第 34 卷第 4 期
2018 年 4 月

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CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.34 No.4
739-749

非对称 Salamo 型 N_2O_3 配体构筑的四核铜(Ⅱ)和锌(Ⅱ)配合物:合成、结构及荧光性质

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摘要:合成了 2 个新设计的 Salamo 型 N_2O_3 配体(H_3L)构筑的四核配合物,$\{Cu(L)(OAc)Cu(H_2O)\}_2$ (**1**)和$\{Zn(L)(OAc)Zn(H_2O)\}_2$ (**2**),并通过元素分析、红外光谱、紫外-可见吸收光谱、荧光光谱及 X 射线单晶衍射等方法对其进行了表征。配合物 **1** 由 2 个完全去质子化的 L^{3-}配体单元、2 个桥联的乙酸根离子和 2 个配位的水分子组成,形成了一种对称的四核结构。铜(Ⅱ)离子均为五配位且分别具有稍微扭曲的三角双锥和四方锥几何构型。该配合物通过 C–H$\cdots\pi$ 相互作用自组装而形成了一种一维链状超分子结构。而配合物 **2** 却为非对称的四核结构,由 2 个完全去质子化的 L^{3-}配体单元、2 个配位的水分子以及 2 个桥联的乙酸根离子组成。该配合物形成了一种三维超分子结构。同时,还研究了配体 H_3L 及配合物 **1** 和 **2** 的荧光性质。

关键词:Salamo 型 N_2O_3 配体;配合物;合成;晶体结构;荧光性质
中图分类号:O614.121;O614.24+1　　**文献标识码**:A　　**文章编号**:1001-4861(2018)04-0739-11
DOI:10.11862/CJIC.2018.070

Tetranuclear Copper(Ⅱ) and Zinc(Ⅱ) Complexes Constructed from an Asymmetrical Salamo-Type N_2O_3 Donor Ligand: Syntheses, Structures and Fluorescence Properties

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Abstract: Two newly designed tetranuclear complexes, $\{Cu(L)(OAc)Cu(H_2O)\}_2$ (**1**) and $\{Zn(L)(OAc)Zn(H_2O)\}_2$ (**2**) derived from an Salamo-type N_2O_3 donor ligand (H_3L) were synthesized and characterized by elemental analyses, IR and UV-Vis spectra, fluorescence spectra and X-ray crystallography. Complex **1** is made up of four Cu(Ⅱ) ions, two deprotonated L^{3-} moieties, two coordinated water molecules and two μ_2-acetate ions. All of the Cu(Ⅱ) ions in **1** are penta-coordinated with slightly distorted tetragonal pyramidal and trigonal bipyramidal symmetries. Complex **1** forms an infinite 1D chain supramolecular structure via C–H$\cdots\pi$ interactions. Complex **2** reveals an asymmetrical tetranuclear structure, and consists of four Zn(Ⅱ) ions, two completely deprotonated L^{3-} units, two μ_2-acetate ions and two coordinated water molecules, which possesses an infinite 3D supramolecular structure. The fluorescent properties of H_3L and complexes **1** and **2** have also been discussed. CCDC: 1484596, **1**; 1484597, **2**.

Keywords: Salamo-type N_2O_3 donor ligand; complex; synthesis; crystal structure; fluorescence property

0 Introduction

It is generally known that Salen-type ligands (R-CH =N-$(CH_2)_2$-N =CH-R) and their metal complexes have been extensively investigated in modern coordination chemistry for several decades[1-5], which have been extensively investigated in potential application in biological fields[6-13], electrochemical conducts[14-15],

收稿日期:2017-08-30。收修改稿日期:2017-12-15。
国家自然科学基金(No.21361015,21761018)资助项目。
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nonlinear optical materials[16-20], magnetic materials[21-25], luminescence properties[26-32] and supramolecular architectures[33-37] and so on. Chemical modifications of substituent or functional groups in the Salen-type N_2O_2 ligands are effective in exchanging the structures or the main functions of complexes, such as Salamo ligand, a Salen analogue, (R-CH=N-O-$(CH_2)_n$-O-N=CH-R) is one of the most versatile ligand[38-43]. In order to study the syntheses, crystal structures and fluorescence properties of the Salamo-type metal complexes, herein, we report two newly designed complexes $\{Cu(L)(OAc)Cu(H_2O)\}_2$ (**1**) and $\{Zn(L)(OAc)Zn(H_2O)\}_2$ (**2**) derived from a N_2O_3 donor bisoxime ligand.

1 Experimental

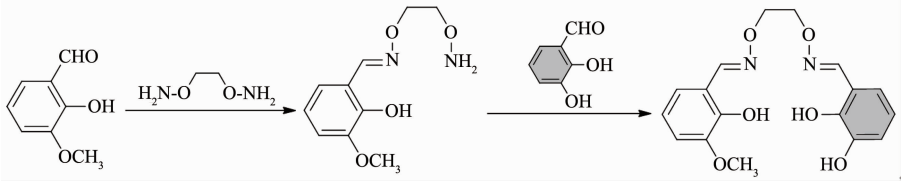
1.1 Materials and physical measurements

3-Hydroxysalicylic aldehyde of 99% purity and 3-methoxysalicylaldehyde of 98% purity were purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory.

C, H and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. Elemental analyses for copper(Ⅱ) and zinc (Ⅱ) were detected with an IRIS ER/S-WP-1 ICP atomic emission spectrometer. Melting points were obtained by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected. IR spectra were recorded on a Vertex70 FT-IR spectrophotometer, with samples prepared as KBr (500~4 000 cm^{-1}) and CsI (100~500 cm^{-1}) pellets. UV-Vis absorption spectra were recorded on a Shimadzu UV-3900 spectrometer. Luminescence spectra in solution were recorded on a Hitachi F-7000 spectrometer. X-ray single crystal structure determinations were carried out on a SuperNova Dual (Cu at zero) diffractometer.

1.2 Synthesis of H_3L

The major reaction steps involved in the synthesis of H_3L is given in Scheme 1. 1,2-Bis(aminooxy)ethane was synthesized following the literature previously reported[44-46].



Scheme 1 Synthetic route to H_3L

Synthesis of 2-(*O*-(1-ethyloxyamide))oxime-6-methoxyphenol: a solution of 3-methoxysalicylaldehyde (304.3 mg, 2 mmol) in methanol (30 mL) was added to a solution of 1,2-bis(aminooxy)ethane (92.00 mg, 1.0 mmol) in methanol (20 mL). The suspension solution was stirred and refluxed at 55 ℃ for 12 h. Then the solution was concentrated in vacuo and the residue was purified by column chromatography (SiO_2, chloroform/ethyl acetate, 30∶1, *V*/*V*) to afford colorless flocculent crystalline solid, which was collected by suction filtration. Yield: 65.4% . Anal. Calcd. for $C_{10}H_{14}N_2O_4$(%): C, 53.09; H, 6.24; N, 12.38. Found(%): C, 52.95; H, 6.20; N, 12.29.

Synthesis of H_3L: a solution of 2-(*O*-(1-ethyloxyamide))oxime-6-methoxyphenol (452.4 mg, 2 mmol) in ethanol (20 mL) was added to a solution of 3-hydroxysalicylic aldehyde (276.3 mg, 3 mmol) in ethanol (20 mL), and the mixture was subjected to heating at 65 ℃ for 4 h. After cooling to room temperature, the resulting yellow powdery solid was collected. Yield: 77.9 %. Anal. Calcd. for $C_{17}H_{18}N_2O_6$(%): C, 58.96; H, 5.24; N, 8.09. Found(%): C, 58.87; H, 5.28; N, 8.02.

1.3 Synthesis of $\{Cu(L)(OAc)Cu(H_2O)\}_2$ (1)

A solution of H_3L (6.92 mg, 0.02 mmol) in 4 mL of acetone was added dropwise to a methanol solution (4 mL) of copper(Ⅱ) acetate monohydrate (7.96 mg, 0.04 mmol). The color of mixing solution turned to dark-brown immediately. The mixture solution was filtered and the filtrate was allowed to stand for about four weeks. Along with partially volatilization of

solvent of the mixed solution and several clear light brown block-shaped single crystals suitable for X-ray crystallographic analysis were obtained. Yield: 55.7%. Anal. Calcd. for $C_{38}H_{40}Cu_4N_4O_{18}$(%): C, 41.68; H, 3.68; N, 5.12; Cu, 23.21. Found (%): C, 41.72; H, 3.63; N, 5.18; Cu, 23.26.

1.4 Synthesis of {Zn(L)(OAc)Zn(H_2O)}$_2$ (2)

A solution of H_3L (6.92 mg, 0.02 mmol) in 4 mL of acetone was added dropwise to a methanol solution (4 mL) of zinc(Ⅱ) acetate tetrahydrate (8.76 mg, 0.04 mmol). The color of mixing solution turned to yellow immediately. The mixture solution was filtered and the filtrate was allowed to stand for about one week. Through partial solvent evaporation, several clear light yellow block-shaped single crystals suitable for X-ray diffraction analysis were obtained. Yield: 48.5%. Anal. Calcd. for $C_{38}H_{40}Zn_4N_4O_{18}$(%): C, 41.40; H, 3.66; N, 5.08; Zn, 23.73. Found(%): C, 41.47; H, 3.72; N, 5.17; Zn, 23.64.

1.5 Crystal structure determinations of the complexes

The crystal diffractometer provides a monochromatic beam of Mo $K\alpha$ radiation (λ=0.071 073 nm) produced using graphite monochromator from a sealed Mo X-ray tube was used to obtain crystal data for the complexes. The Lp corrections were applied by using the SAINT program[47] and Semi-empirical correction were applied by using the SADABS program[48]. The structures were solved by the direct methods (SHELXS-2014)[49]. All hydrogen atoms were added theoretically and difference-Fourier map revealed the positions of the remaining atoms. All non-hydrogen atoms were refined anisotropically using a full-matrix least-squares procedure on F^2 with SHELXL-2014[49]. The crystal data and experimental parameters relevant to the structure determinations are listed in Table 1.

CCDC: 1484596, **1**; 1484597, **2**.

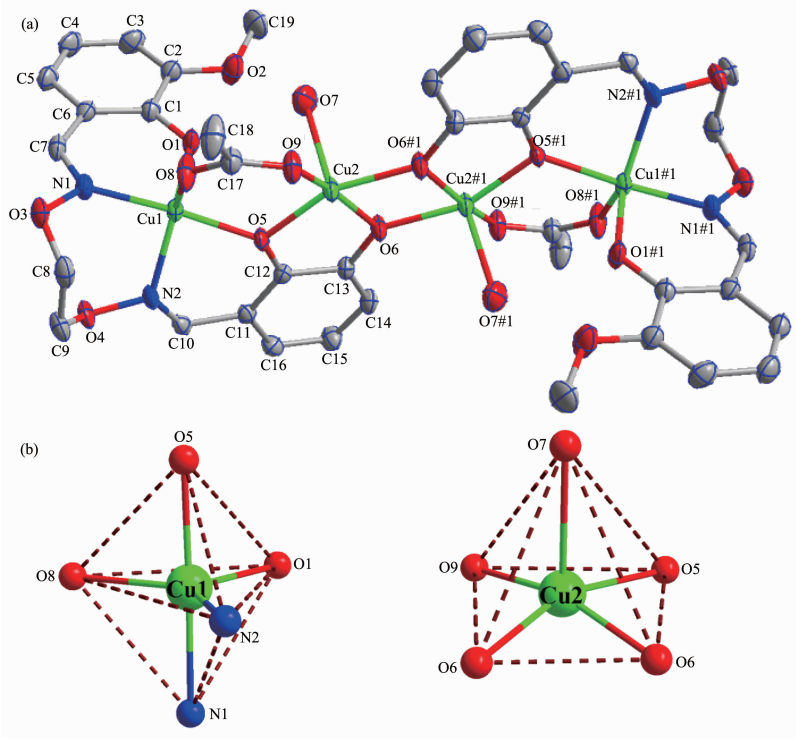
Table 1　Crystal data and structure refinement parameters for complexes 1 and 2

Complex	1	2
Temperature / K	293(2)	294.39(10)
Empirical formula	$C_{38}H_{40}Cu_4N_4O_{18}$	$C_{38}H_{40}Zn_4N_4O_{18}$
Formula weight	1 094.94	1 102.22
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pca2_1$
a / nm	0.987 60(8)	1.687 33(7)
b / nm	1.039 19(10)	1.461 31(7)
c / nm	1.225 40(10)	1.957 51(9)
β / (°)	75.141(7)	
V / nm^3	1.162 67(18)	4.826 7(4)
Z	1	4
D_c / (g·cm^{-3})	1.564	1.517
μ / mm^{-1}	1.879	2.036
F(000)	556	2 240
Crystal size / mm	0.31×0.07×0.03	0.14×0.17×0.21
θ range / (°)	3.332~26.016	3.480~25.010
Limiting indices	$-11 \leqslant h \leqslant 12, -11 \leqslant k \leqslant 12, -14 \leqslant l \leqslant 15$	$-15 \leqslant h \leqslant 20, -17 \leqslant k \leqslant 17, -23 \leqslant l \leqslant 22$
Independent reflection	4 550	8 069
Completeness to θ / %	99.7	99.7
Data, restraint, parameter	4 550, 0, 292	8 069, 71, 582
GOF on F^2	1.037	1.013
Final R indices [$I>2\sigma(I)$]	R=0.052 8, wR=0.114 9	R=0.058 9, wR=0.1117 0
Largest diff. peak and hole / (e·nm^{-3})	683 and −439	493 and −487

2 Results and discussion

2.1 Crystal structure of 1

As shown in Fig.1 and Table 2, **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of four Cu(Ⅱ) ions, two completely deprotonated L^{3-} units, two μ_2-acetate ions and two coordinated water molecules. All of the Cu (Ⅱ) ions in the asymmetric unit of **1** are penta-coordinated, the Cu(Ⅱ) ion at the terminal position is coordinated by two



Hydrogen atoms are omitted for clarity; Symmetry codes: #1: 1–*x*, –*y*, 1–*z*

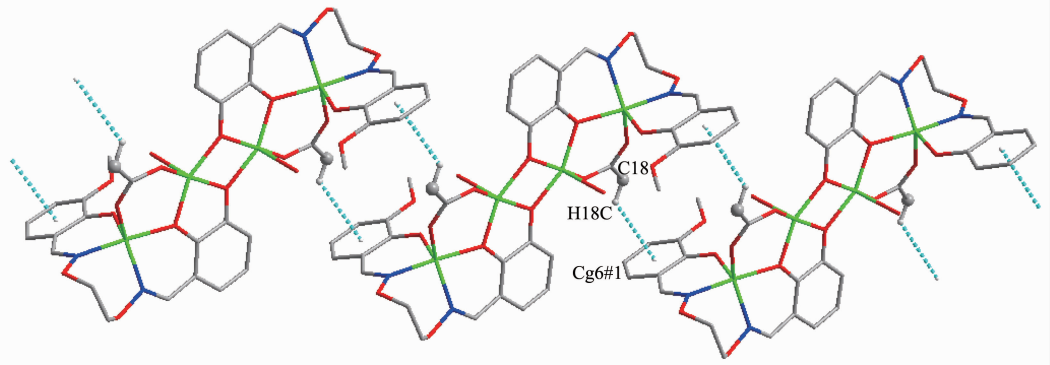
Fig.1 (a) Molecular structure and atom numberings of **1** with 30% probability displacement ellipsoids; (b) Coordination polyhedra for Cu(Ⅱ) ions of **1**

Table 2 Selected bond distances (nm) and angles (°) for 1

			A		
Cu1-O1	0.198 5(3)	Cu1-O5	0.193 9(3)	Cu1-O8	0.205 6(4)
Cu1-N1	0.196 8(4)	Cu1-N2	0.204 4(4)		
O1-Cu1-O8	106.84(17)	O1-Cu1-N2	121.18(17)	O5-Cu1-O1	93.45(13)
O5-Cu1-O8	91.32(14)	O5-Cu1-N1	175.83(15)	O5-Cu1-N2	86.72(14)
N1-Cu1-O1	90.39(14)	N1-Cu1-O8	89.12(16)	N1-Cu1-N2	89.89(16)
N2-Cu1-O8	131.98(17)				
			B		
Cu2-O5	0.197 7(3)	Cu2-O6	0.193 8(3)	Cu2-O6#1	0.197 2(3)
Cu2-O7	0.228 6(4)	Cu2-O9	0.191 8(4)		
O5-Cu2-O7	94.48(15)	O6-Cu2-O5	83.22(13)	O6#1-Cu2-O5	158.47(14)
O6-Cu2-O6#1	77.64(16)	O6-Cu2-O7	97.80(17)	O6#1-Cu2-O7	97.78(15)
O9-Cu2-O5	99.27(14)	O9-Cu2-O6	164.36(16)	O9-Cu2-O6#1	96.63(14)
O9-Cu2-O7	97.39(17)				

Symmetry codes: #1: 1–*x*, –*y*, 1–*z*

phenoxo oxygen (O1 and O5) atoms and two oxime nitrogen (N1 and N2) atoms from L^{3-} moeity and one oxygen (O8) atom from the μ_2-acetate ion. In addition, the phenoxo oxygen (O1) atom, the oxime nitrogen (N2) atom from the L^{3-} unit and one oxygen (O8) atom from the μ_2-acetate ion form the basal plane (Cu1-O1, 0.198 5(3) nm; Cu1-O8, 0.205 6(4) nm; Cu1-N2, 0.204 4(4) nm), and one phenoxo oxygen (O5) atom and one oxime nitrogen (N1) atom occupy together the axial positions where the Cu1-N1 and Cu1-O5 are found to be 0.196 8(4) and 0.193 9(3) nm, respectively. The penta-coordinated central Cu(Ⅱ) ion (Cu2 or Cu2#1) is coordinated by three phenoxo oxygen (O6, O6#1 and O5 atoms) atoms, one oxygen (O9) atom from the μ_2-acetate ion and one oxygen (O7) atom from the coordinated water molecule. Moreover, one oxygen (O9) atom of the μ_2-acetate ion and three phenoxo oxygen (O6, O6#1 and O5) atoms form the basal plane (Cu2-O6, 0.193 8(3) nm; Cu2-O6#1, 0.197 2(3) nm; Cu2-O5, 0.197 7(3) nm; Cu2-O9, 0.191 8(4) nm). One oxygen (O7) atom from the coordinated water molecule occupies the axial position (Cu2-O7, 0.228 6(4) nm). As widely known, tetrahedron or octahedron coordination geometry is commonly reported for Cu(Ⅱ) ion. Herein, we have synthesized a novel structural tetranuclear Cu(Ⅱ) complex, where all the Cu(Ⅱ) ions are penta-coordinated with slightly distorted tetragonal pyramidal and trigonal bipyramidal symmetries by estimating the values of τ_1=0.731 and τ_2=0.098[50-51]. As shown in Fig.2 and Table 3, the molecules of **1** are connected via C18–H18C⋯Cg6 interactions to form an infinite 1D chain structure along the *b* axis[52-57].



Symmetry codes: #1: −*x*, 1−*y*, 1−*z*

Fig.2　View of the 1D supramolecular structure of **1** showing the C–H⋯π stacking interactions

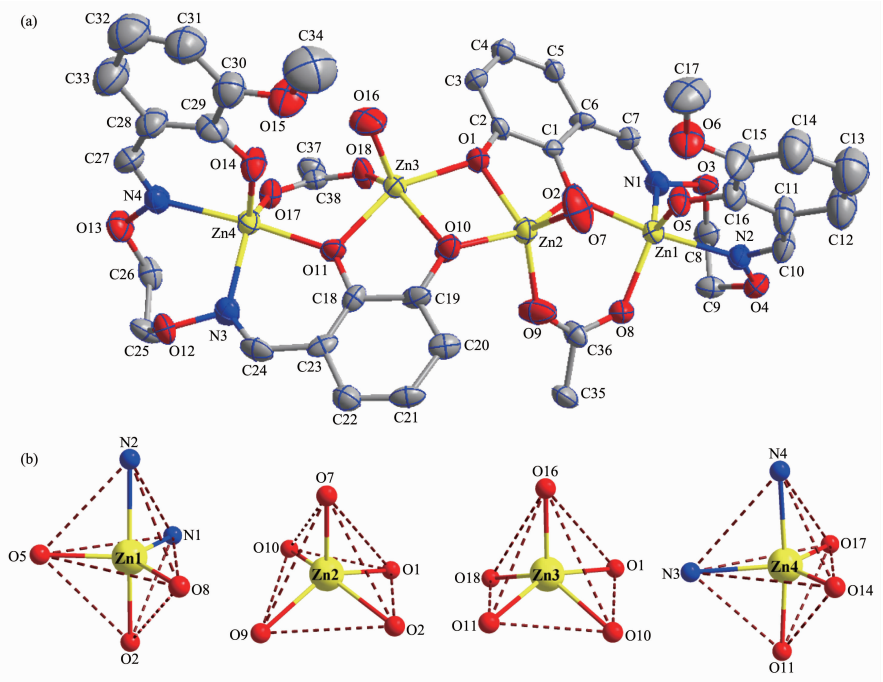
Table 3　Hydrogen bond parameters for complexes 1 and 2

D–H⋯A	*d*(D-H) / nm	*d*(H⋯A) / nm	*d*(D⋯A) /nm	∠D–H⋯A / (°)
		1		
C18–H18C⋯Cg6#1	0.096	0.294 0	0.360 0(7)	127
		2		
C35–H35C⋯O13#1	0.096	0.258 0	0.320 0(2)	122
C9–H9B⋯Cg12#2	0.097	0.272 0	0.344 6(16)	132
C17#3–H17C#3⋯Cg12	0.096	0.292 0	0.361(2)	129
C26–H26B⋯Cg10#4	0.097	0.270 0	0.342 9(16)	133
C34#5–H34B#5⋯Cg10	0.096	0.287 0	0.359(3)	133

Cg6 is the centroids of benzene ring C1~C6 of **1**; Cg10 is the centroids of benzene ring C1~C6 of **2**; Cg12 is the centroids of benzene ring C18~C23 of **2**; Symmetry codes: #1: −*x*, 1−*y*, 1−*z* for **1**; #1: 1/2−*x*, *y*, −1/2+*z*; #2: 1/2+*x*, 1−*y*, *z*; #3: 1/2+*x*, −*y*, *z*; #4: −1/2+*x*, 1−*y*, *z*; #5: −1/2+*x*, −*y*, *z* for **2**.

2.2　Crystal structure of complex 2

As shown in Fig.3 and Table 4, X-ray crystallographic analysis of complex **2** reveals an asymmetrical tetranuclear structure. It crystallizes in the orthorhombic system, space group $Pca2_1$. Its asymmetric unit consists of four Zn(Ⅱ) ions, two completely



Hydrogen atoms are omitted for clarity

Fig.3 (a) Molecular structure and atom numberings of **2** with 30% probability displacement ellipsoids; (b) Coordination polyhedra for Zn(Ⅱ) ions of **2**

Table 4 Selected bond lengths (nm) and angles (°) for 2

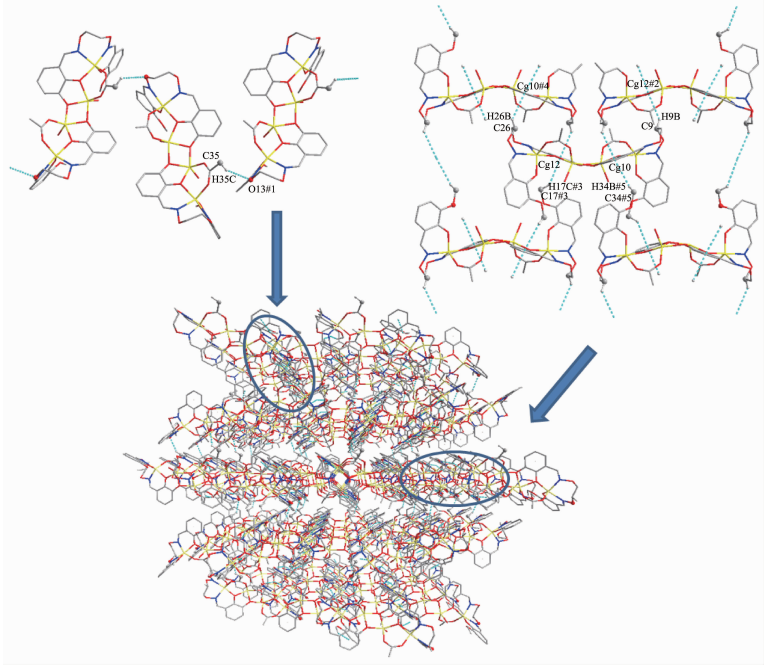
			C		
Zn1-N1	0.211 2(11)	Zn1-N2	0.211 5(13)	Zn1-O2	0.204 4(9)
Zn1-O5	0.192 6(9)	Zn1-O8	0.200 1(10)		
N2-Zn1-N1	88.0(5)	O2-Zn1-N1	84.0(4)	O2-Zn1-N2	171.3(5)
O5-Zn1-N1	121.3(5)	O5-Zn1-N2	87.9(5)	O5-Zn1-O2	93.2(4)
O5-Zn1-O8	116.9(5)	O8-Zn1-N1	121.8(4)	O8-Zn1-N2	95.3(5)
O8-Zn1-O2	92.0(4)				
			D		
Zn2-O9	0.198 9(12)	Zn2-O10	0.199 2(10)	Zn2-O1	0.201 7(11)
Zn2-O2	0.205 5(9)	Zn2-O7	0.196 9(11)		
O9-Zn2-O1	137.9(5)	O9-Zn2-O2	91.8(4)	O7-Zn2-O1	108.9(5)
O10-Zn2-O2	102.2(5)	O2-Zn2-O7	100.2(5)	O7-Zn2-O9	113.1(7)
O10-Zn2-O2	151.8(4)	O9-Zn2-O10	94.8(5)	O1-Zn2-O2	78.4(4)
O10-Zn2-O1	78.4(4)				
			E		
Zn3-O1	0.203 1(9)	Zn3-O10	0.205 7(12)	Zn3-O11	0.205 1(9)
O16-Zn3	0.197 6(10)	Zn3-O18	0.196 8(10)		
O16-Zn3-O11	100.4(4)	O16-Zn3-O10	112.7(5)	O1-Zn3-O16	101.1(5)
O16-Zn3-O18	108.8(6)	O11-Zn3-O18	92.7(4)	O10-Zn3-O18	138.4(4)
O1-Zn3-O18	96.2(4)	O1-Zn3-O10	76.6(4)	O11-Zn3-O10	79.6(4)
O1-Zn3-O11	152.6(4)				

续表 4

F					
Zn4-N3	0.209 0(13)	Zn4-N4	0.214 0(13)	Zn4-O11	0.202 2(10)
Zn4-O14	0.192 1(10)	Zn4-O17	0.200 4(10)		
N3-Zn4-O11	83.7(5)	N4-Zn4-O11	173.9(5)	N3-Zn4-O17	122.1(4)
N4-Zn4-O17	94.5(4)	N3-Zn4-O14	121.7(5)	N4-Zn4-O14	87.7(5)
O14-Zn4-O11	91.9(4)	O14-Zn4-O17	116.1(5)	O17-Zn4-O11	91.2(4)
N3-Zn4-N4	91.3(5)				

deprotonated L^{3-} units, two μ_2-acetate ions and two coordinated water molecules.

The terminal Zn(Ⅱ) ion (Zn1 or Zn4) is penta-coordinated by two oxime nitrogen (N1 and N2) atoms and two phenoxo oxygen (O2 and O5) atoms from the completely deprotonated L^{3-} moiety and one oxygen (O8) atom from the μ_2-acetate ion. Besides, the phenoxo oxygen (O5) atom, oxime nitrogen (N1) atom from the L^{3-} moiety and one oxygen (O8) atom from the μ_2-acetate ion form the basal plane (Zn1-O5, 0.192 6(9) nm; Zn1-O8, 0.2001(10) nm; Zn1-N1, 0.211 2(11) nm), and one phenoxo oxygen (O2) atom and one oxime nitrogen (N2) atom occupy together the axial positions (Zn1-O2, 0.204 4 (9) nm; Zn1-N2, 0.211 5 (13) nm). The central Zn(Ⅱ) ion (Zn2) is also penta-coordinated by three phenoxo oxygen (O1, O2 and O10) atoms, one oxygen (O9) atom from the μ_2-acetate ion and one oxygen (O7) atom from the coordinated water molecule. In addition, one oxygen (O9) atom of the μ_2-acetate ion and three phenoxo oxygen (O1, O2 and O10) atoms form basal plane (Zn2-O9, 0.198 9 (12) nm; Zn2-O2, 0.205 5(19) nm; Zn2-O1, 0.201 7(11) nm; Zn2-O10, 0.199 2(10) nm), and one oxygen (O7) atom of the coordinated water molecule occupies the axial position (Zn2-O7, 0.196 9(11) nm). Thus, we have synthesized a novel asymmetrical structural tetranuclear Zn(Ⅱ) complex, all the Zn(Ⅱ) ions of complex **2** are penta-coordinated with slightly distorted trigonal bipyramidal and tetragonal pyramidal geometries by estimating the values of τ_1=0.825, τ_2=0.232, τ_3=0.237 and τ_4=0.863, respectively[50-51]. Table 3 and Fig.4 show the molecules of complex **2** are interlinked by intermolecular C35–



Symmetry codes: #1: 1/2–x, y, –1/2+z; #2: 1/2+x, 1–y, z; #3: 1/2+x, –y, z; #4: –1/2+x, 1–y, z; #5: –1/2+x, –y, z

Fig.4　View of the 3D supramolecular structure of **2** showing the C–H···O hydrogen bonding and the C–H···π stacking interactions

H35C…O13 and C9–H9B…Cg12, C17–H17C…Cg12, C26–H26B…Cg10 and C34–H34B…Cg10 hydrogen bond interactions leading to a 3D supramolecular structure[58-62].

2.3 FT-IR spectra

The FT-IR spectra of H_3L and its corresponding complexes **1** and **2** exhibit various bands in the 400~4 000 cm^{-1} region (Fig.5). The complexes **1** and **2** have similar structures, which connotes their similarity spectra. The hydroxyl group of H_3L exhibits a characteristic broad band at 3 124~3 410 cm^{-1}, and complexes **1** and **2** show weak band in this region, indicating that the Cu (Ⅱ) and Zn (Ⅱ) ions are coordinated by phenoxo oxygen atoms of L^{3-} moiety.

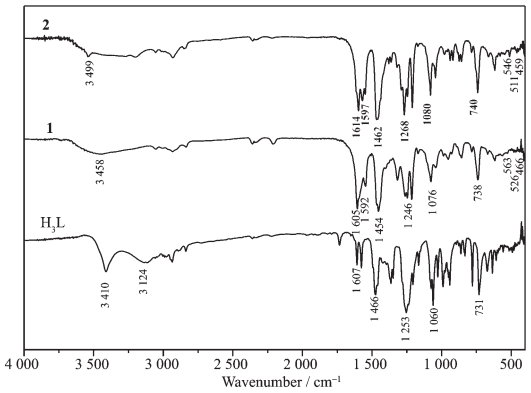


Fig.5 FT-IR spectra of the ligand and complexes **1** and **2**

A typical C=N stretching band of the free ligand H_3L appears at 1 607 cm^{-1}, and those of complexes **1** and **2** appear at 1 592 and 1 597 cm^{-1}, respectively[63]. The changes in the spectra of complexes **1** and **2** show that H_3L coordinated with Cu (Ⅱ) and Zn (Ⅱ) ions. Infrared spectrum of complex **1** shows the expected absorption bands at *ca.* 3 458, 1 605 and 563 cm^{-1} which could be assigned to the coordinated water molecule, as is substantiated by the crystal structure, indicating the presence of the coordinated water molecules[4]. Likewise, complex **2** shows absorption bands at 3 499, 1 614 and 546 cm^{-1} which are typical bands of the coordinated water molecules. The free ligand H_3L exhibits a Ar-O stretching frequency at 1 253 cm^{-1}, while the Ar-O stretching frequencies of complexes **1** and **2** appear at 1 246 and 1 268 cm^{-1}, respectively[64]. The shifts of Ar-O stretching frequencies could be evidence of the Cu-O or Zn-O bond formation between Cu (Ⅱ) or Zn (Ⅱ) ions and oxygen atoms of phenolic groups[65].

The far-IR spectra (500~100 cm^{-1}) of complexes **1** and **2** were also obtained so as to identify the bonds of M-O and M-N frequencies. The bands at 459 and 466 cm^{-1} in complexes **1** and **2** can be attributed to ν_{Cu-O} and ν_{Zn-O}, while the bands at 511 and 526 cm^{-1} are assigned to ν_{Cu-N} and ν_{Zn-N}, respectively[66].

2.4 UV-Vis absorption spectra

The UV-Vis absorption spectra of the free ligand H_3L and complexes **1** and **2** in ethanolic solution (50 $\mu mol \cdot L^{-1}$) at 298 K are shown in Fig.6.

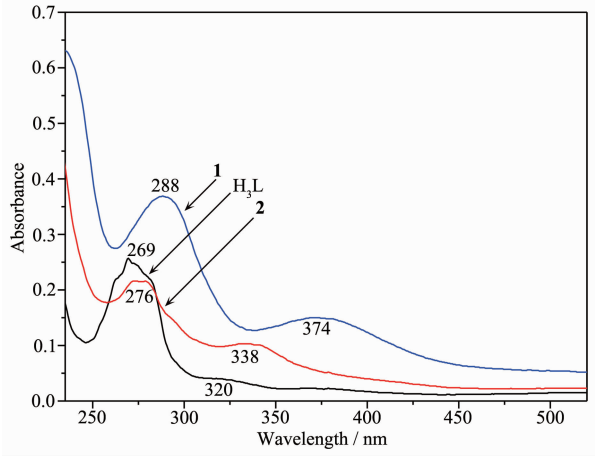


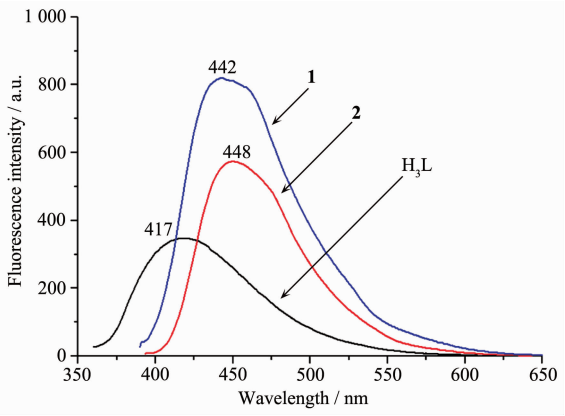
Fig.6 UV-Vis spectra of the free ligand H_3L and complexes **1** and **2**

Obviously, the absorption peaks of the ligand H_3L are different from those of complexes **1** and **2**. The absorption spectrum of the asymmetrical ligand H_3L consists of two relatively intense peaks centered at 269 and 320 nm, which may be assigned to the π-π^* transitions of the phenyl rings and oxime groups[67-68]. Compared with the free ligand H_3L, the absorption peak at 320 nm disappears from the UV-Vis spectra of complexes **1** and **2**, which indicates that the oxime nitrogen atoms are involved in coordination to the Cu(Ⅱ) and Zn(Ⅱ) ions [4]. The intraligand π-π^* transitions of the benzene rings of salicylaldehyde units are shifted in the corresponding Cu (Ⅱ) and Zn (Ⅱ) complexes, and appear at *ca.* 288 and 276 nm for complexes **1** and **2**, respectively. Moreover, the new absorption peaks are observed at *ca.* 374 and 338 nm

for complexes **1** and **2**, respectively, and assigned to L→M charge-transfer (LMCT) transitions which are characteristic of the transition metal Salen-type complexes[4].

2.5 Fluorescence properties

The fluorescent properties of H_3L and complexes **1** and **2** were measured at room temperature (Fig.7). The ligand H_3L exhibits an broad emission at 417 nm upon excitation at 342 nm, which should be assigned to intraligand π-π^* transition[69]. Complexes **1** and **2** show a higher intense photoluminescence with maximum emission at 448 and 442 nm upon excitation at 342 nm, which are slightly red-shifted compared to H_3L. The emission peak positions of complexes **1** and **2** are similar to free ligand H_3L, which may also arise from the intraligand transition. Compared with the emission spectrum of H_3L, enhanced fluorescence intensity of complex **1** or **2** is observed, indicating the intraligand transition has been influenced due to the introduction of M(Ⅱ) ions in the structure [70]. No emission originating from metal-centered or metal-to-ligand/ligand-to-metal charge-transfer excited states are expected for complexes **1** and **2**, and the emission observed in complexes **1** and **2** is tentatively assigned to the (π-π^*) intraligand fluorescence[71].



c=50 μmol·L^{-1}

Fig.7　Emission spectra of H_3L and complexes **1** and **2** in chloroform solution

3 Conclusions

In summary, we have reported the successful syntheses and characterizations of two newly designed tetranuclear complexes $\{Cu(L)(OAc)Cu(H_2O)\}_2$ and $\{Zn(L)(OAc)Zn(H_2O)\}_2$ derived from an asymmetrical Salamo-type bisoxime ligand H_3L. Complex **1** is made up of four Cu(Ⅱ) ions, two μ_2-acetate ions, two L^{3-} units and two coordinated water molecules. All of the Cu(Ⅱ) ions in complex **1** are penta-coordinated with slightly distorted tetragonal pyramidal and trigonal bipyramidal symmetries. Complex **1** forms an infinite 1D chain supramolecular structure via C–H ⋯ π interactions. Similarly, complex **2** includes four Zn(Ⅱ) ions, two L^{3-} units, two μ_2-acetate ions and two coordinated water molecules, and possesses an infinite 3D supramolecular structure. The fluorescent properties indicate that complexes **1** and **2** show a higher intense photoluminescence with maximum emission at ca. 448 and 442 nm, respectively.

Acknowledgements: This work was supported by the Natural Science Foundation of China (Grants No.21361015, 21761018) and the Program for Excellent Team of Scientific Research in Lanzhou Jiaotong University (Grant No.201706), which are gratefully acknowledged.

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