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Cubane-type $\{M_4O_4\}$ ($M = Co^{II}, Zn^{II}, Cu^{II}$) clusters: synthesis, crystal structures, and luminescent and magnetic properties

Qian Gao,^a Yaru Qin,^a Yanmei Chen,^a Wei Liu,^a Haiyan Li,^a Bing Wu,^a Yahong Li^{*a} and Wu Li^b

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The employment of hydroxyl-rich ligand (*E*)-3-((2-hydroxy-3-methoxybenzylidene)amino)propane-1,2-diol (H_3L) in the chemistry of cubane-type $\{M_4O_4\}$ clusters is reported. Three cubane-type clusters of formula $[M_4(HL)_4]$ ($M = Co^{II}$ (**1**), Zn^{II} (**2**), Cu^{II} (**3**)) were achieved by the reactions of metal acetates with H_3L under solvothermal conditions. The structures of **1**, **2** and **3** have been established by single-crystal X-ray diffraction studies. The tetranuclear clusters **1-3** have cubane-type $[M_4(\mu_3-OR)_4]^{4+}$ cores with divalent metal atoms and deprotonated oxygen atoms (originated from the HL^{2-} ligands) occupying alternate vertices. The luminescence studies suggest strong emission for **2** in the solid state at room temperature. The magnetic properties of **1** and **3** have been investigated. The variable-temperature dc magnetic susceptibility studies indicate ferromagnetic $M^{II} \cdots M^{II}$ exchange interactions for **1** and **3**. The ac magnetic susceptibility investigation reveals that complex **1** shows the slow magnetic relaxation (SMM) behavior.

Introduction

The chemistry of high-nuclearity 3d-metal clusters has received increasing attention. The interests in these clusters span from pure academic aspects of chemistry to potential applications as functional materials in biological systems,¹ magnetism² and catalysis.³ Among them, cubane-type $\{M_4O_4\}$ clusters have attracted a renewed interest. The driving forces for this interest include: (i) the desire to discover new Co_4O_4 -type photocatalysts for water oxidation;⁴ (ii) the efforts to construct M_4O_4 -based single molecule magnets,⁵ and (iii) the requests to develop catalysts for bioinorganic systems and organic synthesis.⁶ Ligands used in the synthesis of cubane-type $\{M_4O_4\}$ clusters can be classified into two main classes: (i) hydroxyl incorporated pyridyl, pyrazole, imidazol or benzimidazol ligands and their derivatives⁷ and (ii) hydroxyl-rich Schiff base ligands and their reduction products.⁸ These ligands can function in both bridging and chelating capacities, aggregating metal ions in a cubane-type system.

Recently, we have reported the synthesis and ferromagnetic properties of several cubane-type $\{Ni_4O_4\}$ clusters supported by a variety of Schiff-base ligands.⁹ In order to expand the scopes of cubane-type $\{M_4O_4\}$ clusters and explore their useful properties, we turned our attention to prepare cubane-type $\{Co_4O_4\}$, $\{Zn_4O_4\}$ and $\{Cu_4O_4\}$ clusters by employing another Schiff base (*E*)-3-((2-hydroxy-3-methoxybenzylidene)amino)propane-1,2-diol (H_3L , Scheme 1) as a ligand. The H_3L ligand has previously been incorporated into trinuclear¹⁰ and polynuclear¹¹ manganese

complexes, nanoscale multiferroic manganese clusters,¹² trinuclear Co^{II}/Co^{III} mixed-valence complexes¹³ and Ln_4^{III} clusters.¹⁴ To our surprise, no cubane-type $\{M_4O_4\}$ clusters supported by the H_3L ligand were reported. Herein, we present the synthesis, crystal structures, and photoluminescent and magnetic properties of three cubane-type clusters with formula $[M(HL)]_4$ ($M = Co^{II}$ (**1**), Zn^{II} (**2**), and Cu^{II} (**3**)). To the best of our knowledge, complex **1** is the first reported cubane-type $\{Co_4O_4\}$ cluster supported by Schiff base ligand.

Experimental Section

General procedure

Materials and instruments: All manipulations were performed under aerobic and solvothermal conditions using reagents and solvents as received. The H_3L ligand ($H_3L = (E)$ -3-((2-hydroxy-3-methoxybenzylidene)amino)propane-1,2-diol) was prepared based on reported procedures.¹² The C, H and N microanalyses were carried out with a Carlo-Erba EA1110 CHNO-S elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 400-4000 cm^{-1} on a Nicolet MagNa-IR 500 spectrometer. Powder X-ray diffraction (PXRD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV and 100 Ma with a Cu-target tube and a graphite monochromator. The fluorescent spectra were measured on an FLsp920 fluorescence spectrometer. The dc and ac magnetic susceptibility data were collected using a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants.

Table 1 Crystal data and structure refinement information for complexes **1–3**

	1	2	3
Formula	C ₄₄ H ₅₂ Co ₄ N ₄ O ₁₆	C ₄₄ H ₅₂ N ₄ O ₁₆ Zn ₄	C ₄₄ H ₅₂ Cu ₄ N ₄ O ₁₆
<i>M</i> / g mol ⁻¹	1128.62	1154.38	1147.06
<i>T</i> /K	223(2)	296(2)	296(2)
λ / Å ^a	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Tetragonal
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P4₂/n</i>
<i>a</i> / Å	26.429(5)	26.369(5)	15.4331(19)
<i>b</i> / Å	8.4637(17)	8.4456(13)	15.4331(19)
<i>c</i> / Å	22.736(5)	22.718(4)	9.4388(17)
α / °	90.00	90.00	90.00
β / °	114.74(3)	114.642(6)	90.00
γ / °	90.00	90.00	90.00
<i>V</i> / Å ³	4619.1(16)	4598.6(14)	2248.1(6)
<i>Z</i>	4	4	2
ρ_c / g cm ⁻³	1.623	1.667	1.694
μ / mm ⁻¹	1.487	2.138	1.944
<i>F</i> (000)	2320	2368	1176
θ range / °	3.00 – 27.43	1.70 – 28.46	1.87 to 27.32
Measd/ independent	21211 / 5236	15879 / 5736	14468 / 2546
<i>R</i> _{int} reflections	0.0415	0.0592	0.0424
obsd reflns [<i>I</i> > 2 σ (<i>I</i>)]	5236	5736	2546
GOF on <i>F</i> ²	1.130	0.971	1.045
<i>R</i> ₁ ^b	0.0606	0.0440	0.0331
<i>wR</i> ₂ ^{c,d}	0.1632	0.1052	0.0894
($\Delta\rho$) _{max,min} /e Å ⁻³	1.023, -0.587	0.487, -0.641	0.521, -0.281
^a Mo <i>K</i> α radiation. ^b $R_1 = \Sigma(F_o - F_c) / \Sigma(F_o)$ for observed reflections. ^c $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2] / 3$. ^d $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$ for all data.			

X-ray diffraction crystallography

Data were collected at 223(2) K on Rigaku Mercury CCD X-ray diffractometer for **1** and at room temperature on Bruker Smart Apex II diffractometer for **2** and **3** utilizing Mo *K* α radiation ($\lambda = 0.71073$ Å); the ω and φ scan technique was applied. The structures were solved by direct methods using SHELXS-97¹⁵ and refined on *F*² using full-matrix least-squares with SHELXL-97.¹⁶ Crystallographic data together with refinement details for the new complexes reported in this work are summarized in Table 1. Selected bond lengths and angles for **1–3** are given in the Supporting Informations.

Syntheses of the complexes

[Co₄(HL)₄] (1). A mixture of H₃L (22.5 mg, 0.1 mmol), Co(CH₃COO)₂·4H₂O (24.9 mg, 0.1 mmol), and CH₃OH (1 mL) was sealed in a Pyrex-tube (8 mL). The tube was heated at 120 °C for 3 days under autogenous pressure. Cooling of the resultant solution to room temperature gave red block crystals. The crystals were collected by filtration, washed with CH₃OH (2 mL) and dried in air. Yield: 0.0155 g (55%, based on Co). Anal. Calcd for C₄₄H₅₂Co₄N₄O₁₆: C, 46.82; H, 4.64; N, 4.96. Found: C, 46.66; H, 4.61; N, 4.99%. Selected IR data (KBr, cm⁻¹): 3358 s, 1620 s, 1440 s, 1211 s, 1119 w, 1082 s, 1068 m, 742 m.

[Zn₄(HL)₄] (2). A mixture of H₃L (22.5 mg, 0.1 mmol), Zn(CH₃COO)₂·2H₂O (21.9 mg, 0.1 mmol), and CH₃OH (1 mL)

was sealed in a Pyrex-tube (8 mL). The tube was heated at 120 °C for 3 days under autogenous pressure. Cooling of the resultant solution to room temperature gave yellow block crystals. The crystals were collected by filtration, washed with CH₃OH (2 mL) and dried in air. Yield: 0.0173 g (60%, based on Zn). Anal. Calcd for C₄₄H₅₂N₄O₁₆Zn₄: C, 45.78; H, 4.54; N, 4.85. Found: C, 45.85; H, 4.48; N, 4.78%. Selected IR data (KBr, cm⁻¹): 3346 s, 1631 s, 1444 s, 1212 s, 1122 w, 1071 m, 742 m.

[Cu₄(HL)₄] (3). A mixture of H₃L (11.3 mg, 0.05 mmol), Cu(CH₃COO)₂·H₂O (10 mg, 0.05 mmol), and CH₃CN/CH₃OH (1 mL, v/v = 3:1) was sealed in a Pyrex-tube (8 mL). The tube was heated at 80 °C for 4 days under autogenous pressure. Cooling of the resultant solution to room temperature gave dark green acicular crystals. The crystals were collected by filtration, washed with CH₃CN/CH₃OH (3 mL, v/v = 3:1) and dried in air. Yield: 0.0186 g (65%, based on Cu). Anal. Calcd for C₄₄H₅₂Co₄N₄O₁₆: C, 46.07; H, 4.57; N, 4.88. Found: C, 45.76; H, 4.50; N, 4.73%. Selected IR data (KBr, cm⁻¹): 3385 s, 1637 s, 1443 s, 1221 s, 1043 m, 749 m.

The purity of complexes **1–3** is confirmed by a comparison of experimental and simulated PXRD patterns (Fig. S4–S6). The experimental peaks are in good agreement with those calculated from X-ray single-crystal diffraction data.

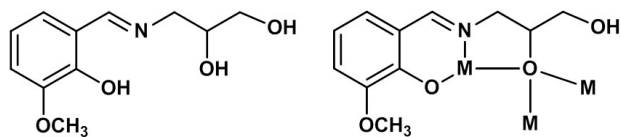
Results and discussion

Syntheses and IR spectra

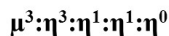
Complexes **1-2** were prepared under solvothermal conditions in CH₃OH. However, the similar reaction between Cu(CH₃COO)₂·H₂O and H₃L in CH₃OH could not afford any crystalline complex. When the reaction of Cu(CH₃COO)₂·H₂O and H₃L was conducted in CH₃CN/CH₃OH (v/v = 3:1), a crystalline tetranuclear species [Cu₄(HL)₄] (**3**) was generated. The mixed MeCN–MeOH solvent mixture was necessary to ensure adequate solubility of all reagents. Furthermore, when EtOH was used, a lot of dark green copper precipitates were obtained, and no clean product could be isolated from the filtrate.

The IR spectra of all the complexes show broad peaks in the range of 3346–3385 cm⁻¹ because of the alcoholic OH group. The strong absorption band occurring at 1620, 1631 and 1637 cm⁻¹ for **1**, **2** and **3**, respectively, can be assigned to the C=N stretching frequency of the coordinated ligands, whereas the same band is observed at ca. 1644 cm⁻¹ for the free ligand. The shift of this band towards lower frequency on complexation with the metals suggests coordination via imino nitrogen atom in all the complexes.¹⁷ The ν(C–O_{phen}) mode is present as a very strong band at about 1211–1221 cm⁻¹. The peaks in the range 1043–1082 cm⁻¹ are assigned to alcoholic C–O stretches. Several weak peaks observed for the complexes in the range 3000–2829 cm⁻¹ are ascribed to the aromatic and aliphatic C–H stretches.

Description of Structures



H₃L



Scheme 1 The structure of H₃L and coordination mode of [HL]²⁻ in **1-3**.

Structures of [M₄(HL)₄] (M = Co^{II} (**1**), M = Zn^{II} (**2**))

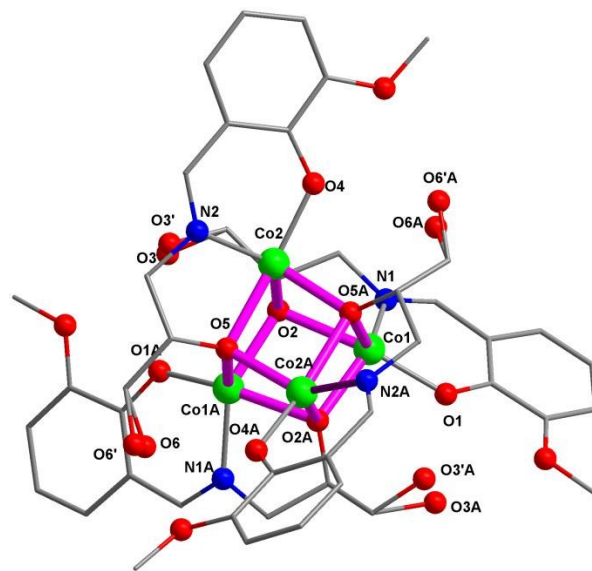
The crystal structure determination reveals that complexes **1** and **2** are isostructural. Thus, the structure of **1** will be discussed here in detail. Complex **1** crystallizes in the monoclinic crystal system in the space group C2/c. As shown in Fig. 1a, the structure of **1** consists of four Co^{II} ions and four doubly deprotonated HL²⁻ ligands. The four Co^{II} centers are linked by μ₃-oxo bridges, generating a cubane-type {Co₄O₄} configuration (Fig. 1b). The HL²⁻ ligand adopts both chelating and bridging modes (μ³:η³:η¹:η¹:η⁰) and coordinates to the metal centers through the imine nitrogen, deprotonated phenolic and alkoxy oxygen atoms (Scheme 1). The coordination environment of each Co^{II} center is identical. Each metal atom is five-coordinated by one imine nitrogen atom, one deprotonated phenolic and one μ₃-alkoxo oxygen atom from one HL²⁻ ligand, and two μ₃-alkoxo oxygen atoms from other two HL²⁻ ligands. The coordination geometry around each Co^{II} center is best described as distorted square pyramid (Fig. 1c) as reflected from the respective τ values (τ = 0.31 for Co1 and Co1A, τ = 0.42 for Co2 and Co2A).¹⁸ The Co–O bond lengths range from 1.944(3) to 2.186(3) Å (Table S1), being in good agreement with the literature values for similar systems.¹⁹ The average Co–N bond length is 1.998 Å, which is longer than that in the above mentioned articles (1.897 Å). A tetrahedron structure with Co···Co separations being in the range of 3.0967(10)–3.1797(10) Å (Fig. 1d) is generated by linking the

adjacent Co^{II} centers. Three different Co···Co distances and five M–O–M angles were found in **1** (Table S1), showing **1** contains a low symmetry cubane core and possesses three types of {M₂O₂} faces. Large thermal coefficients together with residual peaks are found for the non-coordinated alkoxy oxygen atoms, suggesting high thermal motion and/or positional disorder for these atoms. Thus the non-coordinated alkoxy oxygen atoms O3 and O6 were modeled disordered around two positions in 0.5:0.5 ratio. Four intermolecular hydrogen bonds are formed between two neighboring molecules, resulting in a “wave-like” 1D arrangement of the clusters (Fig. 2).

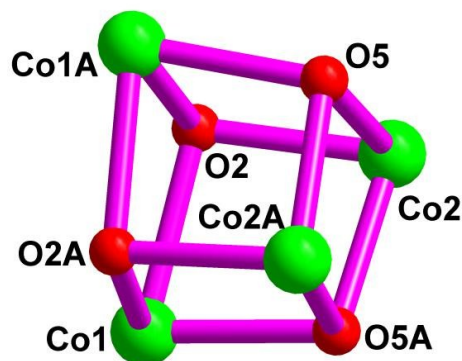
Complex **1** joins a large family of tetranuclear Co^{II} complexes with {Co₄O₄} cubane cores.⁴ Among nearly the 140 {Co₄O₄} clusters found in the Cambridge Structure database, complex **1** is the only one supported by Schiff base, indicating the synthetic novelty of this work.

Complex **2** is one of the members of cubane-type {Zn₄O₄} family. However, among nearly 100 {Zn₄O₄} compounds, only limited numbers of complexes were constructed by Schiff base ligands.²⁰

(a)



(b)



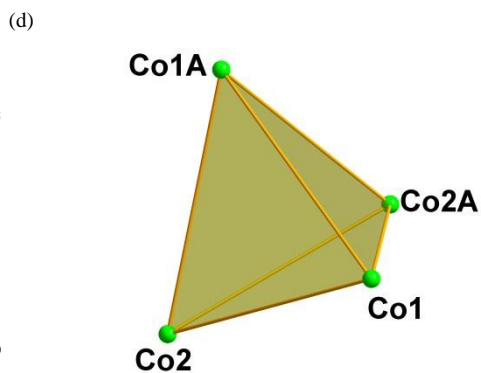
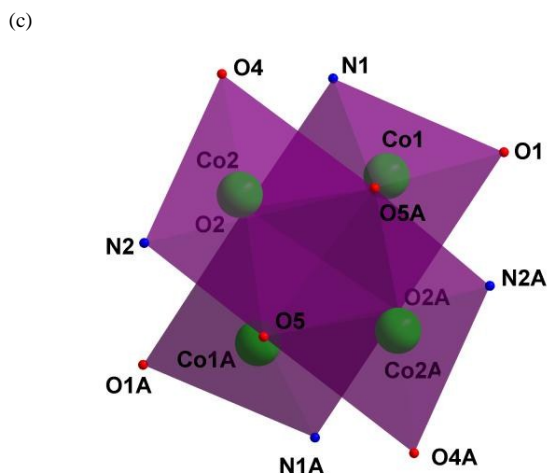


Fig. 1 (a) Molecule structure of **1**; hydrogen atoms have been omitted for clarity. The atoms of O3 and O6 were modeled disordered around two positions in a 0.5:0.5 ratio; (b) The cubane-type $\{Co_4O_4\}$ core in **1**; (c) The coordination environment of each Co^{II} ion; (d) Tetrahedron structure built by Co^{II} centers. Color code: Co^{II} , green; O, red; N, blue; C, gray.

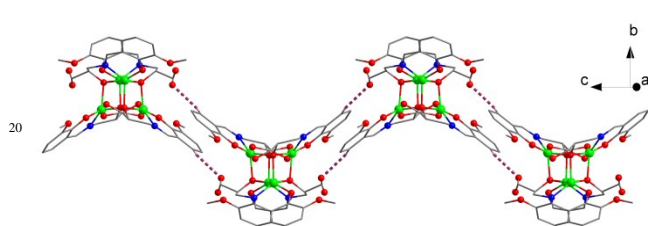


Fig. 2 “Wave-like” 1D hydrogen-bonded double chain of **1**. Color code: Co^{II} , green; O, red; N, blue; C, gray.

Structure of $[Cu(HL)_4]$ (**3**)

Complex $[Cu_4(HL)_4]$ (**3**) crystallizes in the tetragonal space group $P4_2/n$. Compared with **1**, complex **3** has higher symmetry, and crystallographic asymmetric unit only contains one copper center and one doubly deprotonated HL^{2-} ligand. Similar to both **1** and **2**, this compound consists of a tetranuclear core with the metal centers being linked by the μ_3 -alkoxo oxygen atoms (Fig. 3). Each Cu^{II} ion displays distorted square-pyramidal geometry ($\tau = 0.15$). The Cu–O and Cu–N bond lengths in the equatorial plane range from 1.8925(18)–1.9709(17) Å (Table S5), which are shorter than those in **1**. Compared with the axial Co–O bond in **1**, the apical oxygen atom shows longer Cu–O bond length [2.4660(16) Å]. The elongation of the Cu–O axial bond is due to a pseudo-Jahn-Teller distortion of the d^9 Cu^{II} center.²¹ The bridging

Cu–O–Cu angles are in the range of 88.70°–104.93°. In a previous paper,²² P. Alemany had proposed a classification of the cubane structures based on the use of the Cu–Cu distances as a classification criterion. Complex **3** clearly belongs to the 4 + 2 class with the four Cu–Cu separations including Cu1–Cu1A, Cu1–Cu1B, Cu1A–Cu1C and Cu1A–Cu1C being significantly shorter [3.1080(5) Å] than the Cu1–Cu1C and Cu1A–Cu1B distances [3.4317(5) Å]. Complex **3** features weak intermolecular C–H···O hydrogen contacts (C18–H18···O3#3, C to O distance 3.466(7) Å, C7–H7···O3#4 angle 161.3°, symmetry operation $-y+3/2, x, -z+3/2$) between the CH groups of phenolic rings as hydrogen atom donors and oxygen atoms from hydroxy of the neighbor molecules as acceptors. These hydrogen bond interactions connect the neighboring molecules to generate a 1D chain structure (Fig. 4).

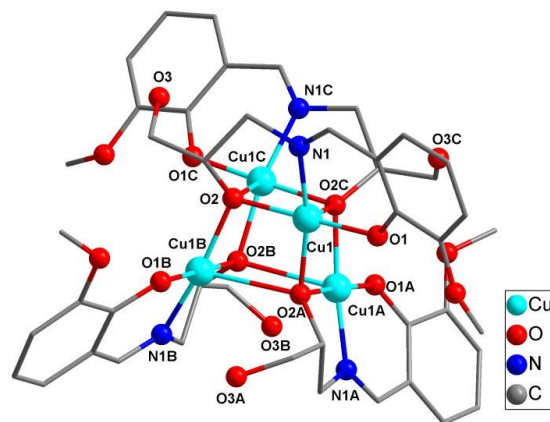


Fig. 3 Molecule structure of complex **3**; hydrogen atoms have been omitted for clarity. Color code: Cu^{II} , light blue; O, red; N, blue; C, gray.

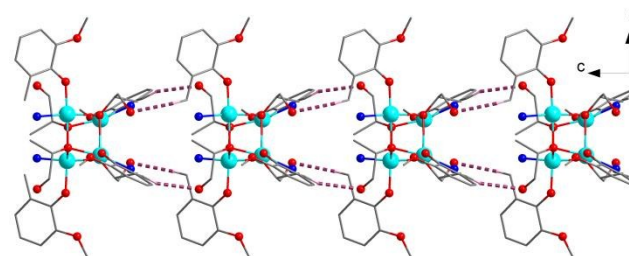


Fig. 4 Chain structure formed by hydrogen bonding interactions in **3**. Color code: Cu^{II} , light blue; O, red; N, blue; C, gray.

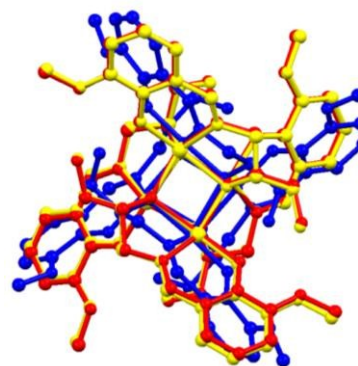


Fig. 5 Overlaid structure of complexes **1-3**. Color code: Co^{II} , yellow (complex **1**); Zn^{II} , red (complex **2**); Cu^{II} , blue (complex **3**).

As the $\{M_4O_4\}$ cluster of the complexes **1-3** is located about a 2-fold rotation axis. The structures of **1-3** are compared by overlaying the complexes (Fig. 5). The r.m.s values between complexes **1** and **2**, **1** and **3**, and **2** and **3** are 0.0297, 0.261 and 0.265, respectively, consisting with the space groups of the three complexes.

Luminescence properties

Photoluminescence studies of the ligand H_3L and the compounds **1-3** were carried out at room temperature in the solid state (Fig. 6). The free ligand H_3L has a moderate fluorescence emission band at 523 nm upon excitation at 370 nm. Complexes **1** and **3** are nonfluorescent and compound **2** has characteristic fluorescence emission. The luminescence of **1** and **3** may be quenched by metal ions. Metal ions can enhance or quench the fluorescence emission of some Schiff base ligands containing aromatic rings, due to magnetic perturbation, redox activity and electronic energy transfer.²³ Compound **2** displays a broad emission band at 473 nm upon excitation at 333 nm. The emission of **2** should be neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in the nature since the Zn^{II} ion is difficult to oxidize or reduce due to its d^{10} configuration.²⁴ Thus, the luminescent band of **2** can probably be ascribed to intraligand $\pi \rightarrow \pi^*$ electron transition.²⁵ The emission intensity of **2** is stronger than that of the ligand. The enhanced fluorescence efficiency of the complex is attributed to the coordination of the ligands to the Zn^{II} ions which effectively increases the rigidity of the ligands and reduces the loss of energy via radiationless thermal vibrations.²⁶

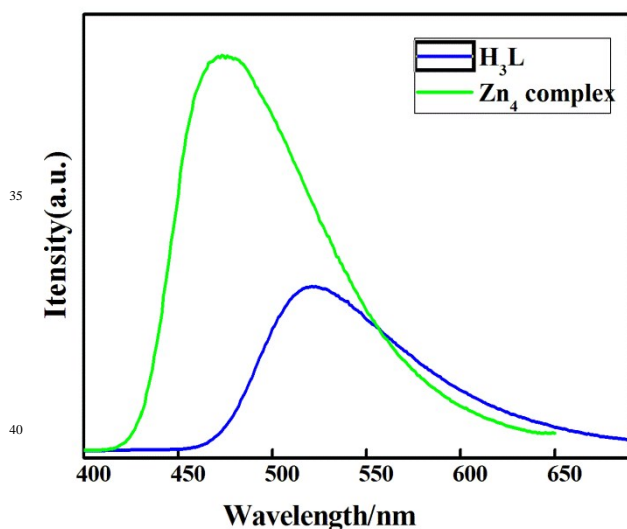


Fig. 6 Emission spectra of H_3L and **2** (green) in the solid state at room temperature (Emission slit = 1 nm).

Magnetic properties of **1** and **3**

Variable-temperature dc magnetic susceptibility data were recorded for polycrystalline samples of **1** and **3** at an applied magnetic field of 1000 Oe in the temperature range of 2-300 K.

The $\chi_M T$ value of **1** at 300 K is $12.22 \text{ cm}^3 \text{ K mol}^{-1}$ (Fig. 7), which is obviously larger than the spin-only value of $7.50 \text{ cm}^3 \text{ K mol}^{-1}$ expected for four $S = 3/2$ uncoupled spins, possibly due to

the orbital contributions of the metal ions.²⁷ Upon cooling from room temperature, $\chi_M T$ per cubane gradually increased to a maximum ($21.99 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) at 3 K and then decreased to $20.82 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. The observed behavior is indicative of the presence of ferromagnetic exchange interactions. The reciprocal magnetic susceptibilities in 2-300 K follow the Curie-Weiss Law of $1/\chi_M = (T - \theta)/C$ with Curie constant $C = 11.95 \text{ cm}^3 \text{ K mol}^{-1}$ and Weiss constant $\theta = 10.64 \text{ K}$, which confirms the existence of the ferromagnetic interactions among the cubane.

The ac magnetic susceptibility **1** is investigated by measurement at frequencies of 100, 500, 1000, 1250 and 1500 Hz (Fig. 8). Complex **1** shows an unnegligible out-of-phase signal above 2 K in the absence of static field, corresponding to the slow magnetic relaxation in magnetization. Below 10 K the out-of-phase susceptibility (χ'') shows strong frequency dependence, suggesting this cubane-type $\{Co_4O_4\}$ complex is a SMM.

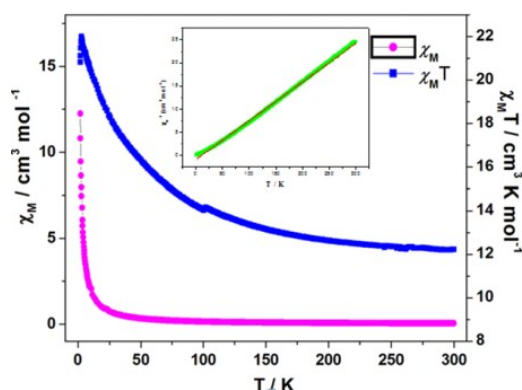


Fig. 7 Temperature dependence of magnetic susceptibilities in the form of $\chi_M T$ vs. T and χ_M vs. T for **1** at 1 kOe. Inset: temperature dependence of magnetic susceptibilities in the form of χ_M^{-1} vs. T for **1** at 1 kOe; the solid line of the χ_M^{-1} vs. T illustration corresponds to the best fit from 300 K to 2 K.

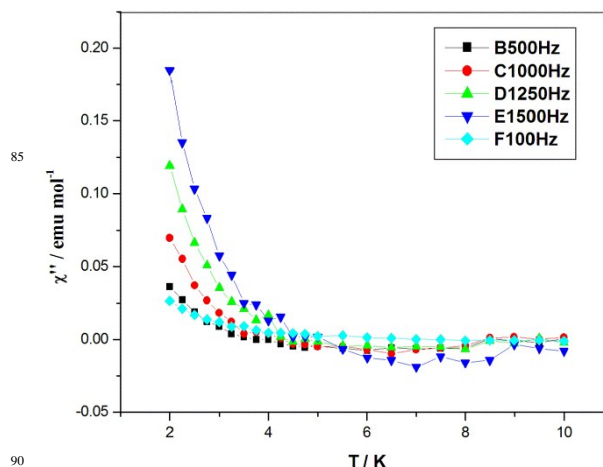


Fig. 8 Variable temperature ac susceptibility data at different frequencies without static field for the complex **1**.

The value of $\chi_M T$ for **3** is $2.05 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K (Fig. 9), which is larger than the sum of the expected value ($1.50 \text{ cm}^3 \text{ K mol}^{-1}$, $g = 2.0$, $S = 1/2$) for four uncoupled Cu^{II} ions. As temperature lowered, the $\chi_M T$ value first increases smoothly to

reach to a maximum value of $2.80 \text{ cm}^3 \text{ K mol}^{-1}$ at 10 K, and then decrease to minimum value of $2.62 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. Fitting the data at 2-300 K with the Curie-Weiss law gives a C of $1.99 \text{ cm}^3 \text{ K mol}^{-1}$ and a θ of 7.99 K. The C value is consistent with the value of $2.05 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K. The positive value of θ indicates the ferromagnetic couplings among the cubane.

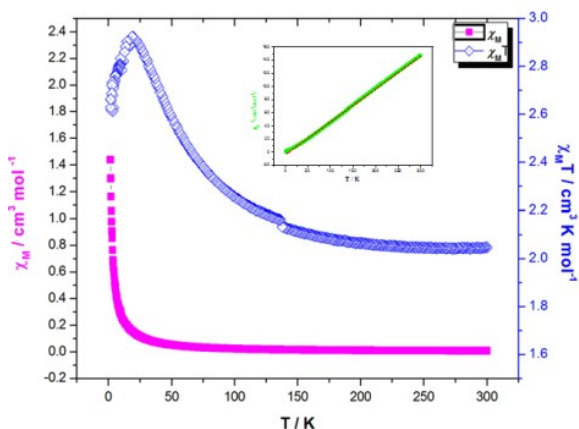


Fig. 9 Temperature dependence of magnetic susceptibilities in the form of $\chi_M T$ vs. T and χ_M vs. T for **3** at 1 kOe. Inset: temperature dependence of magnetic susceptibilities in the form of χ_M^{-1} vs. T for **3** at 1 kOe; the solid line of the χ_M^{-1} vs. T illustration corresponds to the best fit from 300 K to 2 K.

Conclusions

The first use of the hydroxyl-rich ligand (*E*)-3-((2-hydroxy-3-methoxybenzylidene)amino)propane-1,2-diol (H_3L) in the construction of cubane-type $\{\text{M}_4\text{O}_4\}$ clusters was reported. Three new cubane-type complexes $[\text{M}_4(\text{HL})_4]$ ($\text{M} = \text{Co}^{\text{II}}$ (**1**), Zn^{II} (**2**), Cu^{II} (**3**)) have been generated. The three complexes described are valuable additions to the chemistry of tetranuclear Co^{II} , Zn^{II} and Cu^{II} clusters. Complexes **1** and **2** contain low symmetry cubane cores with different $\text{M} \cdots \text{M}$ distances and $\text{M}-\text{O}-\text{M}$ angles, resulting in three types of $\{\text{M}_2\text{O}_2\}$ faces. Complex **3** belongs to the $4 + 2$ class with the four $\text{Cu} \cdots \text{Cu}$ separations being significantly shorter than the other two $\text{Cu} \cdots \text{Cu}$ distances. The photoluminescent studies of **2** indicate the blue shift compared with the H_3L ligand, and the emission intensity of the $\{\text{Zn}_4\text{O}_4\}$ complex is stronger than that of the ligand. Magnetic studies for **1** and **3** suggest that complex **1** is a SMM.

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Notes and references

- ^a Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China. E-mail: liyahong@suda.edu.cn
^b Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China.

CCDC 996947, 996955 and 979727 for complexes **1**, **2** and **3**, respectively. For crystallographic data in CIF, tables of selected bond lengths and angles, and additional figures of these compounds or other electronic format see DOI: 10.1039/b000000x/

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