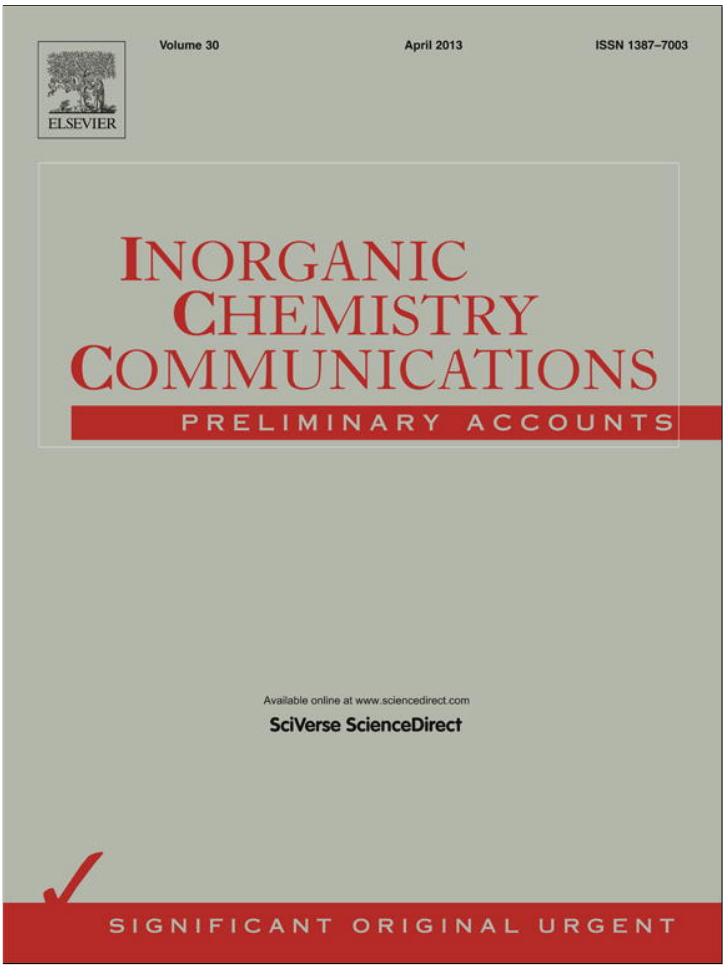

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A novel 3D metal–organic coordination polymer constructed from two types of tetranuclear copper clusters and a flexible bispyridyl-based ligand with amide-$(CH_2)_6$ bridge

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ABSTRACT

A new 3D metal–organic coordination polymer with an unusual 3,3,8,8-connected $\{4.5.6\}_4\{4^2.5^8.6^{12}.7^3.8^3\}\{4^2.5^9.6^{14}.7.8^2\}$ topology has been synthesized under hydrothermal condition, $[Cu_4(BTC)_2(\mathbf{L})(\mu_3\text{-}OH)_2(H_2O)]\cdot 6H_2O$ (**1**) [**L** = N,N′-bis(3-pyridinecarboxamide)-1,6-hexane, H_3BTC = 1,3,5-benzenetricarboxylic acid], which represents the first example of metal–organic frameworks based on two types of tetranuclear copper clusters $[Cu_4(\mu_3\text{-}OH)_2(O_2C\text{-})_6]$ and flexible bis-pyridyl-bis-amided based ligand. Moreover, the electrochemical behavior and magnetic property of **1** have been investigated.

The construction of metal–organic coordination polymers (MOCPs) remains a popular area due to their potential applications in fields as catalysis, photochromic or electrochromic response, medicine, and magnetics [1–3]. A variety of MOCPs with diversified topologies and interesting properties have been prepared through the judicious combination of metal ions and organic ligands with different features, such as shape, functionality, flexibility, symmetry, length, and substituent group [4–6]. Organic ligands as bridging linkers are of the most important factor for the construction of MOCPs because they greatly affect the final frameworks of the coordination polymers. During the assembly of high-dimensional MOCPs, the employment of mixed ligands, especially bridging polycarboxylates and neutral N-donor mixed ligands, has gradually become an effective approach. Moreover, the introduction of various N-donor ligands to metal-carboxylates synthetic systems can modify the structures and physical properties of the overall MOCPs. In this regard, numerous of MOCPs constructed from carboxylates and N-containing ligands have been reported [7–9], in which the bispyridyl-based N-heterocyclic ligands have proven to be excellent N-donor ligands for building novel coordination frameworks [10–12].

Recently, efforts by our group [13–15] and others [16–18] have mainly concentrated on the bispyridyl-based N-heterocyclic ligands with various bridging groups (such as amide-benzene-bridging group, carbonyl-piperazine-bridging group), and have obtained several unique structural motifs. For example, by using the bis(pyridinecarboxamide)-1,4-benzene ligand with amide–benzene bridge, we have obtained a novel 3-fold interpenetrating three-dimensional (3D) metal–organic framework $[Cu_3(4\text{-bpcb})_3(BTC)_2]_3\cdot\sim 12H_2O$ with (3,4)-connected $(6^3)(6^4\cdot 10^2)$ topology [4-bpcb = *N*,*N*′-bis(4-pyridinecarboxamide)-1,4-benzene, H_3BTC = 1,3,5-benzenetricarboxylic acid], in which discrete cage-like $(H_2O)_{12}$ water cluster guests occupy the voids [13]. With bis(pyridylformyl)piperazine ligands containing carbonyl-piperazine bridges, our group has obtained two two-dimensional (2D) layered structures and a novel 3,5-connected binodal 3D topology [15]. LaDuca's group has reported a series of 2D and 3D polymers based on the bis(4-pyridylformyl)piperazine ligand and aromatic dicarboxylate ligands [16,17].

Pursuing our work in this area, we introduce the more flexible amide-$(CH_2)_6$-bridging group into the bispyridyl-based organic ligands and obtain the ligand N,N′-bis(3-pyridinecarboxamide)-1,6-hexane (**L**). Compared with the ligands containing amide–benzene-bridging group or carbonyl-piperazine-bridging group, the ligand **L** with backbone of $\text{-}(CH_2)_6\text{-}$ can bend larger twist-degree to satisfy the coordination request of metal centers, so intriguing structures should be expected. Recently, Chen's group and Cao's group have reported a series of transition metal (Zn, Cd, Hg) complexes based on the flexible bispyridyl-based ligands with amide-$(CH_2)_n$-bridging (n = 0, 4, 10) [19–21]. Comparing **L** with these ligands reported by Chen and Cao (see Scheme S1), we can observe that not only the length of the $\text{-}(CH_2)_n\text{-}$ backbones is distinguishing, but also the sites of N–H and C=O groups in the amide are different, which belong to isomeric ligands for the positions of amide groups. To the best of our knowledge, the related complex constructed by the ligand **L** has not been found up to now. Therefore, we introduce **L** into the metal-BTC system and generate a novel 3D coordination polymer $[Cu_4(BTC)_2(\mathbf{L})(\mu_3\text{-}OH)_2(H_2O)]\cdot 6H_2O$ (**1**) under the hydrothermal condition, which represents the first 3D coordination polymer derived from **L** and aromatic polycarboxylate ligands.

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The ligand **L** was prepared according to the literature method [22]. Complex **1** was obtained by the hydrothermal reaction of $CuCl_2 \cdot 2H_2O$, H_3BTC, **L** and H_2O at 120 °C for 4 days [23]. Single crystal X-ray diffraction analysis [24] reveals that complex **1** is a 3D metal–organic coordination polymer constructed from two types of tetranuclear copper clusters and two kinds of bridging ligands (BTC and **L**). The asymmetric unit of **1** contains four crystallographically independent Cu^{II} ions, two BTC ligands, one **L** ligand, two μ_3-hydroxyl groups, one coordinated water molecule and six lattice water molecules. The coordination environments of four copper ions [Cu(1), Cu(2), Cu(3) and Cu(4)] are shown in Fig. 1. The two types of tetranuclear copper clusters have very similar interatomic distances and angles, and thus only the subunit containing Cu(1), Cu(2) and symmetry equivalents will be discussed in some detail.

The Cu(1) is coordinated by two μ_3-bridging hydroxyl oxygen atoms [Cu(1)–O(13) = 1.975(4) Å, Cu(1)–O(13)#1 = 1.988(4) Å], and three oxygen atoms [O(1), O(6)#2, O(7)] with distance of 1.936(5)–2.225(5) Å from carboxyl groups of three separated BTC anions to complete a five-coordinated environment. The bond angles of O – Cu(1) – O are in the range of 82.92(18)°–170.66(19)°. The Cu(2) ion is five-coordinated by two oxygen atoms belonging to two carboxyl groups from two different BTC ligands [the distances: Cu(2)–O(2), 1.948(4) Å; Cu(2)–O(8)#1, 1.952(4) Å], one μ_3-hydroxyl oxygen atom [Cu(2)–O(13), 1.946(4) Å], an aqua oxygen atom with distance of 2.248(5) Å [Cu(2)–O(15)], and one nitrogen atom from pyridyl group of ligand **L** with the bond distance of 2.067(6) Å [Cu(2)–N(1)], showing a distorted tetragonal pyramidal geometry. The Cu(1), Cu(2) and their symmetry equivalents are connected by four carboxylic groups with bidentate bridging coordination fashion and two carboxylic groups with monodentate mode forming a tetranuclear copper cluster $[Cu_4(\mu_3\text{-}OH)_2(O_2C\text{-})_6]$ (A-type Cu_4 cluster), in which the $[Cu_4(\mu_3\text{-}OH)_2]$ unit of tetranuclear copper cluster exhibits a chair-shaped configuration (Fig. S1a). The non-bonding Cu···Cu distances are 2.9699(10) Å [Cu(1)···Cu(1)#2], 3.2858(12) Å [Cu(1)#1···Cu(2)], 3.4038(12) Å [Cu(1)···Cu(2)], and 5.9954(14) Å [Cu(2)···Cu(2)#1], respectively (Fig. 1a), which are different from those of 3.056, 3.202, 3.471, and 5.938 Å, in chair-shaped tetranuclear copper clusters previously reported [6]. Both Cu(3) and Cu(4) ions are also five-coordinated modes. The coordination mode of Cu(3) is similar to that of Cu(1), and the Cu(2) is similar to Cu(4), but the bond distances and bond angles are slightly different. All the above bond lengths and angles are within the normal ranges (Table S1). Different from the Cu(1) and Cu(2) atoms in A-type Cu_4 cluster, the Cu(3) and Cu(4) atoms are bridged by six carboxyl groups with bidentate bridging mode to give another type of tetranuclear copper cluster $[Cu_4(\mu_3\text{-}OH)_2(O_2C\text{-})_6]$ (B-type Cu_4 cluster) (Fig. 1b and Fig. S1b), in which the adjacent non-bonding Cu···Cu distances are slightly different [Cu(3)···Cu(3)#4 = 2.9802(16) Å, Cu(3)#4···Cu(4) = 3.2535(13) Å, Cu(3)···Cu(4) = 3.3614(14) Å, and Cu(4)–Cu(4)#3 = 5.9064(15) Å].

For complex **1**, without considering the connection of ligands **L**, these two types of Cu_4 clusters are linked by the BTC ligands to form a 3D coordination polymeric framework (Fig. S2). Thus, the crystal structure of **1** can be viewed as an extension of the tetranuclear copper clusters $[Cu_4(\mu_3\text{-}OH)_2(O_2C\text{-})_6]$ into a 3D coordination network. The structure is significantly different from the complex $[Cu_4(BTC)_2(OH)_2(H_2O)_2(NH_3)_4]_n$, which exhibits a bilayer network formed by $[Cu_4(OH)_2(H_2O)_2(NH_3)_4(O_2C\text{-})_6]$ subunit [6]. There have been some reports on tetranuclear copper clusters, however only one example containing a variety of tetranuclear copper clusters simultaneously has been reported [25]. Escuer's group reported the complex $[Cu_4(OH)_2\{(py)C(CN)NO\}_2(O_2CPh)_4]_{2n} \cdot n[Cu_4(OH)_2\{(py)C(CN)NO\}_2(O_2CPh)_4][(py)C(CN)NOH = 2\text{-pyridylcyanoxime}]$ containing three independent Cu_4 subunits, in which two types of Cu_4 subunits give a double chain of tetramers and the third Cu_4 subunit is discrete molecules [25]. As far as we know, the complex **1** represents the first example of 3D coordination polymer including two types of tetranuclear copper cluster constructed from carboxyl groups and μ_3-bridging hydroxyl groups.

A better insight into the structure of complex **1** can be achieved by the procedure of reducing multidimensional structures to simple node and connection nets known as the topological approach [26]. The A-type and B-type Cu_4 clusters are surrounded by eight organic ligands (six BTC and two **L** ligands) and can simply be regarded as an 8-connected node, respectively. (Fig. 2a and b). Ligand BTC adopts two different coordination modes: μ_6-bridging mode (BTC^1) and μ_5-bridging mode (BTC^2) (see Scheme S2a and S2b). For the BTC^1, each of the three carboxyl groups shows bidentate bridging mode and coordinates with two metal Cu^{II} ions. While in the BTC^2, two carboxyl groups coordinate to two different metal Cu^{II} ions with bidentate bridging mode, the third one coordinates to one Cu^{II} ion with monodentate mode. BTC^1 is connected with two A-type Cu_4 clusters and one B-type Cu_4 cluster, while BTC^2 is connected with one A-type Cu_4 cluster and two B-type Cu_4 clusters. Hence, each BTC^1 or BTC^2 is linked to three Cu_4 clusters and can be defined as a 3-connected node, respectively (Fig. 2c and d). The ligand **L** displays only one μ_2-bridging coordination mode (see Scheme S2c) and alternately links two Cu^{II} ions [Cu(2) and Cu(4)] belonging to the adjacent A-type and B-type Cu_4 clusters with the Cu(2)···Cu(4) distance of 17.13 Å to form a 1D chain (Fig. 2e), in which

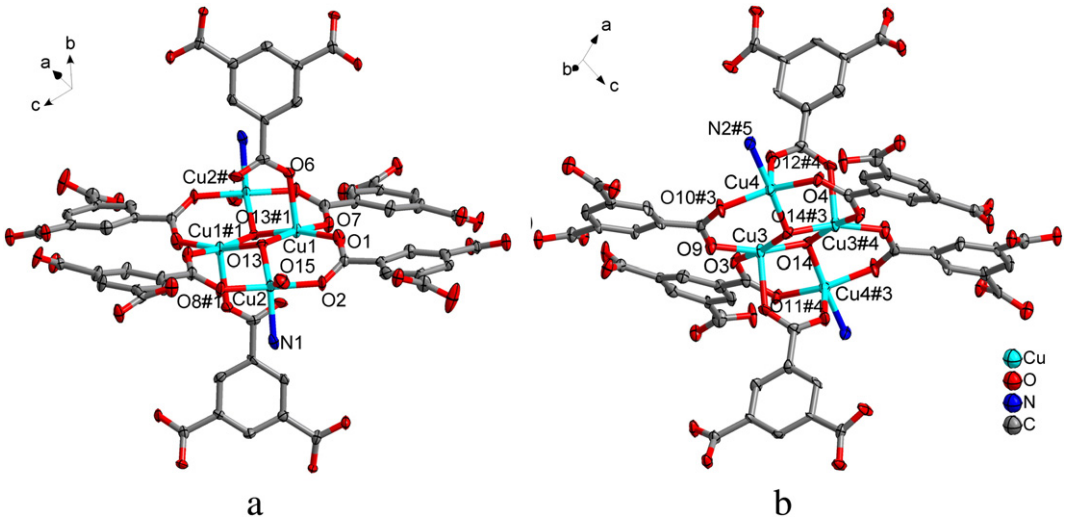

Fig. 1. (a) The coordination environment for Cu(1) and Cu(2) ions in A-type Cu_4 cluster of complex **1**; (b) The coordination environment for Cu(3) and Cu(4) ions in B-type Cu_4 cluster of complex **1** (at 50% probability level). (All H atoms and lattice water molecules are omitted for clarity.)

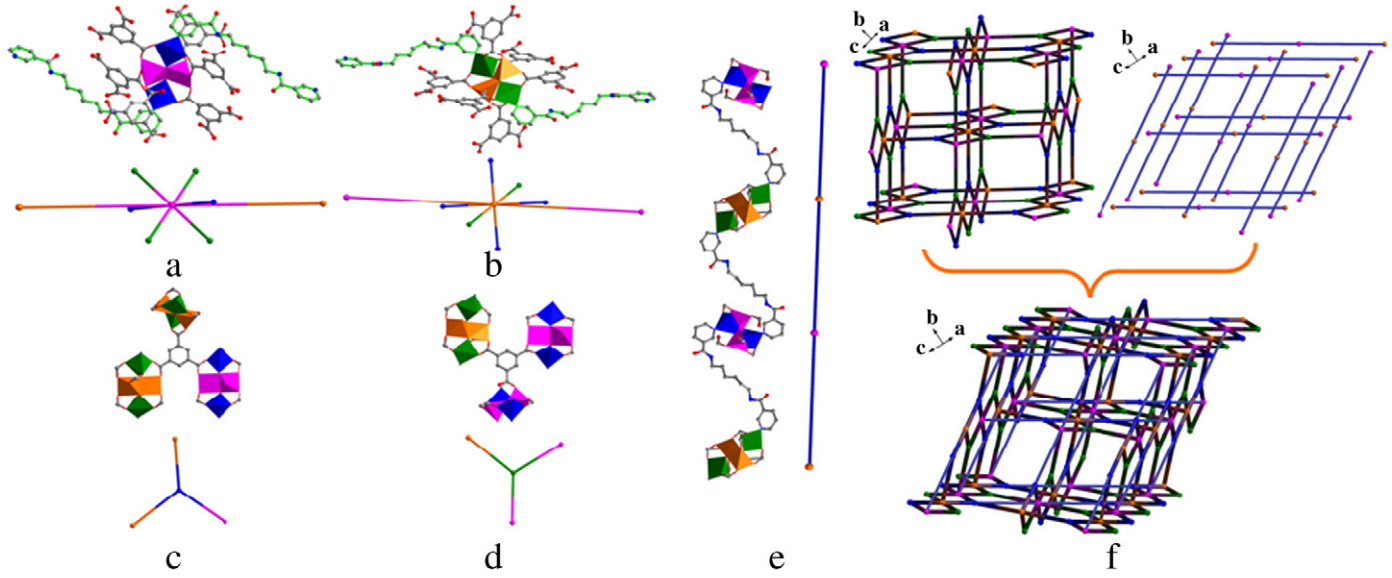

Fig. 2. (a) 8-Connected A type Cu_4 cluster; (b) 8-connected B type Cu_4 cluster; (c) 3-connected BTC[1]; (d) 3-connected BTC[2]; (e) the 1D chain formed by **L** ligands bridging two types of Cu_4 clusters; (f) topologies of (3,3,8,8)-connected 3D network observed in complex **1**.

the corresponding dihedral angle between the pyridyl rings is 35.95°. Considering the two types of Cu_4 clusters and the two kinds of BTC ligands as nodes and keeping the **L** ligands as spacers, the overall topology of the 3D framework is best described as a unique tetranodal 3,3,8,8-connected framework with square-shape cavities [with the length and width dimensions of 17.42 Å and 14.43 Å], as shown in Fig. 2f. Its Schläfli symbol is $\{4.5.6\}_4\{4^2.5^8.6^{12}.7^3.8^3\}\{4^2.5^9.6^{14}.7.8^2\}$.

The design of polynuclear Cu^{II} complexes has attracted much attention owing to their important properties and applications such as in bioinorganic functional compounds, luminescence, magnetic porous materials and catalysts [27–29]. To date, a large number of tetranuclear copper(II) cluster-based complexes have been reported [30–32], in which hydroxyl or carboxyl group is generally the bridge to link the Cu^{II} ions to a Cu_4 cluster core [33,34]. The Cu_4 clusters containing hydroxyl groups have aroused extensive interest because of their effective magnetic interactions by exchanging coupling along the Cu – O – Cu pathways arising from the short metal–metal distances brought about by the $\mu_2(\mu_3)$-OH moieties [33]. For example, Janiak et al. synthesized a tetranuclear μ_3-OH-bridging copper(II) complex $\{[Cu_4(\mu_5\text{-BTC})_2(\mu_3\text{-OH})_2(\mu_4\text{-btre})]\cdot 2H_2O\}$(btre = 1,2-bis(1,2,4-triazol-4-yl)ethane) [34] and investigated its magnetic property. Very recently, Hou et al. reported a 1D double-chain polymer $\{[Cu_4(\mu_3\text{-OH})_2(\mu_4\text{-Cl})(H_2O)_2(L)_2]\cdot Cl(H_2O)_7\}_n$ (H_2L = 1,2-bis[3-(1,2,4-triazolyl)-4-amino-5-carboxylmethylthio]-ethane) with uncommon butterfly-like Cu_4 cluster exhibiting antiferromagnetic behavior and anion exchange characteristic, in which both guest and coordinated Cl^- can be replaced by I^- and NO_3^- in water [35].

In references, the connectivity of Cu_4 cluster is related to the coordination mode of BTC, while the coordination mode of BTC may be relevant to its concentration and systemic reaction temperature. Both the combination of Cu_4 cluster with μ_6- and/or μ_5-bridging BTC can give (3,6)-connected topology. Such as Luo's group got the 3,6-connected rutile network with Cu_4 cluster and μ_6-bridging BTC [36]. Yang et al. obtained a 3,6-connected rutile topology with Cu_4 cluster and μ_5-bridging BTC [37]. In our paper, when ligand **L** was introduced into Cu-BTC system, the complex **1** with (3,3,8,8)-connected topology containing two types of Cu_4 clusters was prepared, in which BTC ligands show μ_6- and μ_5-bridging coordination modes.

The TG curve of complex **1** was determined in the temperature range of 30–650 °C in air. The TG curve displays two obvious weight loss steps. The first gradual weight loss of 11.13% in the region of 115–230 °C is equivalent to the loss of lattice water and coordinated water molecules (calcd 10.91%). The second step in the range of 335–470 °C can be

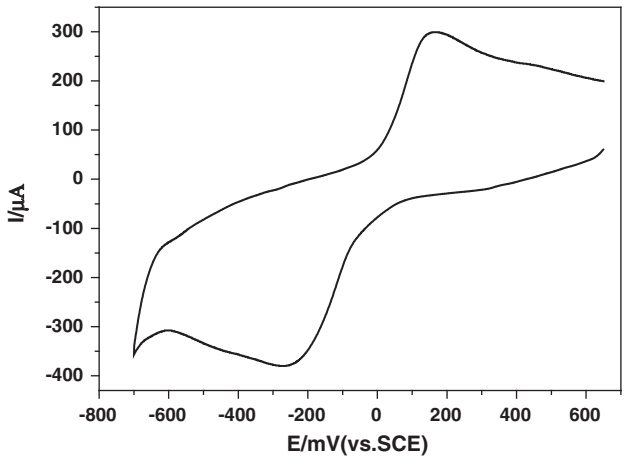

Fig. 3. Cyclic voltammogram of the title complex modified carbon paste electrode (**1**-CPE) in 0.1 M phosphates buffer aqueous solution (pH = 3) in the potential range of 600— −700 mV. Scan rate: 100 mVs^{-1}.

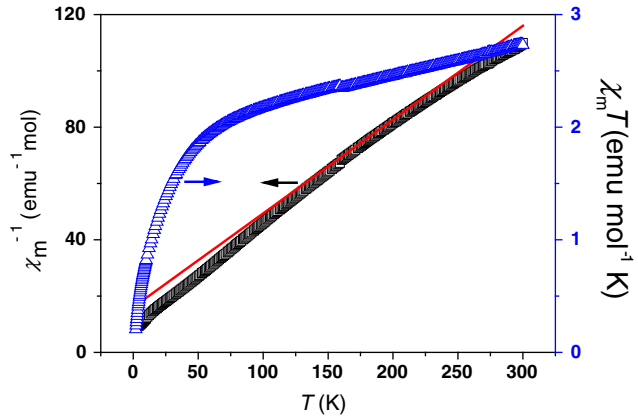

Fig. 4. Plots of χ_m^{-1} *vs. T* and $\chi_m T$ *vs. T* for **1**. Red line is a theoretical fit of χ_m^{-1} *vs. T* plot.

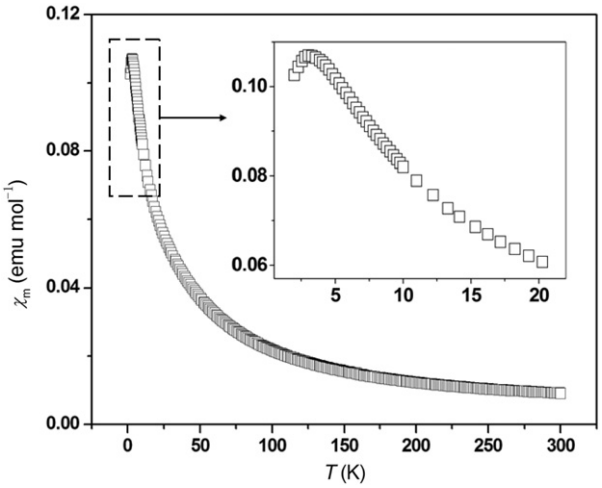

Fig. 5. χ_m *vs. T* plot for complex **1**.

attributed to the decomposition of organic ligands **L** and BTC. The remaining weight (27.20%) is in consistence with the Cu and O components in CuO (calcd 27.71%), indicating that this is the final product. The powder X-ray diffraction pattern of the as-synthesized crystal materials was almost identical to that calculated from the single-crystal structures. The diffraction peaks of the simulated and experimental patterns match well in key positions, indicating the phase purities of the title compound. The TGA plots and XRD spectra are included in the Supporting Information (Fig. S4 and Fig. S5).

The electrochemical properties of copper(II) complexes have inspired more attention for researchers due to their abilities to undergo reversible mono-electron redox process [38,39], so we investigated the electrochemical behavior of complex **1** bulk-modified carbon paste electrode (**1**-CPE). The cyclic voltammogram of **1**-CPE in 0.1 M phosphates buffer aqueous solution (pH = 3) in the potential range of 600 − −700 mV was recorded (Fig. 3), and a quasi-reversible redox peak attributed to Cu^{II}/Cu^{I} was observed [13], in which the mean peak potential $E_{1/2} = (E_{pa} + E_{pc})/2$ was −48 mV. Compared with the reported copper complexes [13,15], the difference of peak potentials may be ascribed to the influence of organic ligands and structure of the complex.

The variable-temperature magnetic susceptibility of **1** was measured in the temperature range of 2–300 K at an applied field of 1000 Oe, owing to the multiple superexchange pathways within the chair-shaped tetranuclear cluster $[Cu_4(\mu_3\text{-}OH)_2(O_2C\text{-})_6]$ for **1**. The χ_m^{-1} *vs. T* and $\chi_m T$ *vs. T* plots are shown in Fig. 4. At 300 K, the $\chi_m T$ value is 2.73 emu mol^{-1} K, which is much higher than the theoretical value (1.50 emu mol^{-1} K) for four spin-only Cu^{II} ions ($S = 1/2$, $g = 2.0$), suggesting that the *g* value of spin carrier in **1** is greater than 2.0 [40,41]. With a decrease of temperature, the $\chi_m T$ value gradually decreases to 0.21 emu mol^{-1} K at 2 K, which indicates a dominant antiferromagnetic interactions between the Cu^{II} ions within the tetranuclear cluster to lead to a $S = 1/2$ spin ground state [42]. Furthermore, the χ_m^{-1} *vs. T* plot in the high-temperature range can be fitted to the Curie–Weiss law with $C = 3.00$ emu mol^{-1} K and $\theta = -41.8$ K, which further suggests the dominant strong antiferromagnetic couplings within the tetranuclear cluster. The antiferromagnetic behavior should be originated from the superexchange interactions between Cu3 (Cu3#4) and Cu4 (Cu4#3) by the mixed *syn,syn*-μ_2-η^1:η^1 − COO^- and μ_3-OH pathways [43,44]. In contrast, the superexchange interactions between Cu3 and Cu3#4 by the double μ_3-OH pathways often result in a weak ferromagnetic coupling [43,44]. A round peak near 3 K in the χ_m *vs. T* curve (Fig. 5) suggests an antiferromagnetic ordering [42]. The field dependent magnetization curve (Fig. S6) of **1** at 1.8 K displays that the magnetization value gradually increases with the field up to 1.34 Nβ at 7 kOe but without reaching saturation (4.00 Nβ for four Cu^{II} ions).

In summary, we have successfully synthesized a new (3,3,8,8)-connected 3D metal–organic framework with the new type of $\{4.5.6\}_4\{4^2.5^8.6^{12}.7^3.8^3\}\{4^2.5^9.6^{14}.7.8^2\}$ topology, in which two types of Cu_4 clusters are linked by the flexible **L** and the bridging BTC ligands with two kinds of coordination modes. Complex **1** represents the first 3D coordination polymer based on two types of tetranuclear copper(II) clusters $[Cu_4(\mu_3\text{-}OH)_2(O_2C\text{-})_6]$ and a flexible bis-pyridyl-bis-amide based ligand. Our work provides a probability for the **L**-like N-donor ligands to be used as flexible bridging ligand in the metal–organic coordination networks.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.01.015.

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[23] A mixture of $CuCl_2 \cdot 2H_2O$ (0.034 g, 0.2 mmol), H_3BTC (0.025 g, 0.12 mmol), **L** (0.033 g, 0.1 mmol), H_2O (12 mL) and NaOH (0.017 g, 0.42 mmol) was stirred for 30 min in air, then transferred and sealed in a 25 mL Teflon reactor, which was heated at 120 °C for 4 days leading to the formation of blue block crystals **1**, and washed by water, dried in air (yield: ~31% based on Cu). Anal. Calcd. for $C_{36}H_{44}Cu_4N_4O_{23}$ (1154.91): C 37.41, H 3.84, N 4.85%. Found: C 37.31, H 3.90, N 4.83%. IR (KBr pellet, cm^{-1}): 3735 (w), 3295 (s), 3098 (w), 2963 (w), 2360 (s), 2335 (m), 1637 (s), 1600 (m), 1563 (s), 1505 (w), 1431 (m), 1364 (s), 1299 (s), 1235 (w), 1178 (w), 1088 (w), 869 (w), 735 (s), 681 (m), 620(w).

[24] Crystal data for compound **1**: $C_{36}H_{44}Cu_4N_4O_{23}$, FW = 1154.91, Monoclinic, space group P 21/c, $a = 18.036(3)$ Å, $b = 13.760(2)$ Å, $c = 17.861(3)$ Å, $\beta = 106.995(3)^o$, $V = 4239.1(12)$ $Å^3$, $Z = 4$, $D_{calc} = 1.810$ mg/m^3, $\lambda = 0.71073$ Å, $T = 273(2)$ K, R_1 (wR_2) = 0.0579 (0.1239), Bruker Smart Apex-II CCD area detector, Mo K_α radiation. The structure was solved by direct methods and refined on F^2 by full-matrix least squares methods using SHELXTL 97. CCDC reference number 860579.

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