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Tetracopper complexes with two-mode cubane-like Cu_4O_4 core from similar hydroxyl-rich salicylaldehyde Schiff bases: Structure and magnetic properties

Bing Yang, Jiali Pan, Xianggao Meng, Jinge Cao, Yuyi Li, Fengping Xiao *, Dongfeng Li *

Department of Chemistry, Central China Normal University, Wuhan 430079, Hubei, China[1]

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The reaction of water-soluble hydroxyl-rich salicylaldehyde Schiff base ligands with the metal salt $Cu(OAc)_2{\cdot}H_2O$ affords three novel tetracopper complexes via solvothermal method: $[Cu_4(H_2L1)_4]{\cdot}CH_3OH$(**1**), $[Cu_4(HL2)_2(Py)_2(OAc)_2]$(**2**), $[Cu_4(HL3)_2(Py)_2(OAc)_2]$(**3**). The X-ray crystal structures reveal the cubane Cu_4O_4 for complex **1** with μ_3-alkoxo bridges and quasi-stepped cubane Cu_4O_4 for **2** and **3** bearing two central copper atoms bridged by two alkoxy groups and two peripheral copper atoms bridged with central copper atoms by one another alkoxy oxygen. Temperature-dependent magnetic measurements indicate that the dominant ferromagnetic interactions among metal ions within the cubic core of **1** with $J_1 = +27.44\ cm^{-1}$, $J_2 = -0.21\ cm^{-1}$ ($g = 2.1157$) while there are antiferromagnetic interactions between two metal centers in **3** with $J_1 = -268\ cm^{-1}$, $J_2 = -297\ cm^{-1}$ ($g = 2.068$).

1. Introduction

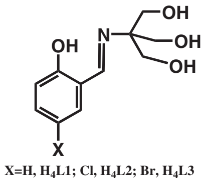
Multinuclear transition-metal complexes have attracted intense interests these years due to their interesting architectures and possible utility in many fields such as catalysis, clathrate separation, molecular sieving, magnetochemistry and bioinorganic chemistry [1–5]. Among them, multinuclear copper(II) complexes, especially the cubane-like Cu_4O_4 complexes, have been studied from a magnetic structure point of view with experimental and theoretical approaches [6,7]. Polydentate ligands bearing endogenous bridging and chelating groups are usually adopted to effectively encapsulate metal ions and promote intramolecular superexchange interactions [8–10]. For example, hydroxy-rich polydentate Schiff-base ligands synthesized via 1,3-diamino-2-propanol/or 2-amino-1,3-propanediol are extensively utilized to bridge metal ions for the preparation of polynuclear complexes with various core structures including Cu, Mn, Fe, Ni and even heteronuclear of Co and Fe, Cu and Mo [11–15]. Some multinuclear complexes constructed by salicylaldehyde Schiff base possessing alkoxyl groups have also been reported besides of pentanuclear Mn complexes with similar ligands from Reedijk and co-workers [15a,16,17].

Inspired by these work mentioned above, three tetranuclear cupric complexes $[Cu_4(H_2L1)_4]{\cdot}CH_3OH$(**1**), $[Cu_4(HL2)_2(Py)_2]{\cdot}(OAc)_2$(**2**) and $[Cu_4(HL3)_2(Py)_2]{\cdot}(OAc)_2$(**3**) have been solvothermally synthesized via the reaction of copper salt and relative Schiff base ligands (H_4L1 = 2-((1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylimino)methyl)phenol), H_4L2 = 2-((1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylimino)methyl)-4-chlorophenol, H_4L3 = 2-((1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylimino)methyl)-4-bromophenol) (Scheme 1) in ethanol.

2. Results and discussion

2.1. Synthesis and characterization

The pentadentate ligands H_4L1-3 were synthesized via amine-aldehyde condensation of salicylaldehyde/or its derivatives with



Scheme 1. The ligands: X = H, H_4L1; Cl, H_4L2; Br, H_4L3.

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* Corresponding authors at: Department of Chemistry, Central China Normal University, 152 Luoyu Road, Hongshan District, 430079 Wuhan, China. Fax: +86 027 67862900.

E-mail addresses: fpxiao@mail.ccnu.edu.cn (F. Xiao), Lidf@mail.ccnu.edu.cn (D. Li).

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2-amino-2-hydroxymethyl-propane-1,3-diol(Tris) in ethanol. The reactions of these ligands and 3 equiv of $Cu(OAc)_2{\cdot}H_2O$ in the presence of pyridine give two kinds of Cu_4O_4 complexes **1**–**3**.

2.1.1. Crystal structure of $[Cu_4(H_2L1)_4]{\cdot}CH_3CH_2OH$ (**1**)

Complex **1** is composed by Cu(II), deprotonation dianionic backbone ligand H_2L1 and one lattice ethanol molecule without second ligand with the rate of them is 4:4:1. But the crystals will become gradual efflorescence at room temperature when they are out of the mother liquor due to the slow loss of the lattice solvent molecules (Fig. S1).

As shown in Fig. 1, complex **1** is cubic tetracopper molecule with the distances of Cu···Cu in "4 + 2" class ($Cu1\cdots Cu1^{\#2}$ = $Cu1\cdots Cu1^{\#3}$ = $Cu1^{\#}\cdots Cu1^{\#3}$ = $Cu1^{\#1}\cdots Cu1^{\#2}$ = 3.1268(3), $Cu1\cdots Cu1^{\#1}$ = $Cu1^{\#2}\cdots Cu1^{\#3}$ = 3.5491(3) Å (Symmetry Code #1: 2 – *x*, 0.5 – *y*, *z*, #2: 0.75 – *y*, 1.25 – *x*, 2.25 – *z*, #3: 1.25 – *y*, 0.75 – *x*, 2.25 – *z*)) (Table S3) and each Cu(II) center is a five-coordinated distorted square-pyramidal coordination sphere (4 + 1) with four O atoms and one N atom from H_2L1. Among of them, one phenol-O atoms, two bridging μ_3-alkoxo- and one N atom form a quasi-square-plane and the axial coordination site is occupied by the rest of μ_3-O(Cu1–O1 = 1.9015(10), Cu1–N1 = 1.9224(12), Cu1–O2 = 1.9428(10), $Cu1–O2^{\#3}$ = 1.94239(10), and $Cu1–O2^{\#1}$ = 2.5407(10) Å). In the other words, the metal centers linked by a μ_3-alkoxo-oxygen atom of the Schiff base to develop a cubic Cu_4O_4 arrangement of the metal and oxygen atoms. More bond lengths and angles were provided in Table S1.

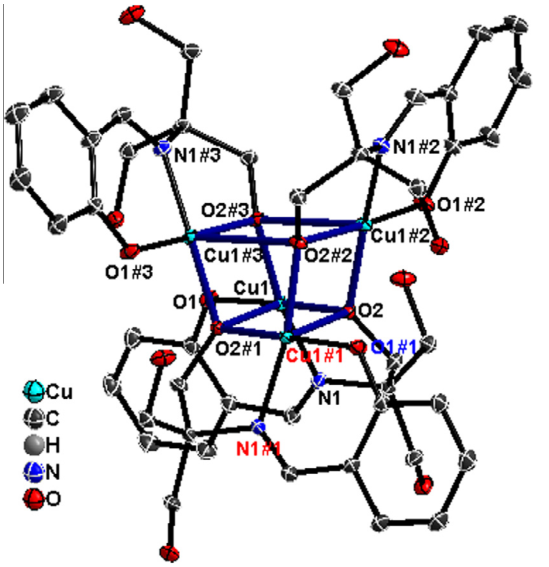
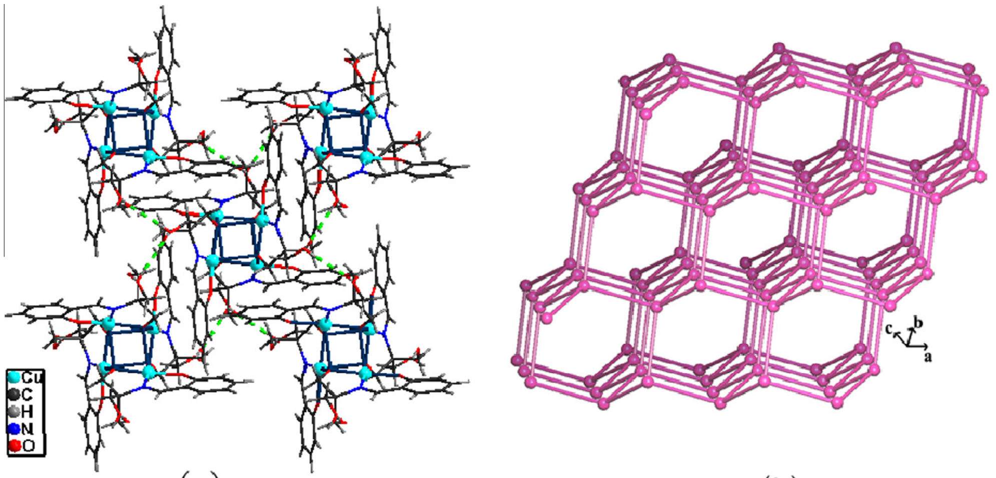


Fig. 1. ORTEP diagram of **1** (in order to clear, the ethanol has been deleted).

Additionally, each ligand in **1** has two uncoordinated hydroxyl groups to form much abundant hydrogen bonds. One molecular interacts with four neighbors via eight hydrogen bonds between uncoordinated O atoms to form a tetrahedral structure (Fig. 2a). The O···O distances of O4–H4A···O1 and O3–H3A···O4 are 2.659(1) and 2.712(1) Å, respectively, and bond angles of them are 174(3)° and 177(2)° (Table S2). Then the tetrahedral structure interacts with neighbors to form 3-D hydrogen bond networks. It is noteworthy that if each cubic tetracopper molecule was considered as a hydrogen-bonded connected node, the final 3D hydrogen-bonded network in complex **1** can be topologically simplified as an uninodal 4-connected net with the long and short schläfli symbol of 6^6 and $6^2.6^2.6^2.6^2.6^2.6^2$, respectively (Fig. 2b).

2.1.2. Crystal structure of $[Cu_4(HL2)_2(Py)_2(OAc)_2]$(**2**)

Complex **2** is a stable tetracopper coordination complex with the ratio of Cu (II) ions:ligand HL2:acetate:pyridine = 4:2:2:2 out of the solution at room temperature (Figs. 3 and S1). And single-crystal X-ray analysis reveals that it is a chair-like/or stepped tetranuclear copper(II) structure although synthesis of it is similar to **1**, in which four copper(II) cations are fixed by two trianionic HL2 and two acetate ions. In **2**, two Cu^{2+} ions are adopted in different types of coordination environments: the Cu1 atom displays square planar geometry (3 + 1) with three oxygen atoms O1 and O2 from Schiff base ligand and O5 from bridging μ_2-OAc^-, one nitrogen atom N3 from HL2 (Cu1–O1 = 1.905(2), Cu1–O2 = 1.931 (2), Cu1–O5 = 1.952(2), and Cu1–N3 = 1.948(2) Å), and the Cu2 center is a five-coordinated distorted square-pyramidal sphere. The centrosymmetric Cu2 and $Cu2^{\#}$ are bridged by two μ_2-alkoxo oxygen atoms (O3 and $O3^{\#}$) which associate with the other coordinated oxygen (O2 and O6/$O2^{\#}$ and $O6^{\#}$) to generate a square-plane ($Cu2–O3^{\#}$ = 1.920(2), Cu2–O2 = 1.941(2), Cu2–O3 = 1.946(2), and Cu2–O6 = 1.982(2) Å (Symmetry Code #: –*x*, 1 – *y*, 1 – *z*)); and the N2 atom of the pyridine occupying the axial site (Cu2–N2 = 2.240(3) Å) results to square-pyramidal sphere (Table S1).



(a) (b)

Fig. 2. (a) Packing structure by hydrogen bonds and (b) topological simplified diagram of the 3D hydrogen-bonded network, in which the tetranuclear copper(II) unit was shown as purple balls. (Colour online.)

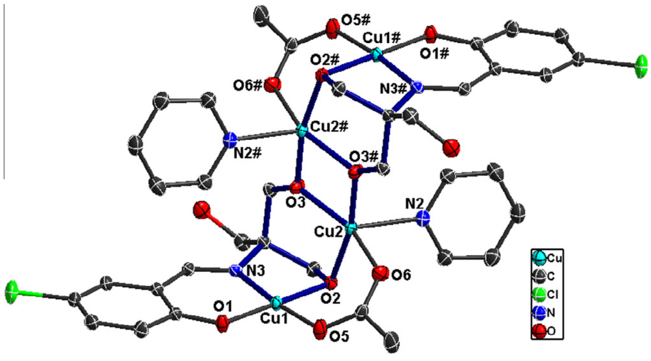


Fig. 3. ORTEP diagram of **2**.

Comparing to **1**, there is only one uncoordinated hydroxyl group in **2**, which results to less hydrogen bonds (Fig. 4). Every molecule interacts with two neighbors to form hydrogen-bonded one-dimensional (1-D) chains via intermolecular hydrogen-bonding interactions between coordinated phenol O atom and hydroxyl O atom. The O···O distance within the chains is 2.8475(35) Å and bond angle of O4–H4···O1^a is 148.759(3)° (Symmetry Code a: $-1+x$, y, z) (Table S2).

2.1.3. Crystal structure of [$Cu_4(HL3)_2(Py)_2(OAc)_2$](**3**)

The single-crystal structure of complex **3** is similar to **2** (Fig. 5) with distance of Cu1···Cu2 = 2.8855(8), Cu2···Cu2$^\#$ = 3.0158(10), Cu1···Cu2$^\#$ = 4.7796(14) and Cu1···Cu1$^\#$ = 7.2970(9) Å (Table S3) and the same packing pattern in addition to intermolecular hydrogen-bonded 1D chain (Fig. S2).

2.2. Electronic spectra

The absorption spectra of **1** and **2** show one weak band centered at 360 and 380 nm, respectively (Fig. 6), which can be attributed to alkoxido- and/or phenoxido-to-copper(II) ligand-to-metal charge-transfer (LMCT) transition [18], while there is no obvious absorption for **3** maybe due to the low dissolubility of it in ethanol. The intense absorption band observed below 250 nm and the shoulder band from 250 to 300 nm should be correlated to the intra-ligand charge-transfer transitions involving the entire conjugation system of ligand ($\pi \rightarrow \pi^*$) associated with C=N linkages ($n \rightarrow \pi^*$). Unfortunately, no low intensity band above 450 nm belonged to the d–d transition of the copper(II) ion has been observed like the literatures [19].

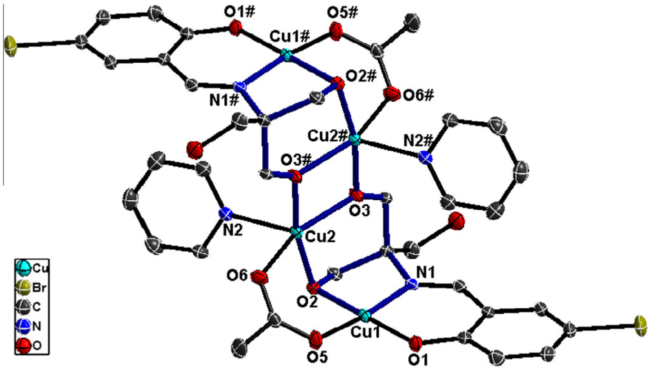


Fig. 5. ORTEP diagram of **3**.

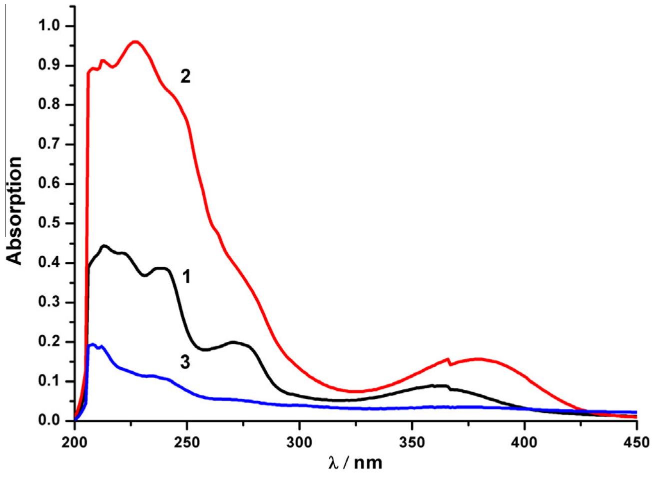


Fig. 6. UV–Vis spectra for complexes **1**–**3** in ethanol.

2.3. Magnetic properties

For complexes **1** and **3** magnetic susceptibility measurements were performed for air-dried powdered samples in the temperature range from 2 to 300 K at an applied field of 1000 Oe. As shown in Fig. 7, the $\chi_m T$ product of complex **1** is 1.811 $cm^3\,K\,mol^{-1}$ at room temperature which is obviously higher than the value expected for four magnetically isolated copper(II) ions (1.5 $cm^3\,K\,mol^{-1}$ for $S_{Cu} = 1/2$, $g = 2$). With the lowering of the temperature, the $\chi_m T$ value increases continuously to reach a maximum of

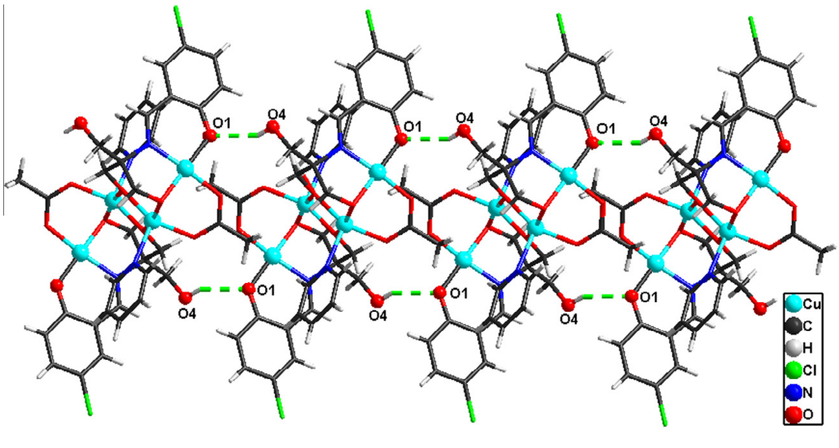


Fig. 4. Self-assembly of the complex **2** via hydrogen bonds into an 1D chain.

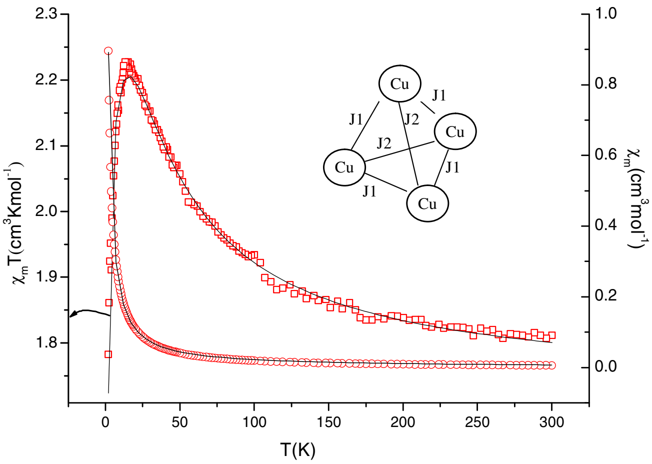


Fig. 7. Plots of $\chi_M T$ vs. T and χ_M vs. T (inset) for complex **1** in the temperature range of 1.8–300 K.

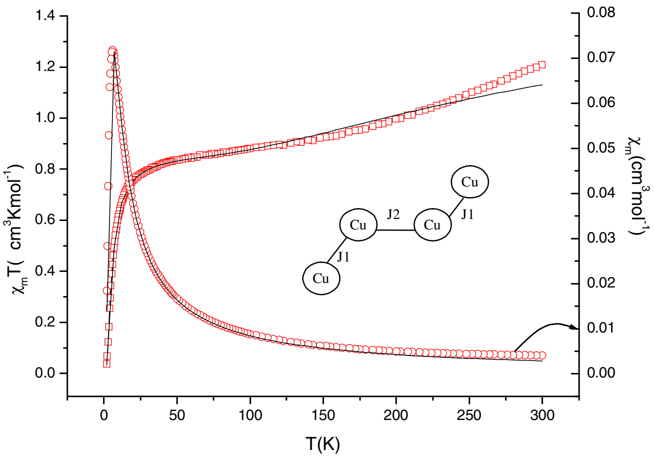


Fig. 8. Plots of $\chi_M T$ vs. T and χ_M vs. T (inset) for complex **3** in the temperature range of 1.8–300 K.

2.23 cm^3 K mol^{-1} around 14 K. Both of them suggest that the total spin ground state of $S_T = 2$ with the four spins ($S = 1/2$) presents dominant ferromagnetic interactions within the cubic unit. Then, the zero-field splitting effects (ZFS) of the $S = 2$ ground state cause the $\chi_m T$ drops suddenly to 1.78 cm^3 K mol^{-1} at 2 K from the maximum [20]. And the temperature-dependence magnetic susceptibilities obeys the Curie–Weiss law $\chi_m = C/(T - \theta)$ with a Weiss constant $\theta = 1.79$ K and a Curie constant $C = 4.15$ cm^3 K mol^{-1}, indicating also a ferromagnetic interaction between the metal centers.

The crystal structure reveals that the Cu_4O_4 core of **1** belongs to the "cubane [4 + 2] class" structure with four short and two long Cu···Cu distances [6] and it belongs to C_{4h} point group. So, the spin Hamiltonian can be considered as two different exchange constants, J_1 and J_2, between the spin S_i. Then, the following spin Hamiltonian (Eq. (1)) has been used.

$$H = -J_1(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_3) - J_2(S_1S_3 + S_2S_4) \qquad (1)$$

In which, S_1, S_2, S_3, and S_4 are the spin operators ($S_1 = S_2 = S_3 = S_4 = 1/2$). A good agreement with the experimental data for complex **1** is obtained with the parameters: $J_1 = +27.44$ cm^{-1}, $J_2 = -0.21$ cm^{-1}, $g = 2.1157$, $R = 1.0 * 10^{-5}$. The dominant ferromagnetic interaction of **1** from the J_1 which depends mainly on the geometry including the value of the Cu–O–Cu angle and the relative orientation of the magnetic orbitals [6c,19b,21], although J_2 exhibits a weak antiferromagnetic coupling. These values of exchange parameters in fit not exactly same with the ones previously reported on the [Cu_4O_4] cubane series with similar ligands because of the different angles of Cu–O–Cu and distances of Cu···Cu [6,22].

The magnetic property of **3** is shown in Fig. 8 with χ_m versus T and $\chi_m T$ versus T. Different from **1**, all of data including the lower $\chi_m T$ value of 1.21 cm^3 K mol^{-1} at room temperature, the continuous decreasing of $\chi_m T$ with lowering temperature and the negative Weiss constant ($C = 1.14$ cm^3 K mol^{-1}, $\theta = -18.4$ K) suggest antiferromagnetic interactions among the stepped cubane unit, even there are a small amount of paramagnetic impurities indicated from the increasing of the χ_m at low temperature. At the same time, the $\chi_m T$ values at low-temperature are nearly consist with an $S_T = 0$ ground state, which are confirmed by the observed change of the χ_m values at low temperatures [23].

For long distances of Cu1···Cu2 and Cu1···Cu1# in complex **3**, the magnetic exchange in the stepped unit can be modeled as Cu(S_1)–J_1–Cu(S_2)–J_2–Cu(S_3)–J_1–Cu(S_4), here, J_1 and J_2 are expected to be different due to the two types of copper atoms: the central copper atoms are bridged by two alkoxy bridges while the peripheral copper atoms are bridged by one alkoxy oxygen [24]. The conventional Hamiltonian (Eq. (2)) can be adopted to the curve fitting of magnetic property for interaction of the tetracopper units.

$$H = -J_1(S_1S_2 + S_3S_4) - J_2S_2S_3 \qquad (2)$$

Then the values giving the best fit (2–300 K) for **3** are, $J_1 = -268$ cm^{-1}, $J_2 = -297$ cm^{-1}, $g = 2.068$, $R = 7.8 * 10^{-7}$. The values of the exchange constants J_1 and J_2 state also strong antiferromagnetic interactions in this stepped cubic Cu_4O_4 core due to the large Cu–O–Cu angles with ∠ Cu1–O2–Cu2 = 96.169(14)° and ∠ Cu2–O3–Cu2# = 101.857(15)° [24,25].

3. Conclusions

In this paper, we present the synthesis and crystal structure of three tetranuclear Cu-containing complexes in two different kinds of mode with similar hydroxyl-rich salicylaldehyde Schiff base ligands. Complex **1** exhibits the "cubane [4 + 2] class" Cu_4O_4 structure with dominant ferromagnetic interactions among four metal centers. And rich hydrogen bonds from the uncoordinated hydroxyl groups result to 3D network with a hexagon topological structure. The four metal ions within **2** and **3** are linked by two trianionic HL2 and HL3 respectively, forming a stepped structure with square-planar and distorted square-pyramidal geometries of copper centers. Different from **1**, the molar paramagnetic susceptibilities χ_m are corrected by the antiferromagnetic interactions among the multinuclear Cu atoms in **3**, and less hydrogen bonds form 1D chain only.

4. Experimental

4.1. Materials and measurements

The starting materials were purchased from commercial sources and used without further purification. ^1H NMR spectra were obtained at a Varian Mercury 400 MHz spectrometer. Chemical shifts are reported in δ relative to TMS. IR spectra were measured as KBr pellets on a Perkin-Elmer spectrometer in the range of 400–4000 cm^{-1}. Elemental analyses were performed on a Vario EL111 CHNSO elemental analytical instrument for C, H, N and Perkin-Elmer OPTIMA 2000 DV Optical Emission Spectrometer for Cu. Powder X-ray diffraction were recorded by Y-2000.

4.2. Preparation

The ligands and their relative complexes have been synthesized according to the route in the Scheme 2.

4.2.1. Preparation of H_4L1

A mixture of tris(hydroxymethyl)methyl aminomethane (1.215 g, 10 mmol) and salicylaldehyde (1.220 g, 10 mmol) in anhydrous ethanol (30 mL) was heated at 100 °C for about 3 h. Then the white crystals of ligand H_4L1 were obtained after removing the solvent in approximate 88% yield. ^1H NMR (400 MHz, DMSO-d_6, 25 °C, δ ppm): $\delta = 14.51$ (1H, s, ArOH), 8.55(1H, s, CH=N), 7.41 (1H, d, *o*-ArH), 7.29 (1H,t, *p*-ArH), 6.08 (2H, t, *m*-ArH), 4.72, (3H, t, -OH), 3.6 (6H, d, $-CH_2$). IR (KBr): $v = 3326$(s) 2809 (m), 1643 (s), 1477 (m), 1052 (m) cm^{-1}.

4.2.2. Preparation of H_4L2

H_4L2 was synthesized similar to ligand H_4L1 with the reaction of tris(hydroxymethyl)methyl aminomethane (1.215 g, 10 mmol) and 5-Cl-salicylaldehyde (1.575 g, 10 mmol) in approximate 95% yield. ^1H NMR (400 MHz, DMSO-d_6, 25 °C, δ ppm): $\delta = 14.68$ (1H, s, ArOH), 8.53 (1H, s, CH=N), 7.51 (IH, d, *o*-ArH),7.28 (1H, t *p*-ArH), 6.75 (1H, d, *m*-ArH), 4.79 (3H, t, –OH), 3.61(6H, d, $-CH_2$). IR (KBr): $v = 3391$ (s), 2928 (w), 2827 (w), 1634 (s), 1541 (m), 1043 (s) cm^{-1}.

4.2.3. Preparation of H_4L3

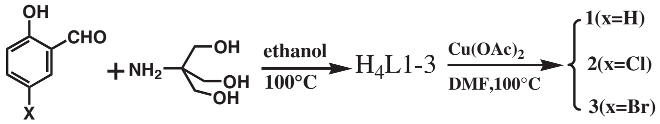
H_4L3 was synthesized via similar the reaction of tris(hydroxymethyl) methyl aminomethane (1.215 g, 10 mmol) and 5-Br-salicylaldehyde (2.009 g, 10 mmol) in approximate 85% yield. ^1H NMR (400 MHz, DMSO-d_6, 25 °C, δ ppm): $\delta = 14.70$ (1H, s, ArOH), 8.52 (1H, s, CH=N), 7.63 (1H, d, *o*-ArH), 7.36 (1H,t, *p*-ArH), 6.72 (1H, d, *m*-ArH), 4.79(3H, t, –OH), 3.61(6H, d, $-CH_2$). IR (KBr): $v = 3400$ (s), 2882 (w), 1625 (s), 1533 (m), 1320 (w) 1172 (w), 1052 (m) cm^{-1}.

4.2.4. Preparation of complexes **1–3**

Similar method has been used to prepare complexes **1–3** with the ratio of backbone ligand:$Cu(OAc)_2 \cdot H_2O$:pyridine = 1:3:2 in ethanol (8 ml) which were heated in a Teflon-lined at 100 °C for 12 h via programmed controlling temperature with 20 °C/h. Then obtain dark-green crystals for X-ray diffraction and the crystal-phase purity of the bulk samples were evidenced by the consistence of theoretical and experimental PXRD patterns (see Fig. S3). Elemental Anal. for complexes: Calc. for **1** ($C_{46}H_{58}Cu_4N_4O_{17}$): Cu, 21.30; C, 46.31; H, 4.90; N, 4.70. Found: Cu, 21.19; C, 46.19; H, 4.91; N, 4.69%; **2** ($C_{18}H_{19}ClCu_2N_2O_6$): Cu, 24.35; C, 41.42; H, 3.67; N, 5.37. Found: Cu, 24.48; C, 41.52; H, 3.65; N, 5.35%; **3** ($C_{36}H_{38}$ Br_2-$Cu_4N_4O_1$): Cu, 22.44; C, 38.17; H, 3.38; N, 4.95. Found: Cu, 24.34; C, 38.07; H, 3.39; N, 4.80%.

4.3. Crystal structure determination

Single-crystal X-ray diffraction measurement for complexes **1–3** were carried out on a Bruker Smart APEX CCD-based diffractometer equipped with a graphite crystal monochromator for data collection at 292(2) K/or 100 K. The determinations of unit cell parameters and data collections were performed with Mo Kα radiation ($\lambda = 0.71073$ Å); and unit cell dimensions were obtained with least-squares refinements. The program Bruke SAINT7 was used for reduction date. All structures were solved by direct methods using SHELXS-97 (Sheldrick, 1990) and refined with SHELXL-97 (Sheldrick, 1997) [26]; non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were treated by a mixture of independent and constrained refinement. Crystallographic data and experimental details for structural analyses are summarized in Table 1.



Scheme 2. The synthesis of the ligands (X = H, H_4L1; Cl, H_4L2; Br, H_4L3) and the relative coordinated multinuclear complexes **1–3**.

Table 1
Crystallographic data of complexes **1–3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{46}H_{58}Cu_4N_4O_{17}$	$C_{18}H_{19}ClCu_2N_2O_6$	$C_{36}H_{38}Br_2Cu_4N_4O_{12}$
Formula weight	1193.12	521.88	1132.68
Temperature (K)	100(2)	296(2)	296(2)
Crystal system	tetragonal	triclinic	triclinic
Space group	*I*4(1)/a	$P\bar{1}$	$P\bar{1}$
a (Å)	17.0466(10)	8.4161(11)	8.389(3)
b (Å)	17.0466(10)	10.7638(14)	10.935(3)
c (Å)	16.7448(10)	11.3804(15)	11.349(4)
α (°)	90°	102.776(2)	103.431(4)
β (°)	90°	101.360(2)	100.988(5)
γ (°)	90°	99.618(2)	99.376(4)
V (Å^3)	4865.8(5)	961.5(2)	970.3(5)
Z	4	2	1
μ (mm^{-1})	1.802	2.390	4.290
Goodness-of-fit (GOF) on F^2	1.057	1.164	1.073
Final R indices [$I > 2\delta(I)$]	$R_1 = 0.0259$, $wR_2 = 0.0717$	$R_1 = 0.0359$, $wR_2 = 0.1089$	$R_1 = 0.0438$, $wR_2 = 0.1224$

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Appendix A. Supplementary data

CCDC 1440270, 1440285 and 1440347 contains the supplementary crystallographic data for complexes **2**, **3** and **1** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.02.042.

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