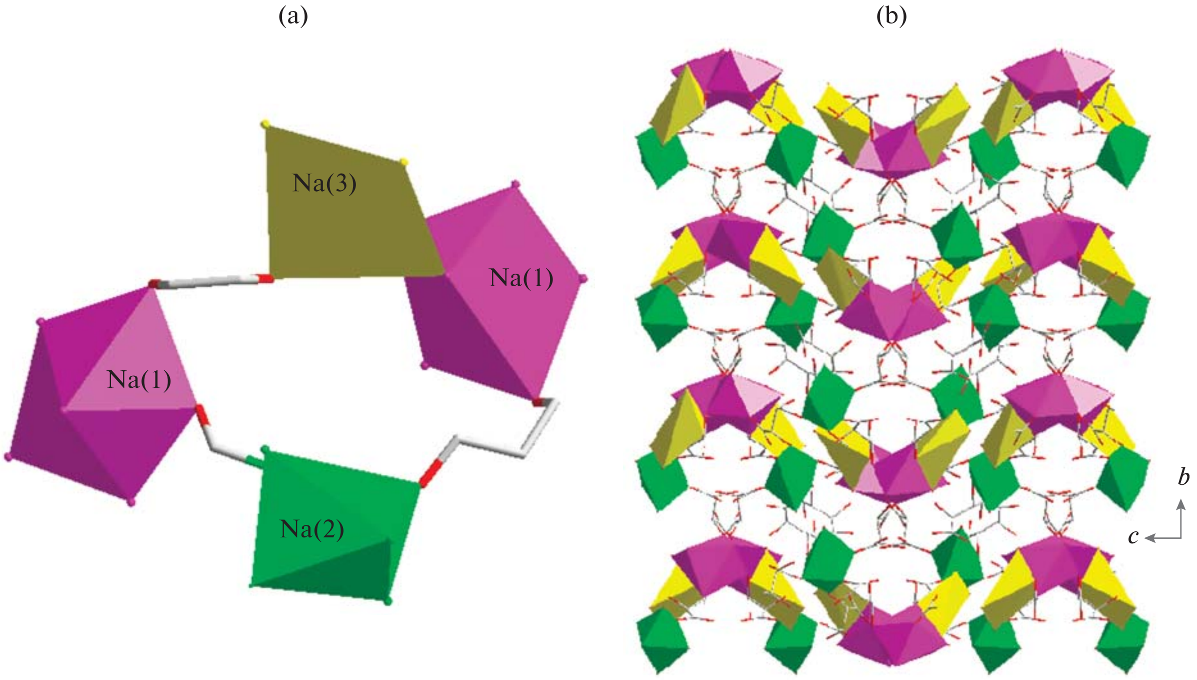


Fig. 3. View of the Na cycle (a); section of the 2D network of Na clusters (b).

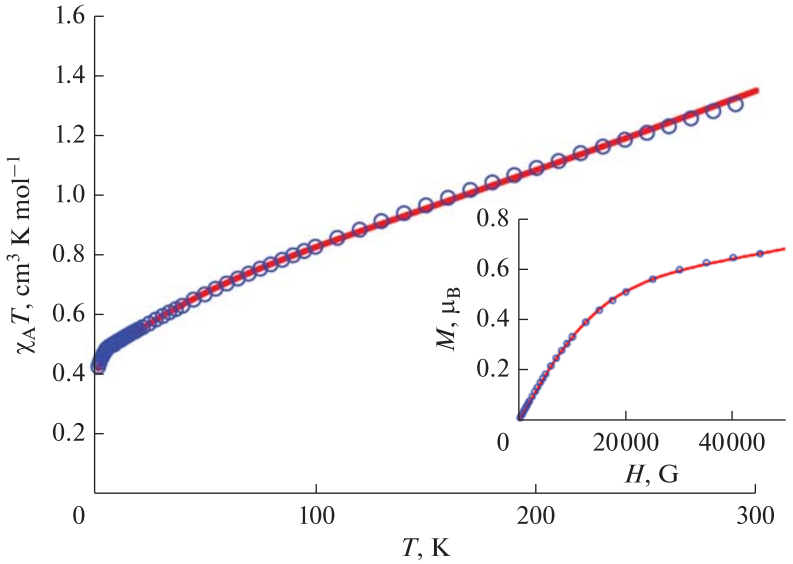


Fig. 4. Temperature dependence of $\chi_m T$ and field dependence of magnetization per Cu at 2 K (insertion).

$J_2 = 64.2$ cm^{-1}, $J_3 = 69.8$ cm^{-1}, $J_4 = -0.01$ cm^{-1}, $J_5 = 0.36$ cm^{-1}, $J_6 = -9.98$ cm^{-1}, $J_7 = -24.7$ cm^{-1}, and TIP = 2.9×10^{-3} cm^3 mol^{-1}, where TIP is the temperature independent paramagnetism per Cu. The theoretical curves are also included in Fig. 4. The large TIP value is explained by decreasing the energy gap between the ground and excited states in the 3D polymer [23]. It is not easy to determine lots of parameters correctly; however, we can conclude that the interaction between the two Cu_5 units in the Cu_{10} unit is antiferromagnetic and that the ground state of the Cu_5 unit corresponds to the $S = 3/2$ state due to the ferromagnetic interactions in the Cu_5 unit.

Thus, a 3D coordination polymer of $[Na_3KCu_5(Tar)_2(HTar)_2(H_2O)_7]$ (H_2Tar = tartaric acid) was designed and synthesized. The title polymer is built up

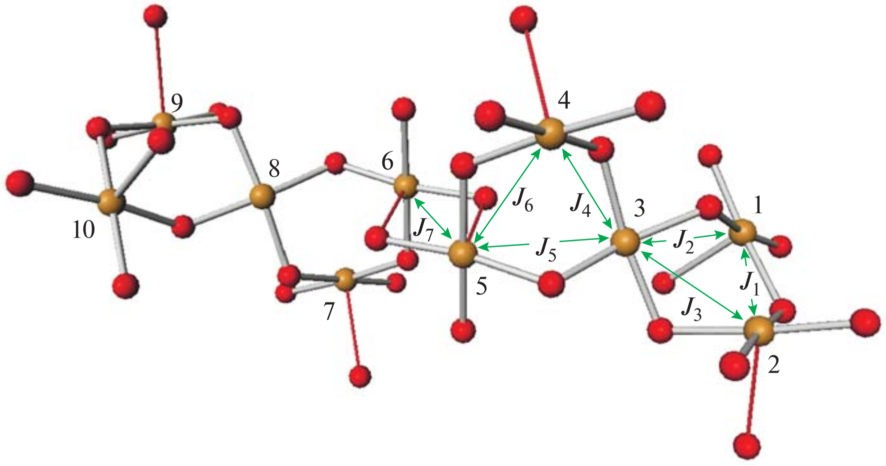


Fig. 5. Cu_{10} model for magnetic analysis in **I** (figures 1–10 are Cu atoms, respectively).

in a shell-like manner based on inner two symmetry-related pentanuclear copper cores and shows a 3D nanoporous architecture. Furthermore, it exhibits antiferromagnetic feature between the two Cu_5 units.

ACKNOWLEDGMENTS

This work was partially supported by the grants from Innovative Entrepreneurial Training Plan of undergraduates in Guangdong Province (nos. 201710571007, 201710571012, 201710571019, 2017105710116, 201710571048, 201710571060, 201710571078), the Public Research and Capacity Building Projects of Department of Guangdong Province (no. 2017A010103022), Natural Science Foundation of Guangdong Province (no. 2017A030313079) and Science Foundation funded project of Guangdong Medical University (nos. Z2016001 and M2016023) and the Japan Society for the Promotion of Science (JSPS) KAKENHI (no. 15K05445).

REFERENCES

1. Kitagawa, S., Kitaura, R., and Noro, S.I., *Angew. Chem., Int. Ed.*, 2004, vol. 43, p. 2334.
2. Eddaoudi, M., Kim, J., Rosi, N., et al., *Science*, 2002, vol. 295, p. 469.
3. Ockwig, N.W., Delgado-Friederichs, O., O'Keeffe, M., et al., *Acc. Chem. Res.*, 2005, vol. 38, p. 176.
4. Moulto, B. and Zaworotko, M.J., *Chem. Rev.*, 2001, vol. 101, p. 1629.
5. Kong, X.J., Long, L.S., Zheng, Z., et al., *Acc. Chem. Res.*, 2010, vol. 43, p. 201.
6. Chen, B., Xiang, S., and Qian, G., *Acc. Chem. Res.*, 2010, vol. 43, p. 1115.
7. Batten, S.R. and Robson, R., *Angew. Chem. Int. Ed.*, 1998, vol. 37, p. 1460.
8. Evans, O.R., Ngo, H.L., and Lin, W.B., *J. Am. Chem. Soc.*, 2001, vol. 123, p. 10395.
9. James, S.L., *Chem. Soc. Rev.*, 2003, vol. 32, p. 276.
10. Rashidipour, M., Derikvand, Z., Shokrollahi, A., et al., *Arabian J. Chem.*, 2017, vol. 10, p. 3167.
11. Rashidipour, M., Derikvand, Z., Shokrollahi, A., et al., *J. Solid State Chem.*, 2015, vol. 225, p. 59.
12. Synoradzki, L., Bernas, U., and Ruskowski, P., *Org. Prep. Proc. Int.*, 2008, vol. 40, p. 163.
13. McCanq, M., Humphreys, F., and McKee, V., *Polyhedron*, 1997, vol. 16, p. 3655.
14. Meng, X., Shi, J.-C., Tong, Q., et al., *J. Coord. Chem.*, 2008, vol. 61, p. 3549.
15. Du, Y.E. and Han, Z.B., *Russ. J. Coord. Chem.*, 2011, vol. 37, p. 506.
16. Xiang, S., Wu, X., Zhang, J., et al., *J. Am. Chem. Soc.*, 2005, vol. 127, p. 16352.
17. Sheldrick, G.M., *SHELXL-97, Program for Structure Determination and Refinement*, Göttingen: Univ. of Göttingen, 1997.
18. Gojon, E., Gaillard, J., Latour, J.M., et al., *Inorg. Chem.*, 1987, vol. 26, p. 2047.
19. Zhou, Y.X., Shen, X.Q., Liu, H.L., et al., *Syn. React. Inorg. Met.*, 2006, vol. 36, p. 563.
20. Laborda, S., Clérac, R., Anson, C.E., et al., *Inorg. Chem.*, 2004, vol. 43, p. 5931.
21. Sakiyama, H., *J. Comput. Chem. Jpn.*, 2007, vol. 6, p. 23.
22. Chilton, N.F., Anderson, R.P., Turner, L.D., et al., *J. Comput. Chem.*, 2013, vol. 34, p. 1164.
23. Wang, J., Li, B., Lu, L., et al., *Dalton Trans.*, 2017, vol. 46, p. 15178.