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双 Salamo 型四肟配体构筑的锌(Ⅱ)配合物：合成，晶体结构和荧光性质

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摘要： 通过二水乙酸锌(Ⅱ)和双 Salamo 型四肟配体 6,6′-二乙氧基-双(2,2′-(乙二氧双(氮次甲基)))四酚(H_4L)的配位反应，合成了 2 种锌(Ⅱ)配合物即：$[Zn_3(L)(OAc)_2(H_2O)]$ (**1**)和$[Zn_3(L)(OAc)_2(H_2O)]\cdot[Zn_3(L)(OAc)_2(CH_3OH)(H_2O)]\cdot 3CH_3OH\cdot H_2O$ (**2**)。该类配合物含有 2 个 Salamo 型 L^{4-}配体和 3 个锌(Ⅱ)离子，其中 2 个锌(Ⅱ)原子位于 Salamo 型螯合单元的 N_2O_2 空腔内。[Zn(L)]螯合物中桥联的酚氧原子进一步和中心的锌(Ⅱ)原子配位。这类结构能通过 2 个桥联的乙酸根配体稳定，从而使配合物 **1** 和 **2** 达到电荷平衡。配合物有 2 种不同的几何构型即扭曲的三角双锥和四方锥(配合物 **1**)或三角双锥和八面体(配合物 **2**)。另外，配合物 **1** 和 **2** 在激发波长为 340 和 337 nm 时能发出强的绿光，其最大发射波长分别为 531 和 536 nm。

关键词： 双 Salamo 型四肟配体；锌(Ⅱ)配合物；合成；晶体结构；荧光性质
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Two Znic(Ⅱ) Complexes Constructed from a Bis(salamo)-type Tetraoxime Ligand: Syntheses, Crystal Structures and Luminescence Properties

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Abstract: Two Zn(Ⅱ) complexes, $[Zn_3(L)(OAc)_2(H_2O)]$ (**1**) and $[Zn_3(L)(OAc)_2(H_2O)]\cdot[Zn_3(L)(OAc)_2(CH_3OH)(H_2O)]\cdot 3CH_3OH\cdot H_2O$ (**2**) have been synthesized via the complexation of zinc(Ⅱ) acetate dihydrate with a bis(salamo)-type tetraoxime ligand H_4L (H_4L=6,6′-diethoxy-bis (2,2′-(ethylenedioxybis (nitrilomethylidyne)))tetraphenol). X-ray crystallographic analyses reveal formation of trinuclear structures consisting of two salamo-type L^{4-} ligands and three Zn(Ⅱ) atoms as expected from the analytical data. Two of the three Zn(Ⅱ) atoms are located in the salamo-type L^{4-} chelate moieties. The μ-phenoxo oxygen atoms of the [Zn(L)] chelates further coordinate to centre Zn(Ⅱ) atom. The trinuclear structure is probably stabilized by the two μ-acetato ligands, which neutralize the whole charge of the complexes **1** and **2**. There are two kinds of coordination geometries (trigonal bipyramidal and square pyramidal or trigonal bipyramidal and octahedral geometries) in complexes **1** and **2**. In addition, complexes **1** and **2** exhibit strong green emission λ_{max}=531 and 536 nm when excited with 340 and 337 nm, respectively. CCDC: 864890, **1**; 1470489, **2**.

Keywords: bis(salamo)-type tetraoxime ligand; Zn(Ⅱ) complex; synthesis; crystal structure; luminescence property

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0 Introduction

The salen-type ligand and its metal complexes were discovered since the 19th century, the synthesis of the salen-type complexes have been extensively investigated for the past several decades[1], At present, some significant applications in the research of the transition metal complexes with salen-type ligands has been observed, and these complexes have been widely used in many areas, such as asymmetric catalysis[2], dioxygen carriers[3], Luminescent and magnetic properties[4-11] and biological activities, for instance, sterilization, anti-virus and anticancer and so on[12-20]. Although the studies of salen-[21-25] or salamo-type[26-37] ligands and their complexes have made great progress, but it is very rarely that the study on bis (salen)-type ligands and their metal complexes[38-39]. These bis(salen)-type ligands containing two salen-type moieties are also fascinating because some novel functions originating from the cooperation of several metal centers are expected. And these bis (salen)-type ligands play an important role in the selective strong binding with metal(Ⅱ or Ⅲ) atoms in coordination chemistry. These metal complexes also have some important practical values[40-41].

In order to further investigate syntheses, crystal structures and properties of metal complexes with bis (salen)-type ligands, herein, we report syntheses, structural characterizations and fluorescent properties of two new bis(salamo)-type Zn(Ⅱ) complexes, $[Zn_3(L)(OAc)_2(H_2O)]$ (**1**) and $[Zn_3(L)(OAc)_2(H_2O)]\cdot[Zn_3(L)(OAc)_2(CH_3OH)(H_2O)]\cdot 3CH_3OH\cdot H_2O$ (**2**) via the complexation of zinc(Ⅱ) acetate dihydrate with a bis(salamo)-type tetraoxime ligand H_4L. Furthermore, the fluorescence behavior of complexes **1** and **2** in DMF are discussed.

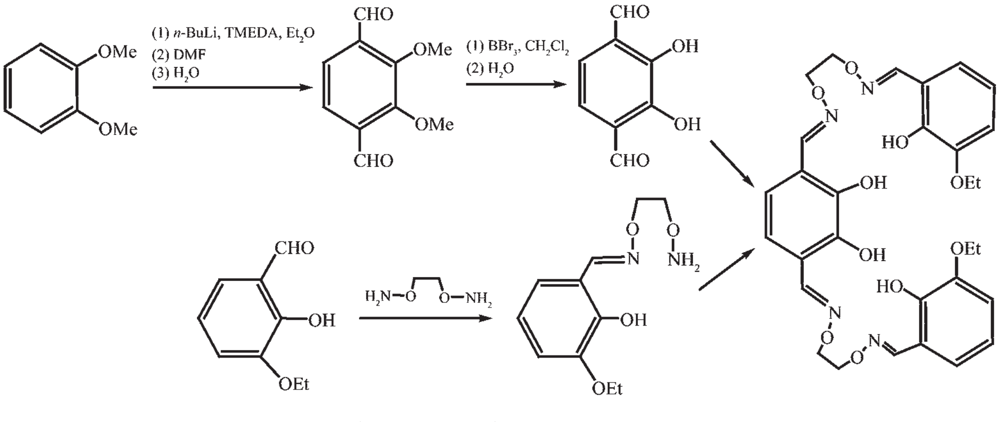
1 Experimental

1.1 Materials and physical measurements

3-Ethoxy-2-hydroxybenzaldehyde was purchased from Aldrich and used without further purification. Other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. Elemental analysis for Zn was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. ^1H NMR spectra were recorded on a Mercury-400BB spectrometer. UV-Vis absorption and fluorescence spectra were recorded on a Shimadzu UV-2550 spectrometer and Perkin-Elmer LS-55 spectrometer, respectively. X-ray single crystal structures were determined on a Bruker Smart APEX CCD area detector. Electrolytic conductance measurements were made with a DDS-11D type conductivity bridge using a 1 mmol·L^{-1} solution in DMF at room temperature. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

1.2 Syntheses of H_4L and its Zn(Ⅱ) complexes 1 and 2

Synthetic route to H_4L is shown in Scheme 1. H_4L



Scheme 1　Synthetic route to H_4L

was synthesized according to an analogous method reported earlier[39,42-45]. m.p. 401~402 K. ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.93 (s, 6H, $-CH_3$), 4.46~4.53 (m, 8H, $-OCH_2CH_2O-$), 4.63 (dt, *J*=5.4, 1.5 Hz, 4H, $-OCH_2-$), 6.77 (s, 2H, Ph-H), 6.78~6.86 (m, 4H, Ph-H), 6.93 (dd, *J*=7.2, 2.2 Hz, 2H, Ph-H), 8.25 (s, 2H, N=CH), 8.28 (s, 2H, N=CH), 9.60 (s, 2H, -OH), 9.69 (s, 2H, -OH). Anal. Calcd. for $C_{30}H_{34}N_4O_{10}$(%): C, 59.01; H, 5.61; N, 9.18. Found(%): C, 59.15; H, 5.57; N, 8.96.

A solution of Zn(Ⅱ) acetate monohydrate (3.26 mg, 0.015 mmol) in ethanol (3.0 mL) was added dropwise to a solution of H_4L (3.03 mg, 0.005 mmol) in $CHCl_3$ (1.0 mL). The color of the mixing solution turned to bright yellow immediately, the mixture was filtered and the filtrate was allowed to stand at room temperature for about two weeks. Along with partially volatilization of solvent of the mixed solution and several yellow block-shaped single crystals suitable for X-ray crystallographic analysis were obtained. Yield: 51.6% (2.4 mg). Anal. Calcd. for $[Zn_3(L)(OAc)_2(H_2O)]$ ($C_{34}H_{38}N_4O_{15}Zn_3$)(%): C, 43.46; H, 4.05; N, 5.97; Zn, 20.93. Found(%): C, 43.41; H, 4.07; N, 5.99; Zn, 20.88.

The single crystals of **2** were grown up by a similar procedure aforementioned taking $Zn(OAc)_2\cdot H_2O$ (3.26 mg, 0.015 mmol) in methanol (3 mL) and H_4L (3.03 mg, 0.005 mmol) in 1.0 mL THF solution. The obtained bright yellow mixture was filtered and the filtrate was allowed to stand was stand at room temperature for three weeks. The solvent was partially evaporated and obtained yellow block-like single crystals suitable for X-ray crystallographic analysis. Yield: 57.7% (3.4 mg). Anal. Calcd. for $[Zn_3(L)(OAc)_2(H_2O)]\cdot[Zn_3(L)(OAc)_2(CH_3OH)(H_2O)]\cdot 3CH_3OH\cdot H_2O$ ($C_{72}H_{93}N_8O_{35}Zn_6$)(%): C, 42.75; H, 4.63; N, 5.54; Zn, 19.40. Found(%): C, 42.39; H, 4.56; N, 5.61; Zn, 18.97.

1.3 Crystal structure determination

X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer at 298(2) K. Using graphite monochromatized Mo *Kα* radiation (λ=0.071 073 nm). The structures were solved using the direct method and refined by full-matrix least-squares on F^2 using the SHELXL-97 program package[46]. All non-hydrogen atoms were refined anistropically and hydrogens were added in calculated positions and refined using a riding model. The X-ray crystallographic data collection, solution and refinement parameters for the Zn(Ⅱ) complexes are summarized in Table 1.

CCDC: 864890, **1**; 1470489, **2**.

Table 1 X-ray crystallographic data and refinement parameters for complexes 1 and 2

Complex	1	2
Empirical formula	$C_{34}H_{38}N_4O_{15}Zn_3$	$C_{72}H_{93}N_8O_{35}Zn_6$
Formula weight	938.79	2 022.76
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / nm	1.639 6(2)	1.233 5(1)
b / nm	1.193 8(1)	2.189 8(2)
c / nm	1.871 2(2)	3.116 8(3)
β / (°)	95.811(1)	94.729(1)
V / nm^3	3.643 7(6)	8.389 9(1)
Z	4	4
D_c / (g·cm^{-3})	1.711	1.601
μ / mm^{-1}	2.038	1.78
F(000)	1 920	4 164
Crystal size / mm	0.38×0.35×0.33	0.23×0.21×0.19
θ range / (°)	2.44~25.02	2.23~25.02
Limiting indices	$-19\leqslant h\leqslant 16, -14\leqslant k\leqslant 11, -21\leqslant l\leqslant 22$	$-11\leqslant h\leqslant 14, -25\leqslant k\leqslant 26, -37\leqslant l\leqslant 37$
Independent reflection	6 340	14 672

Continued Table 1

Completeness to θ / %	99.90	99.80
Data, restraint, parameter	6 340, 0, 509	14 672, 3, 1 116
GOF on F^2	1.091	1.045
Final R indices [$I>2\sigma(I)$]	R=0.066 0, wR=0.196 7	R=0.068 4, wR=0.151 7
Largest diff. peak and hole / ($e \cdot nm^{-3}$)	1 153 and −644	653 and −581

2 Results and discussion

2.1 Molar conductance

Complexes **1** and **2** are soluble in DMF and DMSO, $CHCl_3$, but not soluble in EtOH, MeOH, MeCN, THF, acetone and ethyl acetate. Complexes **1** and **2** display good stability in air at room temperature. Meanwhile, H_4L is soluble in aforementioned solvents. Molar conductance values of complexes **1** and **2** (1 $mmol \cdot L^{-1}$ in DMF) at 298 K are 3.4 and 5.7 $S \cdot m^2 \cdot mol^{-1}$, respectively, indicating complexes **1** and **2** are non-electrolyte.

2.2 FT-IR spectra

The IR spectra of H_4L and its complexes **1** and **2** show a characteristic C=N stretching band. For the free ligand H_4L this band appears at 1 608 cm^{-1}, while the C=N bands of complexes **1** and **2** are observed at 1 616 and 1 612 cm^{-1}, respectively. These shifts toward higher wavenumbers of the C=N absorption of about 8~6 cm^{-1} on going from H_4L to complexes **1** and **2** suggest a weak *p*-accepting ability of the coordinated ligand[47].

The Ar-O stretching frequencies appear as a strong band within the 1 265~1 213 cm^{-1} range, as reported for similar salen-type ligands. These bands occur at 1 265 cm^{-1} for H_4L, 1 260 cm^{-1} for complex **1** and 1 263 cm^{-1} for complex **2**. The Ar-O stretching frequency is shifted to a lower value, indicating that the Zn-O bond was formed between the Zn(Ⅱ) atoms and oxygen atoms of the phenolic groups[27-31,45].

The O-H stretching frequency of H_4L appears at 3 410 cm^{-1}. In addition, the broad absorption centered on 3 384, 3 420 and 3 419 cm^{-1} in complexes **1** and **2**, respectively, which may be assigned to the O-H stretching vibration of water or methanol molecules.

2.3 UV-Vis absorption spectra

The absorption spectra of H_4L and its complexes **1** and **2** in diluted DMF solution are shown in Fig.1. It can be seen that the absorption peaks of complexes **1** and **2** are obviously different from H_4L upon complexation, and the spectral shapes of complexes **1** and **2** are similar to each other. An important feature of the absorption spectrum of H_4L is shown that two absorption peaks are observed at 273 and 310 nm, respectively. The former absorption peak at 273 nm can be assigned to the π-π^* transition of the benzene rings and the latter one at 310 nm can be attributed to the intra-ligand π-π^* transition of the C=N bonds[28-29].

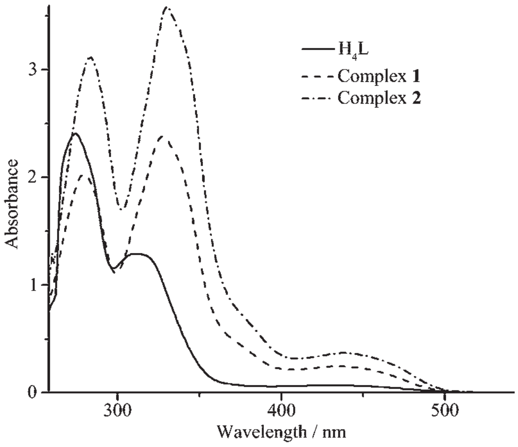


Fig.1 UV-Vis absorption spectra of H_4L and its complexes **1** and **2** in DMF (50 $\mu mol \cdot L^{-1}$)

Compared with the absorption peak of H_4L, there are three absorption peaks in complexes **1** and **2**. The former absorption peak at 273 nm in H_4L was shifted to 285 and 287 nm in complexes **1** and **2**, respectively. Meanwhile, the other absorption peak at 310 nm in H_4L was shifted to 328 and 331 nm in complexes **1** and **2**, which was shifted by *ca.* 18 and 21 nm, respectively. The absorption peaks of 273 and 310 nm were red-shifted upon coordination to the Zn(II) atoms in complexes **1** and **2**, which can be assigned to the π-π^* transitions of the salamo-type ligand. In addition, a new absorption peak at 439 and 442 nm was observed in complexes **1** and **2**, respectively.

2.4 Description of the crystal structures

2.4.1 Crystal structure of complex 1

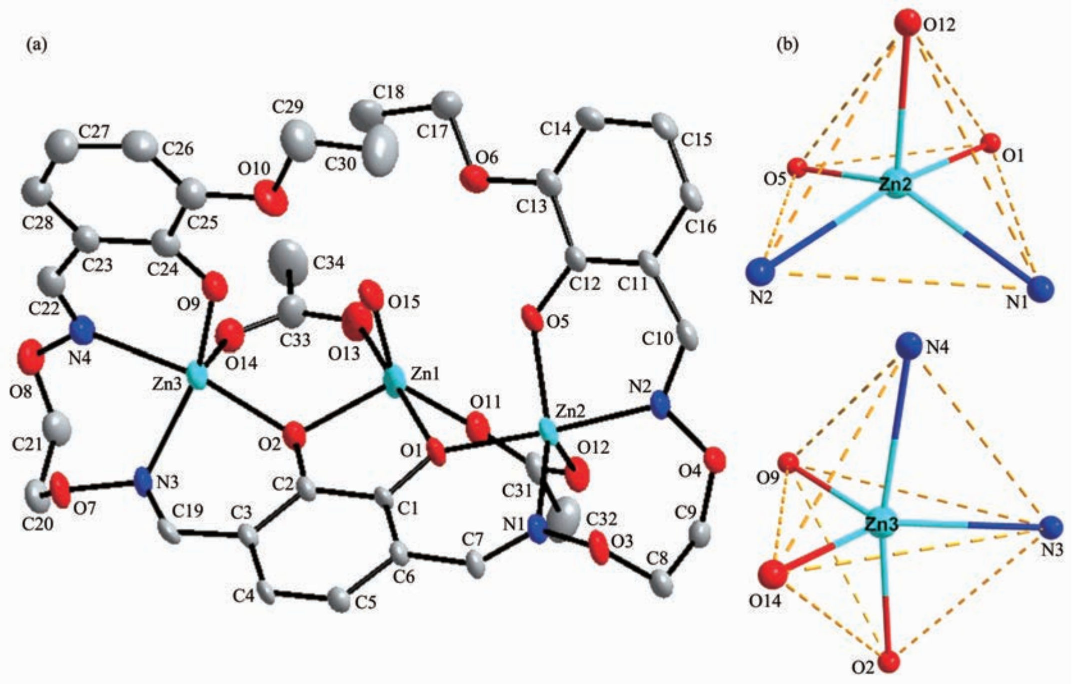
Selected bond lengths and angles for complex **1** are presented in Table 2. Complex **1** crystallizes in the monoclinic system, space group $P2_1/c$. The assembly of three Zn(Ⅱ) atoms, one L^{4-} ligand units, two acetate ions and one coordinated H_2O molecule results in a

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

			1		
Zn1-O11	0.206 1(5)	Zn1-O1	0.200 7(4)	Zn1-O2	0.203 0(4)
Zn1-O15	0.205 4(6)	Zn2-O5	0.198 4(4)	Zn2-O12	0.199 9(5)
Zn2-O1	0.200 3(4)	Zn2-N2	0.210 2(5)	Zn2-N1	0.214 3(5)
Zn3-O9	0.197 6(5)	Zn3-O14	0.199 2(5)	Zn3-O2	0.201 5(4)
Zn3-N3	0.213 4(5)	Zn3-N4	0.214 3(5)		
O13-Zn1-O1	173.4(2)	O13-Zn1-O2	99.8(2)	O1-Zn1-O2	80.7(2)
O13-Zn1-O15	94.7(2)	O1-Zn1-O15	92.0(2)	O2-Zn1-O15	89.7(2)
O13-Zn1-O11	88.3(2)	O1-Zn1-O11	85.9(2)	O2-Zn1-O11	124.0(2)
O15-Zn1-O11	145.2(2)	O5-Zn2-O12	105.6(2)	O5-Zn2-O1	90.4(2)
O12-Zn2-O1	91.2(2)	O5-Zn2-N2	87.8(2)	O12-Zn2-N2	98.7(2)
O9-Zn3-O14	104.3(2)	O9-Zn3-O2	99.9(2)	O12-Zn2-N1	106.1(2)
O9-Zn3-N3	126.4(2)	O14-Zn3-N3	128.9(2)	O2-Zn3-N4	169.2(2)
O9-Zn3-N4	86.5(2)	O14-Zn3-N4	91.7(2)	O2-Zn3-N3	83.1(2)
N3-Zn3-N4	86.1(2)	N2-Zn2-N1	93.1(2)	O14-Zn3-O2	95.1(2)
O1-Zn2-N1	83.3(2)	O5-Zn2-N1	147.7(2)	O1-Zn2-N2	170.1(2)
			2		
Zn1-O11	0.196 1(7)	Zn1-O15	0.202 6(6)	Zn1-O1	0.206 1(6)
Zn1-O5	0.210 5(7)	Zn1-O2	0.214 8(6)	Zn5-N5	0.212 2(9)
Zn2-O1	0.196 8(7)	Zn2-O13	0.199 8(7)	Zn2-O5	0.205 6(9)
Zn2-N2	0.208 5(7)	Zn2-N1	0.219 4(10)	Zn5-O20	0.194 5(7)
Zn5-N6	0.215 8(9)	Zn5-O16	0.206 3(6)	Zn1-Zn2	0.315 2(2)
Zn5-O27	0.199 5(7)	Zn3-O9	0.196 4(7)	Zn3-O2	0.202 2(6)
Zn6-N7	0.209 1(9)	Zn6-N8	0.213 4(9)	Zn3-N4	0.212 4(9)
Zn4-O28	0.200 5(9)	Zn4-O26	0.203 5(8)	Zn4-O16	0.205 0(6)
Zn4-O17	0.206 7(6)	Zn4-O30	0.207 5(8)	Zn4-O31	0.241 3(8)
Zn3-O12	0.203 9(7)	Zn6-O29	0.196 2(8)	Zn6-O17	0.205 9(7)
Zn6-O24	0.195 2(8)	Zn3-N3	0.211 7(10)		
O1-Zn1-O5	76.4(3)	O17-Zn6-N7	84.5(3)	O24-Zn6-N8	87.7(4)
O29-Zn6-N7	120.6(3)	O5-Zn1-O2	153.7(3)	O1-Zn2-O13	126.7(3)
O11-Zn1-O15	126.5(3)	O1-Zn1-Zn2	37.5(2)	O5-Zn1-Zn2	40.96(19)
O2-Zn1-Zn2	113.48(18)	O1-Zn2-O5	78.9(3)	O13-Zn2-O5	101.1(3)
O1-Zn2-N2	121.8(3)	O13-Zn2-N2	111.3(3)	O5-Zn2-N2	86.2(4)
O1-Zn2-N1	84.2(4)	O13-Zn2-N1	96.2(3)	O5-Zn2-N1	160.8(3)
N2-Zn2-N1	95.2(4)	O9-Zn3-O2	101.4(3)	O1-Zn2-O13	126.7(3)
O1-Zn2-Zn1	39.57(2)	O13-Zn2-Zn1	111.6(2)	N2-Zn2-Zn1	116.6(3)
O5-Zn2-Zn1	41.4(19)	N1-Zn2-Zn1	123.5(3)	O9-Zn3-O12	110.7(3)
O2-Zn3-O12	87.5(3)	O9-Zn3-N3	121.7(3)	O2-Zn3-N3	83.8(3)
O16-Zn5-N6	170.2(3)	N5-Zn5-N6	88.2(3)	O24-Zn6-O29	119.9(3)

Continued Table 2

O24-Zn6-O17	97.8(3)	O29-Zn6-O17	90.6(3)	O24-Zn6-N7	119.4(3)
O1-Zn1-O2	77.3(3)	O11-Zn1-O2	90.7(3)	O15-Zn1-O2	90.8(2)
O12-Zn3-N3	127.6(3)	O9-Zn3-N4	87.9(4)	O2-Zn3-N4	170.6(2)
O12-Zn3-N4	91.1(3)	N3-Zn3-N4	89.6(4)	O28-Zn4-O26	91.3(3)
O9-Zn3-O2	101.4(3)	O28-Zn4-O26	91.3(3)	O28-Zn4-O16	154.8(3)
O26-Zn4-O16	96.1(3)	O28-Zn4-O17	94.4(3)	O26-Zn4-O17	174.0(3)
O16-Zn4-O17	79.5(3)	O28-Zn4-O30	102.4(3)	O26-Zn4-O30	87.5(3)
O16-Zn4-O30	101.9(3)	O17-Zn6-N8	173.5(4)	O28-Zn4-O31	71.6(3)
O26-Zn4-O31	88.9(3)	O16-Zn4-O31	84.5(3)	O17-Zn4-O31	94.8(3)
O30-Zn4-O31	172.9(3)	O20-Zn5-O27	117.1(3)	O20-Zn5-O16	97.1(3)
O27-Zn5-O16	94.9(3)	O20-Zn5-N5	116.4(3)	N7-Zn6-N8	89.9(4)
O16-Zn5-N5	82.1(3)	O20-Zn5-N6	88.4(4)	O27-Zn5-N6	89.7(3)
O29-Zn6-N8	89.4(3)	O15-Zn1-O1	106.9(3)	O11-Zn1-O5	104.0(3)
O15-Zn1-O5	97.4(2)	O11-Zn1-Zn2	131.3(2)	O15-Zn1-Zn2	96.1(17)
O11-Zn1-O1	125.5(3)	O17-Zn4-O30	89.4(3)	O27-Zn5-N5	126.3(3)



All hydrogen atoms are omitted for clarity

Fig.2 (a) Molecule structure and atom numberings of complex **1** with 30% probability displacement ellipsoids; (b) Coordination polyhedra for Zn(Ⅱ) atoms of complex **1**

trinuclear Zn(Ⅱ) complex (Fig.2). In molecule unit of complex **1**, three Zn (Ⅱ) atoms are all penta-coordinated. Firstly, the terminal Zn(Ⅱ) atom (Zn2) is penta-coordinated by two oxime nitrogen (N1 and N2) and phenolic oxygen (O1 and O5) atoms of the bis(salamo)-type L^{4-} unit and one oxygen (O12) atom of one chelating acetate ion. Secondly, the centre Zn(Ⅱ) atom (Zn1) is penta-coordinated by two bridging phenolic oxygen (O1 and O2) atoms of the bis(salamo)-type L^{4-} unit, two oxygen (O11 and O13) atoms of the chelating acetate ions and one oxygen (O15) atom from one coordinated water molecule in the apical position. At last, The terminal Zn(Ⅱ) atom (Zn3) is penta-coordinated by two oxime nitrogen (N3 and N4) and phenolic oxygen (O2 and O9) atoms of the bis(salamo)-type L^{4-} unit and one oxygen (O14) atom of the chelating acetate ion. The two chelating acetate ions coordinate to the three Zn(Ⅱ)atoms via a familiar Zn1-O-C-O-Zn2 and Zn1-O-C-O-Zn3 coordinated modes.

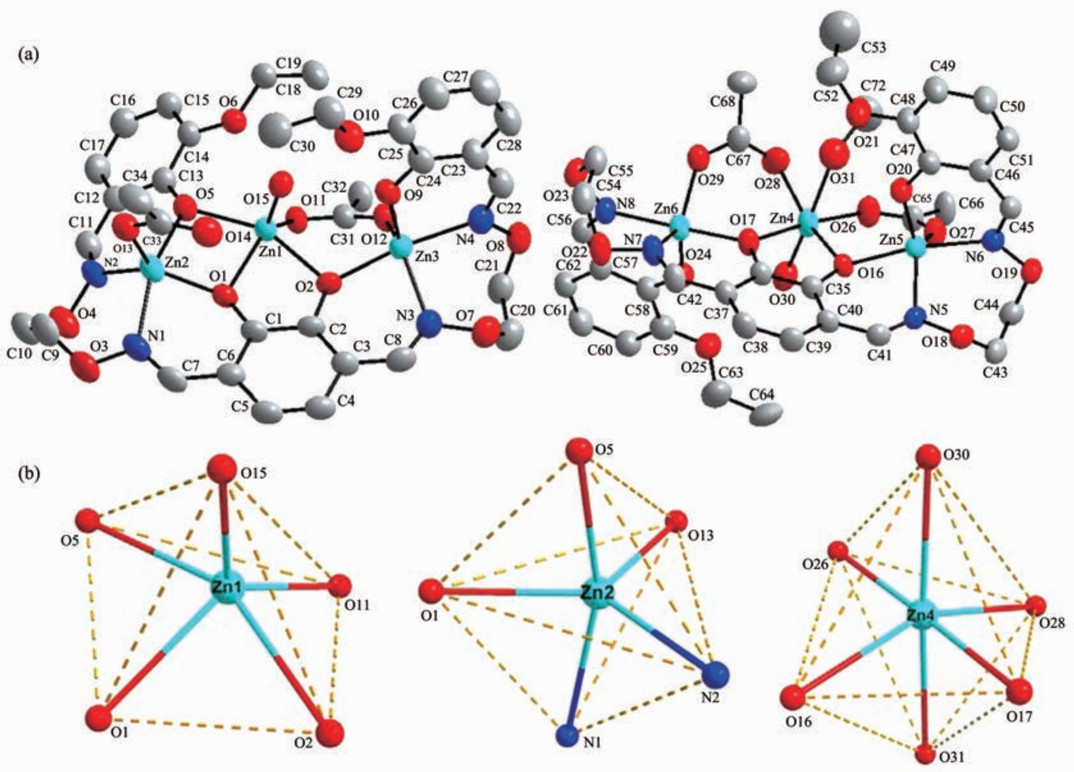
The Zn1 atom adopts a slightly distorted square pyramidal geometry (τ=0.470)[18], which deviate from the mean plane (O1-O2-O11-O13) by 0.029 5(3) nm. The distance of Zn1 atom to the five donor atoms are all different (0.198 8(5)~0.206 1(5) nm). The distances from the four atoms to the mean plane are not equal (0.030 0~0.034 2 nm), and the distances from phenolic oxygen atom (O2) of the bis (salamo)-type L^{4-} unit to the mean plane is 0.221 8(4) nm. The Zn2 atom also adopts a slightly distorted square pyramidal geometry (τ=0.373), Four coordination atoms (O1, O5, N1 and N2) give a mean plane, and the Zn2 atom deviate from the mean plane by 0.037 4(4) nm. The distances from the five coordination atoms to the mean plane are not equal: O1 and N2 above average by 0.021 3(3) and 0.019 1(3) nm, O5 and N1 below average by 0.020 8(4) and 0.019 6(3) nm, respectively. In addition, one oxygen atom (O6) of the acetate ion deviates from the mean plane by 0.236 7(3) nm. The dihedral angle of O1-Zn2-N1 and O5-Zn2-N2 is 32.97(3)°. Interestingly, the geometry of the Zn3 atom is different from the Zn1 and Zn2 atoms. The value of τ=0.671 clearly indicates that the environment of the Zn3 atom is a trigonal bipyramidal geometry in which the axial positions are occupied by O2 and N4 atoms. Which deviate from the mean plane (O9-N3-O14) by 0.007 4(3) nm. The distance of the Zn3 atom to the five donor atoms are all different (0.197 6(5), 0.199 2(5), 0.201 5(4), 0.213 4(5) and 0.214 4(5) nm, respectively). The dihedral angle between the plane of N3-Zn1-O2 and that of N4-Zn1-O9 is 53.10(3)°, which indicates the L^{4-} unit has serious distortion. Thus, two kinds of type coordination geometries (trigonal bipyramidal and square pyramidal) are showed in complex **1**.

2.4.2 Crystal structure of complex 2

Selected bond lengths and angles for complex **2** are presented in (Table 2). Complex **2** crystallizes in the monoclinic system, space group $P2_1/c$, Complex **2** consists of six Zn(Ⅱ) atoms, two completely deprotonated L^{4-} ligand units, four acetate ions, three coordinated water molecules, three crystallizing methanol and one crystallizing water molecules. A perspective view of which is shown in Fig.3 together with the atomic labeling of the coordinated polyhedra.

As shown in Fig.3, the crystal structure of complex **2** consists of two independent molecules A and B, and the two molecules are all trinuclear structures. In molecule A, three Zn(Ⅱ) atoms are all penta-coordinated. The Zn(Ⅱ) atom (Zn1) is penta-coordinated by three phenolic oxygen (O1, O2 and O5) atoms of the bis(salamo)-type L^{4-} unit, one oxygen (O11) atom of the chelating acetate ion and one oxygen atom (O15) from one coordinated water molecule. The Zn(Ⅱ) atom (Zn2) is penta-coordinated by two oxime nitrogen (N1 and N2) and phenolic oxygen (O1 and O5) atoms of the bis (salamo)-type L^{4-} unit and one oxygen (O13) atom of one monochelate acetate ion. In addition, the Zn(Ⅱ) atom (Zn3) is penta-coordinated by two oxime nitrogen (N3 and N4) and phenolic oxygen (O2 and O9) atoms of the bis (salamo)-type L^{4-} unit and one oxygen (O12) atom of the chelating acetate ion. It will be seen from the discussion mentioned above that the coordination environments of the three Zn(Ⅱ) atoms in the molecular A is very similar.

The coordination geometries of the Zn(Ⅱ) atoms (Zn2 and Zn3) are best described as distorted trigonal bipyramidal geometries (Zn2, τ=0.568; Zn3, τ=0.722)[18] in which the axial positions are occupied by O5, N1 and O2, N4 atoms, respectively, and the Zn2 and Zn3 atoms deviate from the mean plane (O13-N2-O1) and (O12-N3-O9) by 0.006 0(3) and 0.001 2(3) nm, respectively. The distance of the Zn3 and Zn2 atoms to the five donor atoms are all different (Zn2: 0.196 8~0.219 4 nm; Zn3: 0.196 4~0.212 4 nm). The dihedral angle between the plane of N2-Zn2-O5 and that of N1-Zn2-O1 is 58.74(3)°, and the dihedral angle between the plane of N3-Zn3-O2 and that of N4-Zn3-O9 is 58.44(3)°, which indicates the structure of the trinuclear core distorts from the ideal symmetry. Interestingly, the geometry of the centre Zn1 atom is different from the other two terminal Zn(Ⅱ) atoms (Zn2 and Zn3). The Zn1 atom have a square pyramidal structure in which the axial sites are occupied by the O1 atom (τ=



All hydrogen atoms and solvent molecules are omitted for clarity

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

0.453), and which deviate from the mean plane (O1-O2-O11-O5) by 0.057 5(3) nm. The distance of the Zn1 atom to the four atoms from the mean plane are all different (0.196 1~0.214 8 nm). The distances from the four atoms to the mean plane are not equal (0.026 1~0.041 4 nm), the dihedral angle between the plane of O1-Zn1-O5 and that of O2-Zn1-O11 is 53.83(3)°. In addition, there exists a four-membered ring (Zn1-O1-Zn2-O5) which adopts a chair-chair conformation. Thus, two kinds of coordination geometries (trigonal bipyramid and square pyramid) are showed in the molecule A.

In the molecule B, Zn5 and Zn6 atoms are penta-coordinated, however, Zn4 atom is hexa-coordinated by two phenolic oxygen (O16 and O17) atoms of the bis(salamo)-type L^{4-} unit, two oxygen (O26 and O28) atoms of the chelating acetate ions and two oxygen (O30 and O31) atoms from the coordinated water and methanol molecules, respectively. The coordination sphere of the terminal Zn(Ⅱ) atom (Zn5) is completed by two oxime nitrogen (N5 and N6) and phenolic oxygen (O16 and O20) atoms of the bis(salamo)-type L^{4-} unit and one oxygen (O27) atom of one chelating acetate ion. The coordination environment of the Zn6 atom is completely consistent with that of the Zn5 atom, and penta-coordinated by two oxime nitrogen (N7 and N8) and phenolic oxygen (O17 and O24) atoms of the bis(salamo)-type L^{4-} unit and one oxygen atom (O29) of one chelating acetate ion. The two chelating acetate ions coordinate to the three Zn(Ⅱ) atoms via a familiar Zn5-O-C-O-Zn4 and Zn4-O-C-O-Zn6 coordinated modes.

The Zn5 and Zn6 atoms have similar trigonal bipyramidal geometries (Zn5, τ=0.732; Zn6, τ=0.882)[30] with approximate molecular symmetry C_3, in which the axial positions are occupied by O16, N6 and O17, N8 atoms, respectively. The Zn5 and Zn6 atoms deviate from the mean plane (O27-N5-O20) and (O24-N7-O29) by 0.004 8(3) and 0.003 0(3) nm, respectively. Although the Zn1 and Zn2 atoms are both penta-coordinated, but the distance of the Zn3 and Zn2 atoms to the five donor atoms are all different. The dihedral angle between the plane of N6-Zn5-O20 and that of N5-Zn5-O16 is 63.46(3)°, and another dihedral angle between the plane of N8-Zn6-O24 and that of N7-Zn6-O17 is 60.64(3)°. These results indicate that the L^{4-} unit has serious distortion. Due to the Zn4 atom is hexa-coordinated, so it is clearly indicates that the coordination environment of the Zn4 atom is an octahedral geometry. The distance of the Zn4 atom to the six donor atoms are all different (Zn4-O28 0.200 5 nm, Zn4-O26 0.203 5 nm, Zn4-O16 0.205 0 nm, Zn4-O17 0.206 7 nm, Zn4-O30 0.207 5 nm and Zn4-O31 0.243 1 nm). In addition, The dihedral angle between the plane of O17-Zn6-O28 and that of O26-Zn4-O16 is 24.20(3)°. So, two kinds of coordination geometries (trigonal bipyramid and octahedron) are showed in the molecule B.

From the above, we can know complex **2** consists of two independent molecules A and B, and the two molecules are all trinuclear structures. There are three kinds of coordination geometries (trigonal bipyramid, square pyramid and octahedron), and every trinuclear structure has serious distortion.

2.5 Supramolecular interaction

2.5.1 Supramolecular interaction of complex 1

The feature of complex **1** is its self-assembling array linked by intramolecular hydrogen bonds and intermolecular C–H···π interactions. The hydrogen bond data and C–H···π interaction data are given in (Table 3).

In the crystal structure, there are four intramolecular O15–H15C···O6, O15–H15C···O9, C9–H9B···O12 and C21–H21A···O14 hydrogen bonds (Table 3) involving the coordinated water, two acetate ions and alkoxy O atoms in each molecule, which is shown in Fig.4. There is also one intermolecular C–H···π (C9–H9A···Cg1) interaction (Table 3). The molecule is interlinked through intermolecular C–H···π interactions into an infinite 1D chain (Fig.5).

Table 3 Intra- and intermolecular hydrogen geometries for complexes 1 and 2

Complex	D–H···A	*d*(D-H) / nm	*d*(H···A) /nm	*d*(D···A) /nm	∠DHA / (°)
1	O15–H15B···O9	0.085	0.188	0.271 0(6)	164
	O15–H15C···O6	0.085	0.189	0.272 8(6)	168
	C9–H9B···O12	0.097	0.239	0.331 3(8)	160
	C21–H21A···O14	0.097	0.255	0.338 1(9)	144
	C9–H9A···Cg1	0.097	0.267	0.353(9)	148
2	O15–H15C···O9	0.085	0.186	0.270 4(9)	169
	O15–H15D···O14	0.085	0.196	0.279 6(10)	170
	O30–H30F···O24	0.085	0.193	0.277 1(9)	172
	O30–H30F···O25	0.085	0.189	0.272 5(18)	167
	O31–H31···O20	0.082	0.183	0.262 0(11)	162
	O33–H33···O35	0.082	0.24	0.319 0(3)	161
	O35–H35C···O34	0.080	0.191	0.273 0(2)	157
	O35–H35D···O25	0.085	0.220	0.304 0(2)	166
	C9–H9A···O13	0.097	0.244	0.335 1(15)	157
	C21–H21B···O12	0.097	0.258	0.339 9(14)	142
	C44–H44B···O27	0.097	0.244	0.327 1(14)	144
	C55–H55B···O29	0.097	0.237	0.319 5(14)	143
	C56–H56···O12	0.03	0.257	0.346 4(14)	160
	C71–H71A···O32	0.096	0.168	0.246(3)	135
	C71–H71B···O26	0.096	0.245	0.323(3)	139
	C50–H50···Cg1	0.093	0.297	0.361 2(7)	130

For the complexes **1** and **2**, Cg1 is the centroids of atoms C11~C16 and C57~C62, respectively.

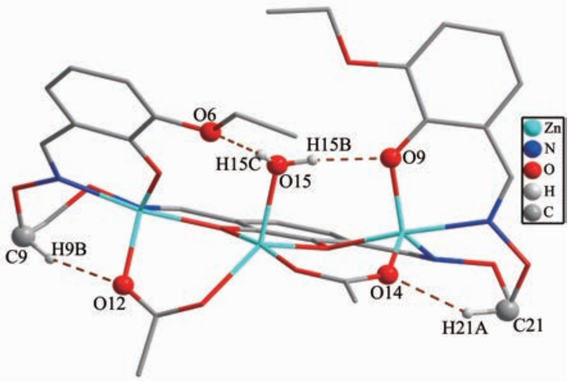


Fig.4　View of the intramolecular hydrogen-bonding interactions of complex **1**

2.5.2　Supramolecular interaction of complex **2**

In the crystal structure of complex **2**, there are twelve intramolecular (O15–H15C⋯O9, O15–H15D⋯O14, O30–H30F⋯O24, O30–H30F⋯O24, O30–H30F⋯O25, O31–H31⋯O20, O33–H33⋯O35, O35–H35C⋯O34, C35–H35D⋯O25, C9–H9A⋯O13, C21–H21B⋯O12, C44–H44B⋯O27, C55–H55B⋯O29, C56–H56⋯O12, C71–H71A⋯O32 and C71–H71B⋯O26) hydrogen bond interactions (Table 3) involving three coordinated water, two acetate ions, crystallizing water molecules and alkoxy O atoms in each molecule, which is shown in Fig.6. Moreover, intramolecular C–H⋯π (C50–H50⋯Cg1) (Table 3) and hydrogen bonding interactions into an infinite wave-like 2D-layer supramolecular structure parallel to the crystallographic plane (Fig.7).

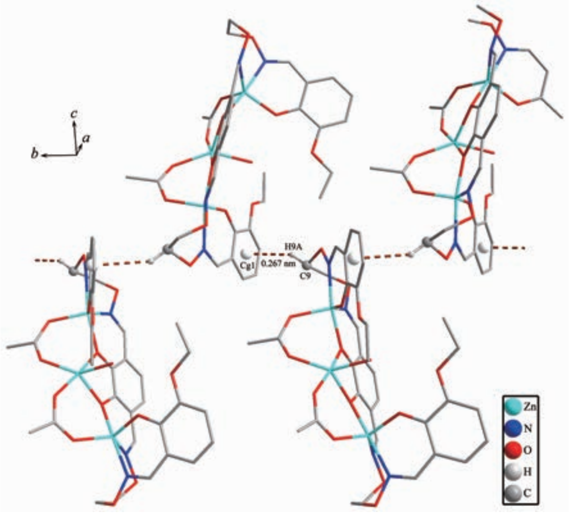


Fig.5　View of intermolecular C–H⋯π interactions of complex **1**

2.6　Luminescence properties

Few reports have appeared so far on the prospective use of fluorescence characteristics on transition metal complexation of bis (salamo)-type tetraoxime ligands. In this work, the fluorescence studies have been employed as independent evidence of complexation between the ligand H_4L and Zn(Ⅱ) atoms.

The fluorescent properties of H_4L and its complexes **1** and **2** were investigated at room temperature (Fig.8). The ligand H_4L exhibits an intense emission peak at 456 nm upon excitation at 340 nm, which should be assigned to the intraligand

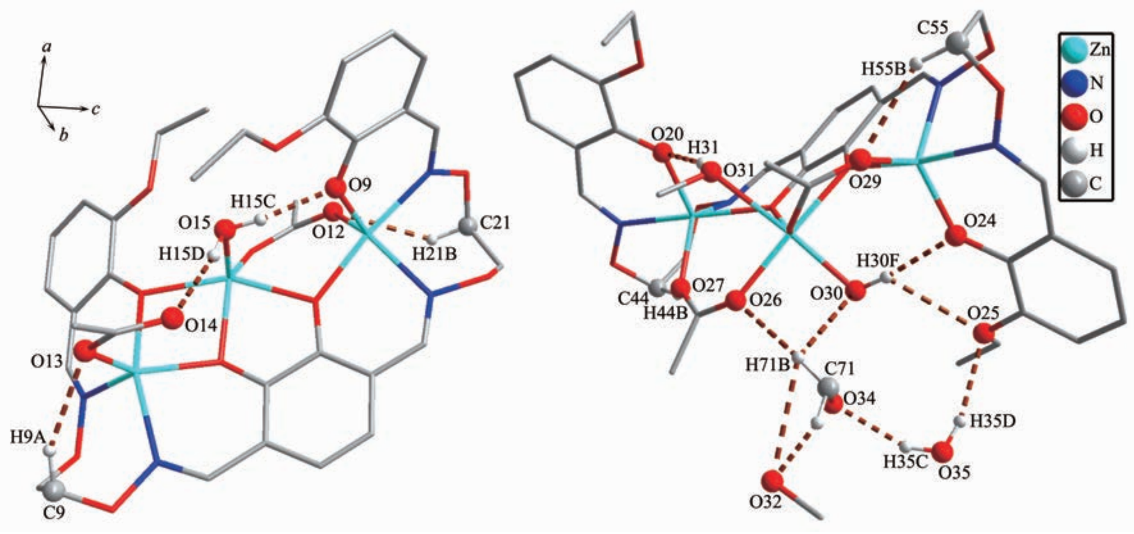


Fig.6　View of the intramolecular hydrogen-bonding interactions of complex **2**

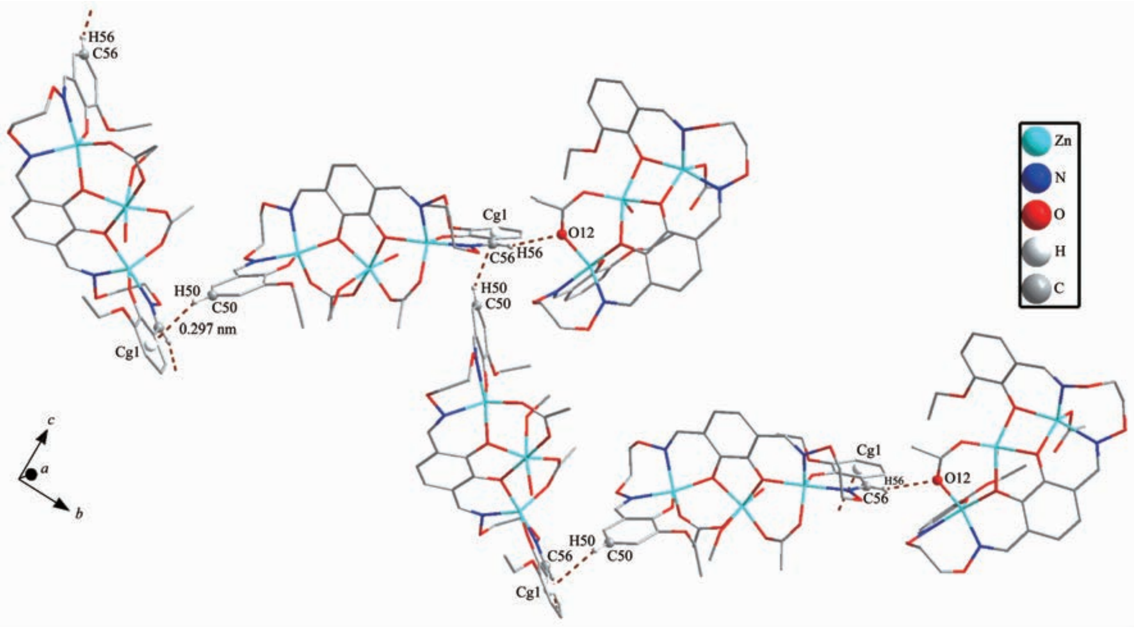


Fig.7 View of intramolecular and intermolecular C-H$\cdots\pi$ interactions of complex **2**

π-π* transition[19]. The emission spectra of complexes **1** and **2** show a main peak at 531 nm (λ_{ex}=340 nm) and 536 nm (λ_{ex}=338 nm), respectively. The two Zn(Ⅱ) complexes **1** and **2** exhibit similar fluorescence emissions because of their similar molecular structures. Meanwhile, it can be seen that complexes **1** and **2** exhibit a red-shift with respect to the bis(salamo)-type tetraoxime ligand H_4L. We tentatively assign it to a ligand-to-metal charge transfer (LMCT)[31]. In addition, compared with the emission spectrum of H_4L, the enhanced fluorescence intensity of complexes **1** and **2** is observed, we attributed it to the following points: (1) the more rigidity of the ligand coordination to Zn(Ⅱ) atom that effectively reduces the loss of energy and increase the emission efficiency; (2) full d^{10} electronic configuration of Zn(Ⅱ) atom; (3) An increased rigidity in structure of the complexes **1** and **2** and a restriction in the photoinduced electron transfer (PET)[48-49]. In addition, The differences of the peak positions may be considered to be a result of the dissimilar coordination of the metal centers because the emission behavior is closely associated to the metal ions and ligands around them[31]. The strong green fluorescence indicates complexes **1** and **2** may be a good candidate for fluorescent materials. Thus, the emission observed in complexes **1** and **2** is tentatively assigned to the LMCT fluorescence.

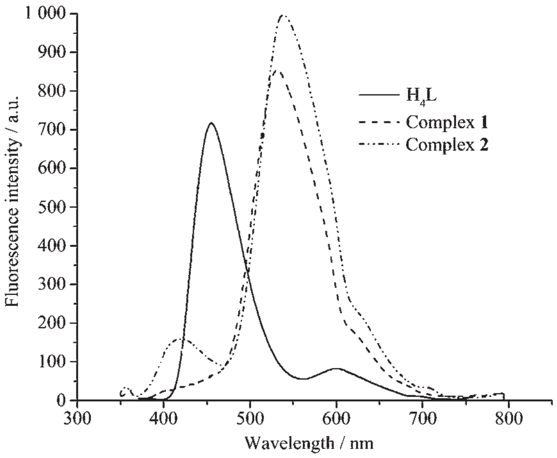


Fig.8 Emission spectra of H_4L and its complexes **1** and **2** in dilute DMF solution (50 μmol·L^{-1}) at room temperature

3 Conclusions

In this paper, two Zn(Ⅱ) complexes **1** and **2** with a bis (salamo)-type tetraoxime ligand H_4L have been synthesized and characterized by elemental analyses, IR, UV-Vis spectra, molar conductance measurements, fluorescence spectra and single crystal X-ray analyses. In complex **1**, three Zn(Ⅱ) atoms are all penta-coordinated (two distorted square pyramid and one distorted trigonal bipyramid). In complex **2**, the crystal structure of complex **2** consists of two independent molecules A and B, and the two molecules A and B are all trinuclear structure. Furthermore, the spectral properties of complexes **1** and **2** have also been studied. And complexes **1** and **2** show greater emission intensity compared to H_4L. Complexes **1** exhibits green emission with λ_{max}=531 nm when excited with 340 nm, meanwhile, complex **2** also exhibits green emission with λ_{max}=536 nm when excited with 338 nm. The strong green fluorescence indicates complexes **1** and **2** may be good candidates for fluorescent materials.

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