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Two unprecedented 1D coordination polymer chains based on tetranuclear copper(II) building blocks

Gaijuan Li, Yan Xing *, Shuyan Song, Ning Xu, Xianchun Liu, Zhongmin Su

College of Chemistry, Northeast Normal University, 5268 Renmin Street, Changchun 130024, PR China

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ABSTRACT

The reaction of copper(II) sulfate with pyridine in DMF or methanol yield two unprecedented Cu(II) coordination polymers $\{[Cu_4(\mu_4\text{–}O)(py)_4(SO_4)_4][\mu\text{–}Cu(py)(DMF)_2]\}_n$ **(1)** and $\{[Cu_4(\mu_4\text{–}O)(py)_4(SO_4)_4][\mu\text{-}Cu(py)_4]\}_n$ **(2)**, respectively. Single-crystal X-ray diffraction indicated that compound **1** crystallizes in the monoclinic system, space group $p2(1)/n$, $a = 14.542(5)$ Å, $b = 16.359(5)$ Å, $c = 18.951(5)$ Å, $\beta = 92.047(5)^\circ$, $V = 4505(2)$ Å^3, $Z = 4$ while **2** is monoclinic $C2/c$, $a = 23.078(5)$ Å, $b = 10.214(5)$ Å, $c = 23.142(5)$ Å, $\beta = 115.471(5)^\circ$, $V = 4925(3)$ Å^3, $Z = 4$. Both of the two compounds consist of tetrahedral tetranuclear $[Cu_4(\mu_4\text{–}O)(py)_4(SO_4)_4]$ clusters that are bridged by pentacoordinated Cu atom for **1** or hexacoordinated Cu atoms for **2** through the sulfate oxygen to form the infinite one-dimensional polymer chains.

1. Introduction

The construction of polynuclear coordination polymer has attracted great interests because of their potential applications and intriguing variety of architectures and topologies [1–3]. In particular, higher nuclearity copper(II) complex is of particular interest, not only because of the fundamental role of copper in numerous catalytic processes in living organisms [4–6], but also owing to the possibility provided by copper(II) polynuclear complexes of exploration of magneto-structural correlations [7–9]. So far, many polynuclear copper(II) complexes have been obtained with such ligands as pyrazole, triazole or their derivatives, which not only exhibit an extensive ability to bridge metal ions to afford polynuclear compounds but also have a superexchange capacity [10–21]. Since Bertrand and Kelley [22,23] characterized the first tetranuclear copper(II) complex of the general formula $[Cu_4OX_{10-n}L_4]^{n-4}$ ($X = $ Br or Cl; $L = $ Lewis-base ligand), a great number of tetranuclear 4-oxo-bridged copper(II) complexes with polydentate ligands has been studied from a magneto-structural point of view [24–30]. However, monotopic ligand has rarely been used in directing construction of polynuclear Cu(II) architectures [31].

In this paper, we report the syntheses and magnetic properties of two new tetranuclear Cu(II) complexes. Both of the structures consist of Cu_4O-based units that are bridged by Cu atom through the sulfate oxygen to form infinite one-dimensional (1D) coordination polymer chains. To the best of our knowledge, it is the first example of the compounds representing the use of tetranuclear copper(II) clusters as building blocks to form 1D networks.

2. Experimental section

2.1. Materials and methods

All chemicals used during the course of this work were of reagent grade and used as received from commercial sources without further purification. Syntheses were carried out in 18 mL Teflon-lined stainless-steel autoclave. Elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. Inductively coupled plasma (ICP) analyses were carried out on a Perkin-Elmer Optima 3300DV spectrometer. Infrared (IR) spectra were recorded within the 400–4000 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The thermalgravimetric analyses (TGA) were performed on Perkin-Elmer TGA 7 thermogravimetric analyzer in the air with a heating rate of 20 °C min^{-1}. Magnetic susceptibility data were collected over the temperature range 300–2 K at a magnetic field of 1000 Oe on a Quantum design MPMS–5 SQUID magnetometer.

2.2. Synthesis of compounds

2.2.1. Synthesis of 1

$\{[Cu_4(\mu_4\text{–}O)(py)_4(SO_4)_4][\mu\text{–}Cu(py)(DMF)_2]\}_n$ was synthesized using mild solvothermal conditions and autogenous pressure.

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* Corresponding author.
E-mail addresses: xingyan69cn@yahoo.com.cn, xingy202@nenu.edu.cn (Y. Xing).

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A reaction mixture of $CuSO_4 \cdot 5H_2O$ (0.125 g, 0.5 mmol), pyridine (0.18 mL, 2.3 mmol) and DMF (10 mL) was stirred for 15 min in air, then transferred to and sealed in a Teflon-lined autoclave. This was heated to 353 K for 72 h, followed by slow cooling down to room temperature. The resulting bright green pillar-like single crystals were isolated by filtration, washed with distilled water and dried in air (yield 0.088 g, ca.70% based on Cu). The ICP and elemental analysis calcd (%) for **1** ($C_{31}H_{39}Cu_5N_7O_{19}S_4$): Cu, 25.21; S, 10.16; C, 29.56; N, 7.78; H, 3.12; found: Cu, 25.15; S, 10.11; C, 29.42; N, 7.85; H, 3.09.

2.2.2. *Synthesis of* **2**

Compound **2** was synthesized in the same method as **1**, except that 10 mL of DMF solvent was replaced by 5 mL of methanol and then green thin block crystals were gained (yield 0.094 g, ca. 75% based on Cu). The ICP and elemental analysis calcd (%) for **2** ($C_{20}H_{20}Cu_{2.5}N_4O_{8.5}S_2$): Cu, 23.51; S, 9.48; C, 35.57; N, 8.30; H, 2.99; found: Cu, 23.58; S, 9.53; C, 35.42; N, 8.37; H, 2.89.

2.3. *Determination of crystal structure*

Crystal data for **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo*K*α radiation ($\lambda = 0.71069$ Å). Data processing was accomplished with the SAINT processing program [32]. Both structures were solved by direct methods with the SHELXTL 97 software package [33]. All non-hydrogen atoms were refined anisotropically. While all H atoms were positioned geometrically and refined as riding mode. Experimental details for the structural determinations of two compounds are presented in Table 1. The selected bond distances and angles are shown clearly in Table 2 for **1** and Table 3 for **2**. CCDC 665524–665525. For crystallographic data in CIF or other electronic format (fax: (+44)-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Table 1
Crystal data and structure refinement for **1** and **2**

	1	2
Empirical formula	C31 H39 Cu5 N7 O19 S4	C20 H20 Cu2.5 N4 O8.5 S2
Formula weight	1259.63	675.37
Temperature	293(2) K	293(2) K
Wavelength	0.71069 Å	0.71069 Å
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*n*	C2/*c*
a (Å)	14.542(5)	23.078(5)
b (Å)	16.359(5)	10.214(5)
c (Å)	18.951(5)	23.142(5)
β (deg)	92.047(2)	115.471(5)
Volume (Å^3)	4505(2)	4925(3)
Z	4	8
D_{calc} (mg m^{-3})	1.857	1.822
Absorption coefficient (mm^{-1})	2.589	2.373
F(000)	2540	2724
Crystal size (mm^3)	0.36 × 0.15 × 0.13	0.34 × 0.34 × 0.15
θ range (deg)	1.64–28.29	1.95–28.28
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0374$, $wR_2 = 0.0922$	$R_1 = 0.0390$, $wR_2 = 0.0896$
R indices (all data)	$R_1 = 0.0566$, $wR_2 = 0.1010$	$R_1 = 0.0598$, $wR_2 = 0.0994$

Table 2
Selected bond lengths (Å) and bond angles (deg) for **1**

N(1)–Cu(1)	2.000(3)	O(19)–Cu(2)	1.936(2)
O(19)–Cu(1)	1.960(2)	O(5)–Cu(2)	2.342(4)
O(5)–Cu(1)	2.037(3)	N(2)–Cu(2)	1.985(2)
O(1)–Cu(1)	1.980(2)	O(16)–Cu(2)	2.076(2)
O(11)–Cu(1)	2.323(3)	O(9)–Cu(2)	2.091(3)
		O(7)–Cu(2)	2.380(3)
O(2)–Cu(3)	2.168(2)	O(6)–Cu(4)	2.194(2)
O(19)–Cu(3)	1.954(2)	O(13)–Cu(4)	2.011(2)
N(3)–Cu(3)	2.003(3)	O(17)–Cu(5)	1.967(2)
O(14)–Cu(3)	1.985(2)	O(18)–Cu(5)	1.949(2)
O(10)–Cu(3)	2.009(3)	O(12)–Cu(5)	1.986(3)
N(4)–Cu(4)	1.993(3)	N(5)–Cu(5)	2.038(3)
O(19)–Cu(4)	1.933(2)	O(4)–Cu(5)	2.124(2)
O(3)–Cu(4)	2.078(2)	O(9)–S(3)	1.489(3)
O(1)–S(1)	1.481(2)	O(10)–S(3)	1.447(3)
O(2)–S(1)	1.465(2)	O(11)–S(3)	1.431(3)
O(3)–S(1)	1.471(2)	O(12)–S(3)#1	1.430(3)
O(4)–S(1)	1.465(2)	O(13)–S(4)	1.473(2)
O(5)–S(2)	1.516(3)	O(14)–S(4)	1.481(2)
O(6)–S(2)	1.473(2)	O(15)–S(4)	1.441(2)
O(7)–S(2)	1.443(3)	O(16)–S(4)	1.469(2)
O(8)–S(2)	1.404(3)		
O(5)–Cu(1)–O(11)	89.31(14)	O(5)–Cu(1)–Cu(2)	50.62(11)
O(19)–Cu(1)–Cu(2)	38.76(6)	O(11)–Cu(1)–Cu(2)	78.73(9)
O(1)–Cu(1)–Cu(2)	132.34(6)	O(19)–Cu(2)–N(2)	172.55(9)
N(1)–Cu(1)–Cu(2)	141.32(8)	O(19)–Cu(2)–O(16)	94.06(9)
N(1)–Cu(1)–O(11)	88.62(11)	N(2)–Cu(2)–O(16)	93.32 (9)
N(2)–Cu(2)–O(7)	84.02(10)	O(19)–Cu(2)–O(9)	91.49(9)
O(16)–Cu(2)–O(7)	96.79(10)	N(2)–Cu(2)–O(9)	87.50(10)
O(9)–Cu(2)–O(7)	156.80(12)	O(16)–Cu(2)–O(9)	105.24(12)
O(5)–Cu(2)–O(7)	59.06(9)	O(19)–Cu(2)–O(5)	76.84(9)
O(19)–Cu(2)–Cu(1)	39.32(6)	N(2)–Cu(2)–O(5)	96.09(10)
N(2)–Cu(2)–Cu(1)	133.26(7)	O(7)–Cu(2)–Cu(1)	87.40(6)
O(16)–Cu(2)–Cu(1)	133.35(7)	O(9)–Cu(2)–O(5)	100.65(11)
O(9)–Cu(2)–Cu(1)	82.79(8)	O(19)–Cu(2)–O(7)	94.15(9)
O(5)–Cu(2)–Cu(1)	42.24(7)	O(16)–Cu(2)–O(5)	152.77(10)
O(19)–Cu(3)–N(3)	174.47(10)	O(14)–Cu(3)–O(2)	112.56(10)
O(14)–Cu(3)–N(3)	86.55(11)	N(3)–Cu(3)–O(2)	92.04(10)
O(19)–Cu(3)–O(10)	93.79(12)	O(10)–Cu(3)–O(2)	93.94(11)
O(14)–Cu(3)–O(10)	152.24(13)	O(19)–Cu(3)–O(14)	92.82(9)
O(19)–Cu(3)–O(2)	93.27(8)	N(3)–Cu(3)–O(10)	84.31(14)
O(19)–Cu(4)–N(4)	177.86(10)	O(18)–Cu(5)–O(17)	174.33(11)
O(19)–Cu(4)–O(13)	95.11(9)	O(18)–Cu(5)–O(12)	91.79(12)
N(4)–Cu(4)–O(13)	86.46(9)	O(17)–Cu(5)–O(12)	85.86(12)
O(19)–Cu(4)–O(3)	91.92(8)	O(18)–Cu(5)–N(5)	88.02(10)
N(4)–Cu(4)–O(3)	88.23(10)	O(17)–Cu(5)–N(5)	90.87(10)
O(13)–Cu(4)–O(3)	128.19(10)	O(18)–Cu(5)–O(4)	88.63(9)
O(19)–Cu(4)–O(6)	88.31(9)	N(5)–Cu(5)–O(4)	112.02(10)
N(4)–Cu(4)–O(6)	89.57(11)	O(12)–Cu(5)–N(5)	144.23(12)
O(13)–Cu(4)–O(6)	129.53(10)	O(18)–Cu(5)–O(4)	88.63(9)
O(3)–Cu(4)–O(6)	101.89(10)	O(17)–Cu(5)–O(4)	96.95(10)
O(12)–Cu(5)–O(4)	103.73(12)	O(18)–Cu(5)–O(17)	174.32(11)

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

3. Results and discussion

3.1. *Structure determination of* **1** *and* **2**

Compounds $\{[Cu_4(\mu_4\text{–}O)(py)_4(SO_4)_4][\mu\text{–}Cu(py)(DMF)_2]\}_n$ (**1**) and $\{[Cu_4(\mu_4\text{–}O)(py)_4(SO_4)_4][\mu\text{–}Cu(py)_4]\}_n$ (**2**) were solvothermally synthesized from a mixture of copper(II) sulfate and pyridine in DMF or methanol medium, respectively. The structures of **1** and **2** are both characterized by the presence of the tetrahedral $[Cu_4(\mu_4\text{–}O)(py)_4(SO_4)_4]$ cores, which can be considered as the building blocks for construction of the 1D architecture of these compounds. Figs. 1(a) and 2(a) show the molecular structures of tetrahedral tetranuclear Cu(II) cluster of **1** and **2**, respectively. In both **1** and **2**, each tetranuclear cluster consists of a distorted tetrahedron of four Cu(II) atoms coordinating to a central μ_4-oxygen atom. The tetranuclear Cu(II) cluster in **2** is crystallographic axis-symmetrical. The Cu-to-central oxygen atom distances (average 1.946 Å (**1**); 1.925 Å (**2**)) and Cu–O–Cu bond angles (range from 101.92(9)° to 117.23(10)° (**1**); 99.82(13)° to 119.52(14)° (**2**)) are in the normal range of tetranuclear complexes having $\{Cu^{II}_4(\mu_4\text{–}O)\}$ units [25,28]. The Cu⋯Cu distances range from 3.026 to 3.341 Å for **1** and from 2.933 to 3.341 Å for **2**. This is comparable to the Cu⋯Cu distances in some of the μ_4-oxo tetracopper complexes that have been reported [28,31].

In the building block of **1**, there exists two different coordination polyhedra around the four copper atoms, Cu(1) and Cu(2) display distorted octahedral geometries: four O donors from three different sulfate groups define the equatorial plane, the axial positions are occupied by one pyridine N atom and the central μ_4-oxo atom (O(19)). While the coordination of Cu (3) and Cu (4) atoms is distorted trigonal bipyramidal, a nitrogen atom from the pyridine molecule and the μ_4-oxide occupy the axial positions, and three bridging sulfate O atoms coordinate the equatorial sites. The way of coordination of the sulfate is an interesting structural aspect of this compound. **1** contains two tridentate sulfato ligands (S(2) and S(4)) and two tetradentate bridging sulfato groups (S(1) and S(3)). Both of the two tridentate sulfato groups bind three different Cu atoms of the same building unit. The S–O$_{terminal}$ distances [1.422(2) Å av.] are shorter than those for the coordinated oxygens [1.476 Å av.]. Interestingly, each of the tetradentate sulfato groups connect to three different Cu atoms from the same building unit and the forth coordination is from the unique Cu(II) atom, Cu(5). As far as we know, this is the first structurally characterized complex containing not only tridentate, but also tetradentate bridging sulfato ligands. The single copper atom, Cu(5), placed on a special position, is five-coordinated, with two O atoms from solvent molecules (DMF), one N atom from the pyridine and two O atoms from two tetradentate sulfate groups, completing a distorted CuO_4N trigonal bipyramidal geometry (as shown in Fig. 1(b)). It is noteworthy that tetrahedral tetranuclear building blocks are covalently linked to single Cu(5) atoms through Cu(II)–sulfato O interactions [Cu(5)–O(4) and Cu(5)–O(12) bond lengths are 2.124(2) and 1.986(3), respectively], thus generating an unusual polymeric 1D zigzag chain running along the [010] direction (Fig. 3). To the best of our knowledge, this is the first example of polynuclear Cu(II) 1D chains complexes in which the tetrahedral tetranuclear units are connected to each other through single Cu(II) atom bridges. Obviously, the sulfate anions acting as tetradentate metal linker have a significant effect on the formation of the chain.

Table 3
Selected bond lengths (Å) and bond angles (deg) for **2**

N(1)–Cu(1)	2.002(3)	N(2)–Cu(2)	1.974(3)
O(4)–Cu(1)#1	2.095(2)	O(9)–Cu(2)	1.9168(18)
O(5)–Cu(1)	2.085(2)	O(6)–Cu(2)	2.017(2)
O(1)–Cu(1)	2.028(2)	O(2)–Cu(2)	1.975(2)
O(9)–Cu(1)	1.9336(15)	O(1)–S(1)	1.479(2)
Cu(3)–N(4)#2	2.012(3)	O(2)–S(1)	1.492(2)
Cu(3)–N(3)#2	2.016(3)	O(3)–S(1)	1.445(2)
N(3)–Cu(3)	2.016(3)	O(4)–S(1)	1.470(2)
N(4)–Cu(3)	2.012(3)	O(5)–S(2)	1.500(3)
Cu(1)–Cu(2)#1	3.0517(10)	O(6)–S(2)	1.495(2)
Cu(2)–Cu(2)#1	2.9329(10)	O(7)–S(2)	1.454(3)
Cu(2)–Cu(1)#1	3.0517(10)	O(8)–S(2)	1.437(2)
O(9)–Cu(1)–N(1)	175.67(8)	O(9)–Cu(2)–N(2)	164.27(9)
O(9)–Cu(1)–O(1)	92.90(7)	O(9)–Cu(2)–O(2)	93.21(9)
N(1)–Cu(1)–O(1)	91.13(10)	N(2)–Cu(2)–O(2)	93.69(10)
O(9)–Cu(1)–O(5)	85.91(10)	O(9)–Cu(2)–O(6)	91.90(9)
N(1)–Cu(1)–O(5)	92.69(11)	N(2)–Cu(2)–O(6)	92.71(11)
O(1)–Cu(1)–O(5)	130.00(11)	O(2)–Cu(2)–O(6)	136.83(10)
O(9)–Cu(1)–O(4)#1	90.83(8)	O(9)–Cu(2)–Cu(2)#1	40.09(6)
N(1)–Cu(1)–O(4)#1	85.97(10)	N(2)–Cu(2)–Cu(2)#1	131.66(8)
O(1)–Cu(1)–O(4)#1	116.49(11)	O(2)–Cu(2)–Cu(2)#1	133.28(6)
O(5)–Cu(1)–O(4)#1	113.51(11)	O(6)–Cu(2)–Cu(2)#1	62.71(7)
O(9)–Cu(1)–Cu(2)#1	37.38(4)	O(9)–Cu(2)–Cu(1)#1	37.76(3)
N(1)–Cu(1)–Cu(2)#1	139.00(8)	N(2)–Cu(2)–Cu(1)#1	131.11(9)
O(1)–Cu(1)–Cu(2)#1	129.01(7)	O(2)–Cu(2)–Cu(1)#1	77.28(7)
O(5)–Cu(1)–Cu(2)#1	57.06(8)	O(6)–Cu(2)–Cu(1)#1	126.56(7)
O(4)#1–Cu(1)–Cu(2)#1	82.84(7)	Cu(2)#1–Cu(2)–Cu(1)#1	64.896(17)
N(4)#2–Cu(3)–N(4)	180.0(2)	N(4)#2–Cu(3)–N(3)	90.69(12)
N(4)#2–Cu(3)–N(3)#2	89.31(12)	N(4)–Cu(3)–N(3)	89.31(12)
N(4)–Cu(3)–N(3)#2	90.69(12)	N(3)#2–Cu(3)–N(3)	180.0(2)

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

In the tetranuclear Cu(II) cluster of **2**, two different types of Cu atoms can be distinguished, Cu(1) and Cu(2). Cu(1) is coordinated by one pyridine N atom, one central μ_4-O atom (O(9)) and three O atoms from three sulfate groups, forming a distorted CuO_4N trigonal bipyramid, while Cu(2) is ligated by four sulfate O atoms (Cu(2)–O(5) and Cu(2)–O(6) distances of 2.596 and 2.692 Å, respectively, are indicative of a weak Cu–sulfate interactions) [34], one N atom from pyridine, and one μ_4-O atom to furnish a distorted CuO_5N octahedron. The tetrahedral sulfate groups of **2** are all tridentate bridging ligands, $S(1)O_4$ group binds three different Cu atoms from the tetranuclear cluster, while $S(2)O_4$ group binds Cu(2) atom from the building block through O(5) and O(6), and a third coordination is from the single Cu(II) atom, Cu(3). The S–O$_{terminal}$ average distance of 1.441(2) Å is shorter than those for the coordinated oxygens [1.482 Å av.]. The coordination environment of the unique Cu(3) atom is perfect octahedron (as shown in Fig. 2(b)): four N donors from four pyridine molecules, and two O atoms from two tridentate sulfate groups. The tetrahedral tetranuclear Cu(II) clusters are connected to single

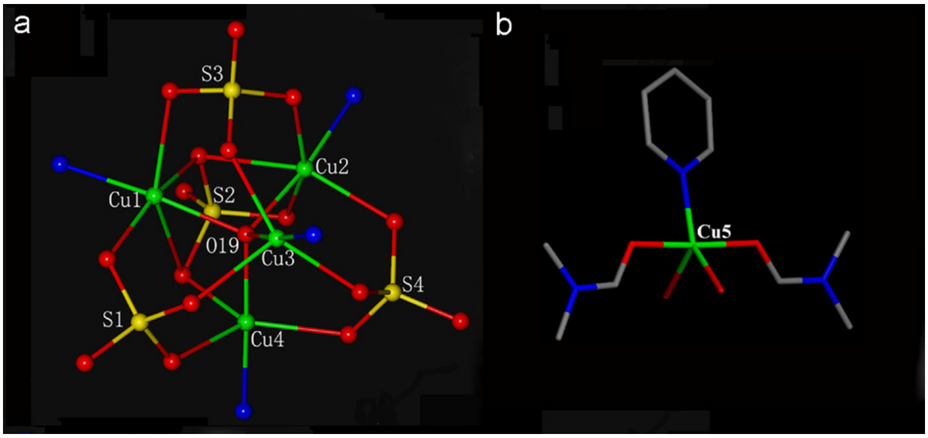

Fig. 1. (a) The molecular structure of tetrahedral tetranuclear Cu(II) clusters and (b) the coordination environment of unique bridged Cu(5) atom in compound **1**.

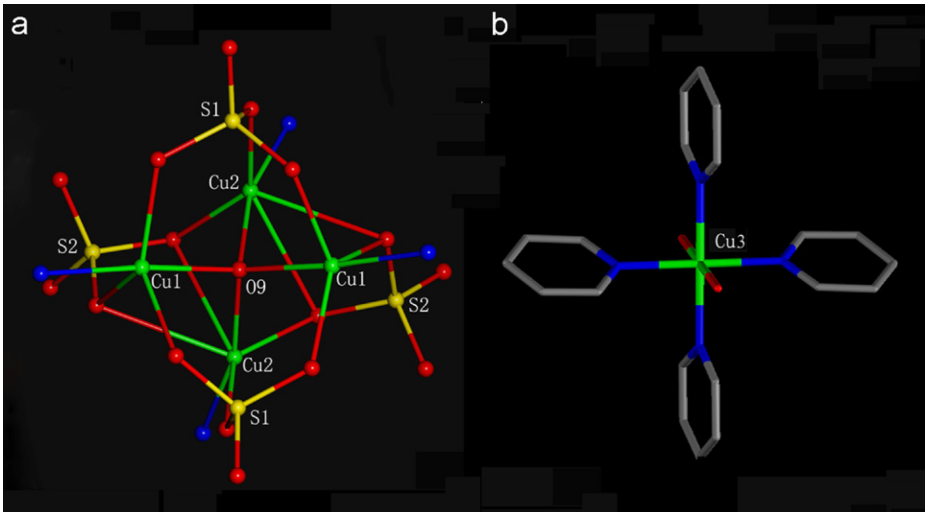

Fig. 2. (a) The molecular structure of tetrahedral tetranuclear Cu(II) clusters and (b) the coordination environment of unique bridged Cu(3) atom in compound **2**.

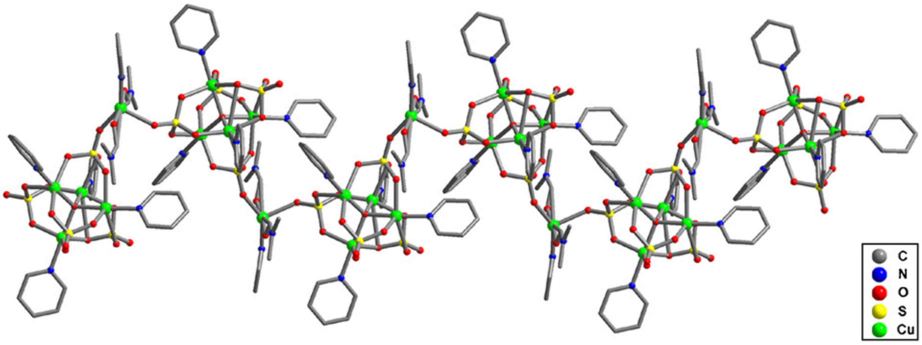

Fig. 3. The fragment of the polymeric chain of **1**.

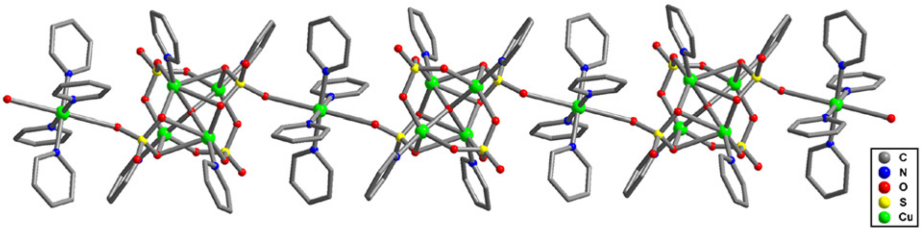

Fig. 4. The fragment of the polymeric chain of **2**.

Cu(3) atoms through weak Cu–sulfate interactions with Cu(3)–O(7) distance of 2.801 Å [35,36], giving rise to the 1D infinite chain (Fig. 4).

3.2. *Characterization*

3.2.1. *TGA*

In order to examine the thermal stability of **1** and **2**, TGA under air atmosphere were carried out. The TGA curves (Fig. 5) of **1** and **2** show that they both are stable below 200 °C. The thermal decomposition of **1** is initiated between 200 and 330 °C by a weight loss of 44.34 wt%, corresponding to the loss of the organic parts (calc. 43.00 wt%). There is a further 24.48 wt% weight loss in the continuous steps from 330 to 500 °C, which compares with the sulfates decomposition (calc. 25.24 wt%). For **2**, there is a 47.17 wt% weight loss in the range 200–380 °C, corresponding to the loss of the organic pyridine (calc. 46.85 wt%). The following losing step (20.96%) indicates the decomposition of the residual inorganic sulfates (calc. 21.69 wt%).

3.2.2. *IR*

Both of the compounds examined exhibit strong IR absorptions at 572 and 564 cm^{-1} for **1** and **2**, respectively, characteristic of the T_2 vibrational mode of the $\{Cu_4O\}$ core [28].

3.2.3. *Magnetic properties*

A preliminary magnetic study of the two complexes has been performed. The temperature dependence of the molar magnetic (χ) and the inverse molar magnetic susceptibilities (χ^{-1}) of the complexes **1** and **2** in the range 2–300 K are shown in Figs. 6 and 7, respectively. The thermal evolution of χ for complex **1** follow the Curie–Weiss law at temperature range from 30 to 300 K with

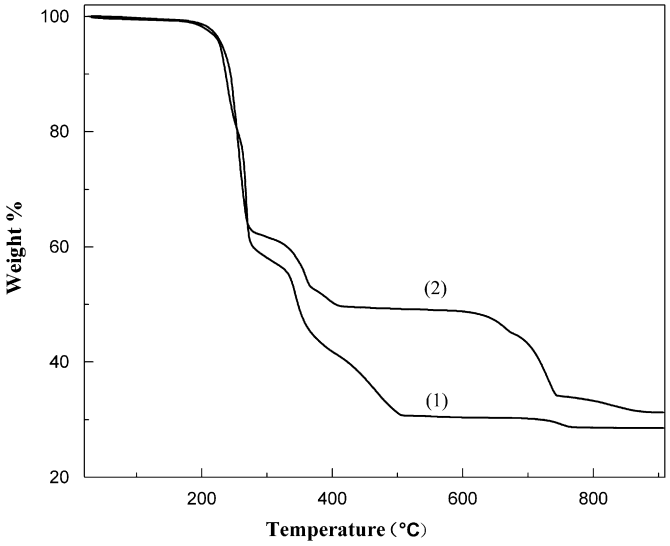

Fig. 5. The TG curves of **1** and **2**.

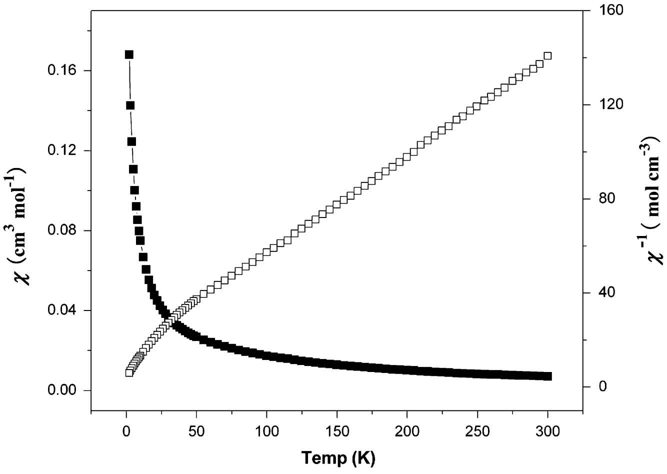

Fig. 6. Thermal evolution of χ and χ^{-1} for **1**.

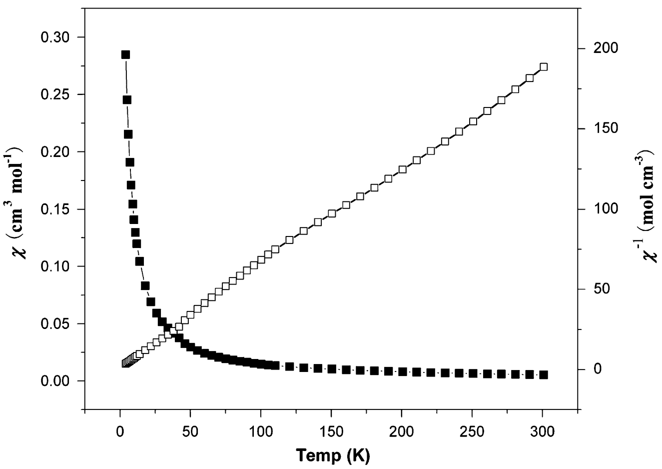

Fig. 7. Thermal evolution of χ and χ^{-1} for **2**.

$C = 2.421\,\text{cm}^3\,\text{K}\,\text{mol}^{-1}$ and $\theta = -38.60\,\text{K}$, and **2** obeys the Curie–Weiss law above 50 K, where $C = 1.686\,\text{cm}^3\,\text{K}\,\text{mol}^{-1}$ and $\theta = -12.05\,\text{K}$. There have existed the antiferromagnetic interactions both in **1** and **2**. The negative Weiss constants indicate operative antiferromagnetic interactions both in **1** and **2**. More detailed studies are currently carried out to evaluate the magnetic interactions in this system.

4. Conclusions

In conclusion, two 1D coordination polymers based on tetrahedral tetranuclear copper(II) building blocks have been successfully synthesized solvothermally. Individual tetranuclear copper cluster is bridged each other by unique Cu(II) atom through the sulfate oxygen. The sulfate groups acting as tridentate or tetradentate metal linker play an important role in the formation of the 1D polymeric structures of **1** and **2**. Our future studies will be aimed at further expansion of the polynuclear Cu(II) complex family and its interesting magnetic property.

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Appendix A. Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.05.045.

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