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PII:	S1386-1425(17)30315-3
DOI:	doi: 10.1016/j.saa.2017.04.061
Reference:	SAA 15114
To appear in:	Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy
Received date:	10 January 2017
Revised date:	30 March 2017
Accepted date:	18 April 2017

Please cite this article as: Wen-Kui Dong, Shan-Shan Zheng, Jin-Tong Zhang, Yang Zhang, Yin-Xia Sun , Luminescent properties of heterotrinuclear 3d–4f complexes constructed from a naphthalenediol-based acyclic bis(salamo)-type ligand. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Saa(2017), doi: 10.1016/j.saa.2017.04.061

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# Luminescent properties of heterotrinuclear 3d-4f complexes constructed from a naphthalenediol-based acyclic bis(salamo)-type ligand

Wen-Kui Dong,<sup>\*</sup> Shan-Shan Zheng, Jin-Tong Zhang, Yang Zhang, Yin-Xia Sun

#### Abstract

Heterotrinuclear 3d-4f complexes with a naphthalenediol-based acyclic bis(salamo)-type ligand have been synthesized and structurally characterized. titrations clearly show the heterotrinuclear Spectral that complexes  $[Zn_2(L)Ce(OAc)_3]$ (2) $[Zn_2(L)La(OAc)_3]$ (1),and  $[Zn_2(L)Dy(OAc)_3(CH_3OH)]$ ·CH<sub>2</sub>Cl<sub>2</sub> (3) are acquired by the substitution reaction of the obtained homotrinuclear Zn(II) complex with 1 equiv of  $Ln(NO_3)_3$  ( $Ln^{3+}$  =  $La^{3+}$ ,  $Ce^{3+}$  and  $Dy^{3+}$ ). Two Zn(II) ions are penta- and hexa-coordinated with geometries of distorted tetragonal pyramid and octahedron. La(III) ion is deca-coordinated, adopting a distorted bicapped square antiprism geometry. Ce(III) ion is nona-coordinated with geometry of distorted capped square antiprism as well as Dy(III) ion. The different coordination modes of acetate ions in complexes 1, 2 and 3 lead to different coordination numbers of the lanthanide(III) ions. Furthermore, the structures and fluorescence properties have been discussed.

*Keywords:* Heterotrinuclear complex; Bis(salamo)-type ligand; Synthesis; Luminescent property

#### 1. Introduction

Salen-type [1-7] and salamo-type [8-19] complexes are well known for their potential applications in many areas, such as biological fields [20-25], nonlinear optical materials [26], catalysis [27-28], magnetism [29-32]. As the superior functional

<sup>&</sup>lt;sup>\*</sup> School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P. R. China. E-mail: dongwk@126.com; Tel: +86 931 4938703

<sup>†</sup> CCDC: numbers 1520694-1520696

properties in optoelectronic devices, medicine, separation, ions recognition, lanthanide complexes have recently attracted much attention [33-39]. Meanwhile, trivalent lanthanide ions possess large radius, high coordination numbers and flexible coordination geometries [40]. Especially, lanthanide ions have variable coordination environments and a special 4f electron configuration with large spin moments and strong spin-orbit coupling, so that the lanthanide complexes display amazing optical and magnetic properties [41-42]. Based on the sharp *f-f* transitions and high quantum yields, it is often thought that lanthanide complexes are the most important components in pursuit of new luminescence materials [43-46].

Herein, as an extension of our previous studies [47-49], a novel bis(salamo)-type tetraoxime ligand H<sub>4</sub>L is synthesized by introducing a naphthalenediol ring on the ligand, which has a greater conjugation system and coordination ability, can be expected to form lanthanide complexes with better optical properties. It is well known that acetate ions often play an important role in coordination chemistry which can adopt various binding modes such as terminal monodentate, chelating to one metal centre, bridging bidentate in a syn-syn, syn-anti and anti-anti, and bridging tridentate to two metal centres [50]. In this paper, heterotrinuclear complexes  $[Zn_2(L)La(OAc)_3]$  (1),  $[Zn_2(L)Ce(OAc)_3]$  (2) and  $[Zn_2(L)Dy(OAc)_3(CH_3OH)] \cdot CH_2Cl_2$  (3), have been synthesized and structurally characterized. In complex 1, two acetate ions bridge  $Zn^{2+}$ and  $La^{3+}$  ions in a common  $\mu_2$ -fashion, another acetate ion chelates  $La^{3+}$  ion as a bidentate ligand. While in complex 2, all acetate ions bridge  $Zn^{2+}$  and  $Ce^{3+}$  ions via  $\mu_2$ -fashion. It is unexpected that one acetate ion of complex 3 only coordinates with  $Zn^{2+}$  ion as a monodentate ligand. Thus, these monodentate and chelating bidentate configurations of the coordinated acetate ions rarely exist in the documented salamo-type complexes to the best of our knowledge [17-19, 51].

#### 2. Experimental

#### 2.1. Materials and instrumentation

2-Hydroxy-3-methoxybenzaldehyde (99%) was purchased from Alfa Aesar. The other reagents and solvents were purchased from Shanghai Darui Chemical

Fine Chemicals Company. All chemicals were of analytical grade and used without further purification. C, H, and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. Melting points were obtained by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected. <sup>1</sup>H NMR spectra were recorded using a Mercury-400BB spectrometer at 400 MHz. IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (4000-400 cm<sup>-1</sup>) pellets. UV–Vis absorption spectra were recorded on a Hitachi U-3900H spectrometer. Luminescence spectra in solution were recorded on a Hitachi F-7000 spectrometer.

#### 2.2. Synthesis of the ligand $H_4L$

The reaction steps involved in the synthesis of the bis(salamo)-type tetraoxime ligand (H<sub>4</sub>L) are shown in Scheme 1 [52-57].



Scheme 1 Synthesis route to bis(salamo)-type ligand H<sub>4</sub>L

The mixture ethanol solution of 2,3-dihydroxynaph-thalene-1,4-dicarbaldehyde (175.2 mg, 0.80 mmol) and 2-[*O*-(1-ethyloxyamide)]oxime-6-methoxyphenol (449.0 mg, 1.98 mmol) was heated at 55 °C for 2h. After cooling to room temperature, the precipitate was filtered off, obtained light yellow crystalline solid. Yield: 423.4 mg, 83.7%. m.p.:

172-174 °C. *Anal.* calc. for C<sub>32</sub>H<sub>32</sub>N<sub>4</sub>O<sub>10</sub> (%): C, 60.75; H, 5.10; N, 8,86. Found (%): C, 60.64; H, 5.23; N, 8.94. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): δ 11.03 (s, 2H), 9.82 (s, 2H), 9.14 (s, 2H), 8.29 (s, 2H), 7.97 (q, J = 3.2 Hz, 2H), 7.41 (q, J = 6.0, 2.9 Hz, 2H), 7.06-6.68 (m, 6H), 4.58 (t, 8H), 3.89 (s, 6H). IR (KBr; cm<sup>-1</sup>): 1607 [ $\nu$ (C=N)], 1250 [ $\nu$ (Ar–O)], 3172 [ $\nu$ (O–H)], UV–Vis [in chloroform/methanol (1:1)],  $\lambda_{max}$  (nm) (log ε) [3.0 × 10<sup>-5</sup> M]: 269 (4.42), 342 (4.03), 360 (4.12), 378 (4.05).

#### 2.3. Synthesis of homotrinuclear Zn(II) complex

A solution of  $Zn(OAc)_2 \cdot 2H_2O$  (6.58 mg, 0.030 mmol) in methanol (3 mL) was added to a solution of the ligand H<sub>4</sub>L (6.32 mg, 0.010 mmol) in chloroform (3 mL) at room temperature. The color of the solution immediately turned yellow. The mixture was filtered and the filtrate was allowed to stand at room temperature for about four weeks. The solvent was partially evaporated and several yellow prismatic single crystals were obtained. Yield: 5.63 mg, 41.2 %; *Anal.* Calc. for C<sub>41</sub>H<sub>45</sub>C<sub>19</sub>N<sub>4</sub>O<sub>16</sub>Zn<sub>3</sub> (%): C 36.07; H 3.32; N 4.10. Found (%): C 35.96; H 3.40; N 3.97. IR (KBr; cm<sup>-1</sup>): 1604 [ $\nu$ (C=N)], 1245 [ $\nu$ (Ar–O)], 3392 [ $\nu$ (O–H)], UV–Vis [in chloroform/methanol (1:1)],  $\lambda_{max}$  (nm) (log  $\varepsilon$ ) [3.3 × 10<sup>-5</sup> M]: 280 (4.35), 370 (4.04), 396 (3.99), 416 (3.92).

#### 2.4. Preparation of heterotrinuclear complexes 1, 2 and 3

A solution of  $Zn(OAc)_2 \cdot 2H_2O$  (6.58 mg, 0.030 mmol) in methanol (1 mL) and  $La(OAc)_3 \cdot H_2O$  (3.34 mg, 0.010 mmol) in water/methanol (1:3, 2 mL) were added to a solution of H<sub>4</sub>L (6.32 mg, 0.010 mmol) in chloroform (3 mL), and the resulting solution was concentrated to dryness. The solid was redissolved in chloroform/methanol/ethanol (3:2:1, 6 mL). The mixture was filtered and the filtrate was allowed to stand at room temperature for several weeks. Complexes **2** and **3** were prepared by a similar procedure as complex **1**.

Complex **1**, yellow crystals. Yield: 7.0 mg, 65.2 %. Elemental analysis: *Anal.* calc. for  $C_{38}H_{37}LaN_4O_{16}Zn_2$  (%): C 42.44; H 3.47; N 5.21. Found (%): C 42.39; H 3.51; N 5.15. IR (KBr; cm<sup>-1</sup>): 1610 [ $\nu$ (C=N)], 1242 [ $\nu$ (Ar–O)], UV-Vis [in chloroform/methanol (1:1)],  $\lambda_{max}$  (nm) (log  $\varepsilon$ ) [3.3 × 10<sup>-5</sup> M]: 280 (4.61), 370 (4.29), 396 (4.25), 416 (4.20).

Complex 2, yellow crystals. Yield: 7.3 mg, 67.4 %. Elemental analysis: Anal. calc.

for C<sub>38</sub>H<sub>37</sub>CeN<sub>4</sub>O<sub>16</sub>Zn<sub>2</sub> (%): C 42.39; H 3.46; N 5.20. Found (%): C 42.35; H 3.52; N 5.17. IR (KBr; cm<sup>-1</sup>): 1610 [ $\nu$ (C=N)], 1237 [ $\nu$ (Ar–O)], UV-Vis [in chloroform/methanol (1:1)],  $\lambda_{max}$  (nm) (log  $\varepsilon$ ) [3.3 × 10<sup>-5</sup> M]: 280 (4.60), 370 (4.29), 396 (4.25), 416 (4.20).

Complex **3**, yellow crystals. Yield: 8.2 mg, 67.3 %. Elemntal analysis: *Anal.* calc. for C<sub>40</sub>H<sub>43</sub>Cl<sub>2</sub>DyN<sub>4</sub>O<sub>17</sub>Zn<sub>2</sub> (%): C, 39.51; H, 3.56; N, 4.61. Found (%): C 39.44; H 3.53; N 4.65. IR (KBr; cm<sup>-1</sup>): 1610 [v(C=N)], 1240 [v(Ar–O)], 3434 [v(O–H)], UV-Vis [in chloroform/methanol (1:1)],  $\lambda_{max}$  (nm) (log  $\varepsilon$ ) [3.3 × 10<sup>-5</sup> M]: 280 (4.60), 370 (4.29), 396 (4.25), 416 (4.21).

#### 2.5. X-ray Crystallographic Analysis

Intensity data for complex **1** were collected on a Bruker Smart 1000 CCD area detector with Mo K $\alpha$  radiation (k = 0.71073 Å) at 293.33(10) K. While intensity data for complex **2** and **3** were collected on a SuperNova (Dual, Cu at zero, Eos) diffractometer with Mo K $\alpha$  radiation (k = 0.71073 Å) at 293.33(10) and 293.78(10) K, respectively. Data collection and reduction were performed using CrysAlisPro and then processed with Olex2. The structures were solved with ShelXS-2018 and refined with ShelXL-2015.All hydrogen atoms were added in calculated positions. The crystallographic data are summarized in Table 1.

Complex	1	2	3
Empirical formula	$C_{38}H_{37}LaN_4O_{16}Zn_2$	$C_{38}H_{37}CeN_4O_{16}Zn_2$	$C_{40}H_{43}Cl_2DyN_4O_{17}Zn_2$
Formula weight	1075.36	1076.57	1215.92
Temperature (K)	293.33(10)	293.33(10)	293.78(10)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic
Space group	$\overline{P}1$	$\overline{P}1$	<i>P</i> 2 <sub>1</sub> /c
<i>a</i> (Å)	10.4562(4)	13.4231(12)	12.6510(3)
<i>b</i> (Å)	14.5979(7)	13.5379(12)	13.6894(3)
<i>c</i> (Å)	18.4521(7)	15.6521(13)	26.8174(7)
$\alpha$ (°)	73.452(4)	64.689(9)	90
$\beta(^{\circ})$	75.215(3)	78.336(8)	103.515(3)

Table 1 Crystallographic data and refinement parameters for complexes 1, 2 and 3

<u> </u>	4	•	2
Complex	1	2	3
$\gamma(^{\rm o})$	77.263(4)	70.323(8)	90
Volume (Å <sup>3</sup> )	2577.05(19)	2415.4(4)	4515.77(19)
Z	2	2	4
Calculated density (g·cm <sup>-3</sup> )	1.386	1.480	1.788
Absorption coefficient (mm <sup>-1</sup> )	1.799	1.977	2.887
$\theta$ range for data collection (°)	3.298 to 26.021	3.372 to 26.021	3.312 to 26.022
<i>F</i> (000)	1076.0	1078.0	2428.0
h/k/l(min, max)	-12, 13/-19, 18/-24, 22	-16, 11/-16, 16/-18, 19	-15, 15/-16, 16/-33, 32
Crystal size (mm)	$0.35 \times 0.36 \times 0.38$	$0.09 \times 0.12 \times 0.21$	$0.34 \times 0.35 \times 0.36$
Collected reflections	19108	16682	33323
Unique reflections	9912	9506	8876
<i>R</i> <sub>int</sub>	0.035	0.090	0.048
parameters / restraints	555 / 0	555 / 0	604 / 0
$R_1(I > 2\sigma(I))^a$	0.0353	0.0717	0.0402
$wR_2(I > 2\sigma(I))^a$	0.0787	0.1441	0.1044
$R_1(\text{all data})^b$	0.0470	0.1625	0.0525
$wR_2(\text{all data})^b$	0.0737	0.1122	0.0951
Goodness-of-fit for $(F^2)^c$	0.985	0.983	1.082
Largest difference peak and hole (e $\text{\AA}^{-3}$ )	0.83, -0.70	0.77, -0.61	1.50, -0.85

*a.*  $R_1 = \Sigma ||F_o| - ||F_c||/\Sigma ||F_o||$ ; *b.*  $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$ ,  $w = [\sigma^2 (F_o^2) + (0.0784P)^2 + 1.3233P]^{-1}$ , where  $P = (F_o^2 + 2F_c^2)/3$ ; *c.* GOF  $= [\Sigma w (F_o^2 - F_c^2)^2 / n_{obs} - n_{param})]^{1/2}$ ;

#### 3. Results and discussion

The substitution reaction of the Zn(II) complex with 1 equiv of  $La^{3+}$  has been used to synthesize complex 1, meanwhile, complexes 2 and 3 are prepared by the same way. The ligand H<sub>4</sub>L and its corresponding complexes 1, 2 and 3 are stable in air. The ligand has remarkably soluble in chloroform, DMF and DMSO, but slightly soluble in methanol, ethanol, acetone and ethyl acetate. Complex 1 could dissolve in the methanol, chloroform and DMF, but slightly soluble in ethanol. The similar solubility of complexes 2 and 3 is measured. Mixing solution of methanol and chloroform as a

benign solvent is selected to accomplish spectral experiments.

#### 3.1. IR spectra

IR spectra of the free ligand H<sub>4</sub>L and its corresponding complexes 1, 2 and 3 exhibit various bands in the region of 4000-400 cm<sup>-1</sup>. The most important bands are given in Table 2 including the ligand H<sub>4</sub>L, Zn(II) complex and 3d-4f complexes 1, 2 and 3. The O-H stretching band of the free ligand H<sub>4</sub>L has been observed at 3172 cm<sup>-1</sup>. This band is disappeared in the spectra of complexes 1 and 2, which indicates that the phenolic OH groups of H<sub>4</sub>L have been completely deprotonized and coordinated to the metal ions [58-59]. The characteristic band of the OH group is found in complex 3 at 3419 cm<sup>-1</sup>, which belongs to the coordinated methanol molecule.

The free ligand H<sub>4</sub>L exhibits characteristic band of C=N at 1607 cm<sup>-1</sup>, which are shifted by 3 cm<sup>-1</sup> in complexes **1**, **2** and **3**, indicating that the metal ions are coordinated by N<sub>2</sub>O<sub>2</sub> donor atoms of (L)<sup>4-</sup> units, which is similar to previously reported Zn(II) complexes [60-61].

The Ar-O stretching frequency appears at 1250 cm<sup>-1</sup> for the ligand H<sub>4</sub>L, while the Ar-O stretching frequencies in complexes **1**, **2** and **3** are observed at 1242, 1237 and 1240 cm<sup>-1</sup>, respectively, which are shifted to a lower frequencies, implying that the M-O bonds are formed between the metal ions and oxygen atoms of phenolic groups [62]. The above facts are in agreement with the results determined by X-ray diffraction.

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Compound	$\mathcal{V}_{(C=N)}$	V <sub>(Ar-O)</sub>	$\mathcal{V}_{(O-H)}$
H <sub>4</sub> L	1607	1250	3172
Zn(II) complex	1604	1244	3387
Complex 1	1610	1242	-
Complex 2	1610	1237	-
Complex 3	1610	1240	3419

Table 2 The IR data for the free ligand  $H_4L$ , Zn(II) complex and heterotrinuclear complexes 1, 2 and 3

#### 3.2. UV-Vis absorption spectra

It can be seen from the spectrum of the free ligand H<sub>4</sub>L, there are four absorption peaks at *ca*. 269, 342, 360 and 378 nm (Fig. 1). The absorption peak at 269 nm can be assigned to the  $\pi$ - $\pi$ \* transition of the benzene rings. The other three absorption peaks can be attributed to the  $\pi$ - $\pi$ \* transition of the oxime groups [14-17]. The Zn(II) complex shows four absorption bands at 280, 370, 396 and 416 nm which can be observed in the heterotrinuclear complexes **1**, **2** and **3** with absorbance intensity changes. Compared with the absorption peaks of the free ligand H<sub>4</sub>L, the corresponding absorption peaks of complexes **1**, **2** and **3** are bathochromically shifted by *ca*. 11, 28, 36 and 38 nm, respectively, indicating the coordination of metal ions with the (L)<sup>4–</sup> unit.





In the UV-Vis titration experiments of complex **1**, the colour of the solution of Zn(II) complex in chloroform/methanol (1:1) changed inconspicuously when the solution of  $La^{3+}$  was added. With the increasing concentration of  $La^{3+}$ , the absorbance of the solution from 320~407 nm enhanced, and from 407~500 nm reduced. The absorbance of the solution hardly changed after  $La^{3+}$  was added up to 1 equiv. The

spectroscopic titration clearly indicated that the ratio of the replacement reaction was 1:1 (Fig. 2). Similar changes also appeared in complexes 2 and 3, which gave the same conclusions.





Fig. 2 UV–Vis spectral changes of complexes by the addition of  $Ln(NO_3)_3$  (CHCl<sub>3</sub>/CH<sub>3</sub>OH (1:1), [complex 1] =  $3.3 \times 10^{-5}$  M): (a)  $Ln^{3+} = La^{3+}$ , (b)  $Ln^{3+} = Ce^{3+}$ , (c)  $Ln^{3+} = Dy^{3+}$ 

#### 3.3. Fluorescence spectra

As can be seen from the spectra of the free ligand H<sub>4</sub>L and its corresponding complexes **1**, **2** and **3** (Fig. 3), the absorption peaks are bathochromically-shifted from that of the ligand H<sub>4</sub>L at 397 nm, which is due to the intraligand  $\pi$ - $\pi$ \* transition [63-65]. It is obvious that the La(III) enhanced of the fluorescence intensity and Ce(III) fluorescence quenching.



Fig. 3 Emission spectra of the free ligand H<sub>4</sub>L and complexes 1, 2 and 3 in CHCl<sub>3</sub>/CH<sub>3</sub>OH (1:1)

The excitation spectra using chloroform and methanol as the solvent are detected at the peak wavelength of the corresponding emission spectra at room temperature. The emission spectrum of complex **1** in this solvent at room temperature is shown in Fig. 4. The emission spectrum of complex **1** from 431 nm wavelength excitation exhibits broad visible photoluminescence at the range of 450 to 600 nm. Furthermore, the fluorescence intensity of complex **1** is much stronger than the reported heterotrinuclear complexes with alkaline earth ions. Two reasons lead to the enhancement of the fluorescence intensity, on one hand, the naphthalene ring have larger conjugate system which is good for optical properties, on the other hand, La(III) ion is usually used to synthesizing luminescent complexes.



**Fig. 4** (a) The excitation and emission spectra of complex **1**. (b) Fluorescence spectral changes of Zn(II) complex by the addition of La(NO<sub>3</sub>)<sub>3</sub> (CHCl<sub>3</sub>/CH<sub>3</sub>OH (1:1), [Zn(II) complex] =  $5.0 \times 10^{-5}$  =M).

The emission spectrum of complex 2 in the same solvent at room temperature is shown in Fig. 5. Complex 2 shows fluorescence quenching with maximum emission at *ca*. 502 nm upon excitation at 437 nm, which may result from  $Ce^{3+}$ ion itself and the fluorescence of  $Ce^{3+}$  ion is rarely reported in the literature. Both the absorbance of the solutions hardly changed after  $La^{3+}$  or  $Ce^{3+}$  was added up to 1 equiv. The spectroscopic titration clearly indicated that the ratio of the replacement reaction was 1:1, which obtained the same conclusion with UV-Vis

#### titration.



**Fig. 5** (a) The excitation and emission spectra of complex 2. (b) Fluorescence spectral changes of Zn(II) complex by the addition of Ce(NO<sub>3</sub>)<sub>3</sub> (CHCl<sub>3</sub>/CH<sub>3</sub>OH (1:1), [Zn(II) complex] =  $5.0 \times 10^{-5}$  M).

Complex **3** having maximum emission at ca. 481 nm upon excitation at 420 nm, the emission spectra are shown in Fig. 6. Here, fluorescence enhancement of complex **3** is observed with obvious blue shift, which is just stronger than the Zn(II) complex but far from complex **1**. The emission spectrum of complex **3** from 420 nm wavelength excitation exhibits broad visible photoluminescence at the range of 425 to 600 nm. Additionally, no characteristic emission peaks of  $Dy^{3+}$  ion are existed in the spectrum, which may result from the ligand H<sub>4</sub>L cannot be an antenna group to sensitize  $Dy^{3+}$  ion through an efficient intramolecular energy transfer process [66].

Fluorescence titration experiments of the lanthanide ions with the crystal of Zn(II) complex dissolved in the solvent show the same conclusion compared with the UV-Vis titration experiments. The fluorescence intensity of the solution hardly changed after lanthanide ion was added up to 1 equiv. With fluorescence enhancement and quenching, the spectroscopic titration of complexes 1 and 2 clearly indicated that the ratio of the replacement reaction was 1:1.



**Fig. 6** (a) The excitation and emission spectra of complex **2**. (b) Fluorescence spectral changes of Zn(II) complex by the addition of Dy(NO<sub>3</sub>)<sub>3</sub> (CHCl<sub>3</sub>/CH<sub>3</sub>OH (1:1), [Zn(II) complex] =  $5.0 \times 10^{-5}$  M).

The difference of heterotrinuclear complexes **1**, **2** and **3** is great. It indicates that the preparation of 3d-4f complexes by substitution reaction is effective. Through the spectral titration, high transformation rate and high yield could be predicted.

#### 3.4. Crystal structure descriptions

The heterotrinuclear complexes **1**, **2** and **3** were synthesized by using  $La^{3+}$ ,  $Ce^{3+}$  and  $Dy^{3+}$  ions to replace the central  $Zn^{2+}$  ion of homotrinuclear complex,  $[Zn_3(L)(OAc)_2(CH_3OH)_2]\cdot 3CHCl_3$ , respectively. All the structures of complexes **1**, **2** and **3** were determined by single-crystal X-ray diffraction. Selected bond lengths and bond angles are listed in Table 3.

Complex 1							
La1-O1	2.828(2)	La1-O2	2.595(2)	La1-O5	2.591(2)	La1-O6	2.578(2)
La1-09	2.591(2)	La1-O10	2.886(2)	La1-O11	2.476(2)	La1-O13	2.465(2)
La1-O15	2.615(3)	La1-O16	2.600(2)				
O1-La1-O2	56.73(7)	01-La1-O5	99.91(7)	O1-La1-O6	128.70(7)	01-La1-O9	123.54(7)
O1-La1-O10	124.56(7)	O1-La1-O11	64.77(7)	O1-La1-O13	127.16(8)	O1-La1-O15	64.83(7)
O1-La1-O16	67.49(7)	O2-La1-O5	59.18(7)	O2-La1-O6	117.31(7)	O2-La1-O9	177.18(7)
O2-La1-O10	125.90(7)	O2-La1-O11	103.60(7)	O2-La1-O13	76.12(7)	O2-La1-O15	109.67(8)

Table 3 Selected bond lengths (Å) and angles (°) of complexes 1, 2 and 3

O2-La1-O16	73.14(7)	O5-La1-O6	58.75(7)	O5-La1-O9	118.43(7)	O5-La1-O10	130.10(7)
O5-La1-O11	90.45(8)	O5-La1-O13	70.94(7)	O5-La1-O15	164.69(7)	O5-La1-O16	127.48(7)
O6-La1-O9	60.12(7)	O6-La1-O10	100.34(7)	O6-La1-O11	69.14(8)	O6-La1-O13	91.83(8)
O6-La1-O15	128.96(8)	O6-La1-O16	163.41(7)	O9-La1-O10	56.61(7)	O9-La1-O11	74.58(7)
O9-La1-O13	104.76(8)	O9-La1-O15	72.36(7)	O9-La1-O16	109.64(7)	O10-La1-O11	126.36(7)
O10-La1-O13	64.70(7)	O10-La1-O15	64.37(7)	O10-La1-O16	63.58(7)	O11-La1-O13	158.73(8)
O11-La1-O15	81.88(8)	O11-La1-O16	122.85(8)	O13-La1-O15	118.59(8)	O13-La1-O16	77.82(8)
O15-La1-O16	49.86(8)					Z	
Complex 2					0-		
Ce1-O1	2.688(7)	Ce1-O2	2.458(7)	Ce1-O5	2.437(6)	Ce1-O6	2.481(7)
Ce1-O9	2.485(7)	Ce1-O10	2.747(6)	Ce1-O11	2.459(7)	Ce1-O13	2.499(7)
Ce1-O15	2.471(7)						
O1-Ce1-O2	60.6(2)	01-Ce1-O5	130.5(2)	01-Ce1-O6	149.7(2)	01-Ce1-O9	119.0(2)
O1-Ce1-O10	69.5(2)	01-Ce1-O11	73.6(2)	01-Ce1-O13	108.1(2)	O1-Ce1-O15	77.5(2)
O2-Ce1-O5	74.0(2)	O2-Ce1-O6	134.8(2)	O2-Ce1-O9	150.2(2)	O2-Ce1-O10	97.7(2)
O2-Ce1-O11	129.7(2)	O2-Ce1-O13	69.5(2)	O2-Ce1-O15	73.4(2)	O5-Ce1-O6	61.9(2)
O5-Ce1-O9	110.1(2)	O5-Ce1-O10	139.3(2)	O5-Ce1-O11	132.4(2)	O5-Ce1-O13	70.1(2)
O5-Ce1-O15	71.4(2)	O6-Ce1-O9	62.7(2)	O6-Ce1-O10	121.8(2)	O6-Ce1-O11	79.6(2)
O6-Ce1-O13	102.2(2)	O6-Ce1-O15	83.3(2)	O9-Ce1-O10	59.2(2)	O9-Ce1-O11	70.4(2)
O9-Ce1-O13	83.9(2)	O9-Ce1-O15	136.4(2)	O10-Ce1-O11	83.9(2)	O10-Ce1-O13	69.7(2)
O10-Ce1-O15	145.6(2)	O11-Ce1-O13	150.2(2)	O11-Ce1-O15	77.7(2)	O13-Ce1-O15	132.1(2)
Complex 3	$\mathbf{G}$						
Dy1-O1	2.595(3)	Dy1-O2	2.318(4)	Dy1-O5	2.335(4)	Dy1-O6	2.355(3)
Dy1-O9	2.367(4)	Dy1-O10	2.643(3)	Dy1-O11	2.407(4)	Dy1-O13	2.375(4)
Dy1-O17	2.472(4)						
O1-Dy1-O5	128.78(12)	O1-Dy1-O6	144.45(12)	O1-Dy1-O9	112.19(12)	O1-Dy1-O10	65.47(12)
O1-Dy1-O11	117.53(13)	O1-Dy1-O13	69.18(13)	O1-Dy1-O17	72.87(14)	O2-Dy1-O5	73.24(12)
O2-Dy1-O6	137.92(11)	O2-Dy1-O9	149.24(12)	O2-Dy1-O10	91.04(13)	O2-Dy1-O11	75.74(13)
O2-Dy1-O13	125.99(13)	O2-Dy1-O17	73.98(14)	O5-Dy1-O6	65.34(10)	O5-Dy1-O9	119.03(12)

O5-Dy1-O10	142.53(11)	O5-Dy1-O11	71.97(12)	O5-Dy1-O13	126.50(12)	O5-Dy1-O17	70.88(12)
O6-Dy1-O9	65.14(10)	O6-Dy1-O10	126.71(11)	O6-Dy1-O11	97.56(12)	O6-Dy1-O13	77.01(11)
O6-Dy1-O17	85.56(12)	O9-Dy1-O10	61.74(11)	O9-Dy1-O11	81.63(12)	O9-Dy1-O13	71.78(12)
O9-Dy1-O17	135.68(12)	O10-Dy1-O11	71.24(12)	O10-Dy1-O13	90.40(12)	O10-Dy1-O17	138.01(13)
O11-Dy1-O13	152.72(13)	O11-Dy1-O17	137.26(13)	O13-Dy1-O17	69.60(13)		

#### 3.4.1. Crystal structure of complex 1

The crystal structure of complex 1 and the coordination environment of La1 and Zn2 are shown in Fig. 7. Complex 1 crystallizes in the triclinic space group  $\overline{P}$ 1. X-ray crystallography clearly showed the formation of complex 1, which was isolated as yellow crystals. Interestingly, the formation process of complex 1 was highly cooperative. In the crystal structure of complex 1, two acetate ions bridge  $Zn^{2+}$  and  $La^{3+}$ ions in a  $\mu_2$ -fashion. Meanwhile, two oxygen ions of another acetate ion coordinate to  $La^{3+}$  synchronously, which probably contribute to the cooperative formation of complex 1. Zn1 and Zn2 are both penta-coordinated with geometries of distorted tetragonal pyramid, which were deduced by calculating the value of  $\tau_1 = 0.3175$ ,  $\tau_2 = 0.3778$ , respectively [67]. La1 is located in the cavity that consists of six oxygen atoms, the four are phenoxy oxygen atoms while the two others come from methoxy groups. Besides, three acetate ions provide remaining four oxygen atoms, so La1 is ten-coordinated with geometry of distorted bicapped square antiprism. The distances between La1 and the coordination oxygen atoms are ranged from 2.578(2) to 2.886(2) Å. Such structure is similar to the reported work earlier, in which  $La^{3+}$  is also ten-coordinated and no solvent molecules coordinate to the metal ions [68]. The high coordination number of  $La^{3+}$  ion is determined by its longer ionic radius and smaller winding angles.



Fig. 7 X-ray crystal structure of complex 1 and the coordination environment of La1 and Zn2



Fig. 8 View of an infinite 1D chain motif of complex 1 units along the c axis.

In the crystal structure of complex **1**, there are significant intermolecular hydrogen bonds (C7-H7…O16) and C-H… $\pi$  interactions (C21-H21…*Cg*6 (C11-C12-C17-C18-C19-C20), C14-H14…*Cg*8 (C25-C30)), which link the units together efficiently, especially, the units are interlinked by the intermolecular hydrogen bonds into a 1D chain supra-molecular structure along the *c* axis (Fig. 8).

#### 3.4.2. Crystal structure of complex 2

The crystal structure of complex 2 and the coordination environment of Ce1 are shown in Fig. 9. Complex 2 also crystallizes in the triclinic space group  $\overline{P}1$ . Ce1 is also located in the O<sub>6</sub> cavity, differently, three acetate ions all bridge Zn<sup>2+</sup> and Ce<sup>3+</sup> ions in a  $\mu_2$ -fashion, which provide other three oxygen atoms. As the three coordinated acetate ions, Zn1 is hexa-coordinated with geometry of

distorted octahedron. Zn2 is peta-coordinated with geometry of distorted tetragonal pyramid. Ce1 is nine-coordinated with geometry of distorted capped square antiprism. The distances between Ce1 and the four phenoxy oxygen atoms of the salamo moieties coordinate are ranged from 2.437(6) to 2.485(7) Å, however, the distances of the oxygen atoms of acetates ions are all in this range. The distances with methoxy groups (Ce1-O1 2.688(7) Å, Ce1-O10 2.747(6) Å) are clearly longer than those of above oxygen atoms. Negative charge of the oxygen atoms would be the main reason, which enhances the coordination ability of the oxygen atoms.



Fig. 9 X-ray crystal structure of complex 2 and the coordination environment of Ce1 and Zn ions



Fig. 10 View of a dipolymer motif of two complex 2 units.

In the crystal structure of complex **2**, just three intermolecular hydrogen bonds (C8-H8B···O14, C22-H22A···O12, C24-H24···O13) were observed. Here, complex **2** units are interlinked by one pair intermolecular hydrogen bonds into a dipolymer (Fig. 10). No supramolecular structures were observed in complex **2**.

#### 3.4.3. Crystal structure of complex 3

The crystal structure and atom numbering of complex **3** is shown in Fig. 11. Complex **3** crystallizes in the monoclinic space group  $\overline{P}2_1/c$  which is different from the former complexes. The Zn<sup>2+</sup> ions of complex **3** have similar coordination environments and coordination geometries with complex **2**. Zn1 is hexa-coordinated with geometry of distorted octahedron, and Zn2 is peta-coordinated with geometry of distorted tetragonal pyramid. Unexpectedly, the third acetate ion only coordinates with Zn1 as a monodentate ligand, and another methanol molecule coordinates to Dy<sup>3+</sup> ion instead of it. So Dy1 is nine-coordinated consisting of six oxygen atoms from bis(salamo)-type ligand, two oxygen atoms of two acetate ions and one oxygen atom of coordinated methanol molecule, with geometry of distorted capped square antiprism. The same phenomena were observed that the coordination bonds of Dy1 with negative charged oxygen atoms have shorter distances.

In the crystal structure of complex **3**, there are significant intermolecular hydrogen bonds (C24-H24···O11, C15-H15···O16) and C-H··· $\pi$  interactions (C8-H8A··· *Cg*8 (C25-C30)), which link the units together efficiently, especially, complex **3** units are interlinked by the intermolecular hydrogen bond and C-H··· $\pi$  interactions into a 2D supra-molecular structure along the *ab* plane (Fig. 12).



Fig. 11 X-ray crystal structure of complex 3 and the coordination environment of Dy1.



Fig. 12 View of an infinite 2D supra-molecular network of complex 3 units on the *ab* plane. As we see, the three lanthanide complexes have their own structure characteristics. The three acetate ions coordinate to the metal ions result in two main effects, the one is to make crystal structure stable, the other is to make the charge balance. With the coordinated methanol molecules, complex 3 having similar structure with complex 2 owns more intermolecular interactions.

#### 4. Conclusions

We had designed and synthesized a novel naphthalenediol-based acyclic

bis(salamo)-type ligand and its corresponding homotrinuclear Zn(II) complex. Here, the heterotrinuclear 3d-4f complexes were acquired by the substitution reaction of the homotrinuclear Zn(II) complex with 1 equiv of Ln(NO<sub>3</sub>)<sub>3</sub> (Ln<sup>3+</sup> = La<sup>3+</sup>, Ce<sup>3+</sup> and Dy<sup>3+</sup>). Spectral titrations and X-ray crystallography clearly show that the stoichiometry of the homotrinuclear Zn(II) complex is 1:3 (ligand/Zn<sup>2+</sup>) and those of the heterotrinuclear complexes are all 1:2:1 (ligand/Zn<sup>2+</sup>/Ln<sup>3+</sup>), respectively. The different optical properties and peak wavelength variation of the heterotrinuclear complex clearly show the success of transformation from homotrinuclear to heteronuclear complexes, which could be used in host–guest systems. Furthermore, by analyzing the structures of these complexes, another acetate ion coordinate to the metal ions compared with the alkaline earth ion that we had reported, which makes the crystal structure more stable.

#### Acknowledgments

This work was supported by the National Natural Science Foundation of China (21361015), which is gratefully acknowledged.

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**Abstract**: Heterotrinuclear 3d-4f metal complexes with an naphthalenediol-based acyclic bis(salamo)-type ligand have been synthesized and structurally characterized. The coordination modes of three acetate ions are different in the complexes **1-3**. Spectral titration clearly shows that the heterotrinuclear complexes  $[Zn_2(L)La(OAc)_3]$  (**1**),  $[Zn_2(L)Ce(OAc)_3]$  (**2**) and  $[Zn_2(L)Dy(OAc)_3(CH_3OH)]\cdot CH_2Cl_2$  (**3**) were acquired by the substitution reaction of the reported homotrinuclear Zn(II) complex with 1 equiv of  $Ln(NO_3)_3$  ( $Ln^{3+} = La^{3+}$ ,  $Ce^{3+}$  and  $Dy^{3+}$ ).



#### Highlights

Novel naphthalenediol-based acyclic bis(salamo)-type ligand was synthesized.

Spectral titrations clearly show the success of transformation from homotrinuclear to heterotrinuclear complexes.

The 3d-4f complexes have been synthesized and characterized structurally.

The different coordination modes of acetate ions in complexes 1, 2 and 3 have been observed.

Fluorescence properties of complexes 1, 2 and 3 have been discussed.

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