

Article

Self-Assembly of 3d-4f Zn^{II}-Ln^{III} (Ln = Ho and Er) Bis(salamo)-Based Complexes: Controlled Syntheses, Structures and Fluorescence Properties

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Abstract: Two new hetero-trinuclear 3d-4f complexes $[Zn_2(L)Ho(\mu_2-OAc)_2(OAc)(MeOH)]\cdot CH_2Cl_2$ (1) and $[Zn_2(L)Er(\mu_2-OAc)_2]OAc$ (2), derived from a bis(salamo)-based ligand H₄L, were synthesized and characterized via elemental analyses, IR, UV–Vis, fluorescence spectra and X-ray crystallography. The X-ray crystal structure analyses demonstrated that two μ_2 -acetateanions bridge the Zn^{II} and Ln^{III} (Ln = Ho (1) and Er (2)) atoms in a μ_2 -fashion forming similar hetero-trinuclear structures, respectively. In complex 1, one methanol molecule as coordinating solvent participates in the coordination, the two Zn^{II} atoms are six- and five-coordinated and have geometries of slightly distorted tetragonal pyramid and octahedron, and the Ho^{III} atom is nine-coordinated and has the geometry of a mono-capped square antiprism. In complex 2, the two Zn^{II} atoms both possess five-coordinated tetragonal pyramid geometries, and the Er^{III} atom is eight-coordinated with a square antiprism geometry. Furthermore, the fluorescence properties of complexes 1 and 2 were determined.

Keywords: bis(salamo)-type compound; hetero-trinuclear 3d-4f complex; preperation; structure; fluorescence property

1. Introduction

As we know, due to easy preparation and strong coordination abilities, modified Salen-type ligands [1–8] containing tetradentate N_2O_2 site have been used for the synthesis of metal complexes [9–13] in the past few decades. The potential applications of Salen-type compounds and their corresponding metallic complexes in modern coordination chemistry and organometallic chemistry have attracted considerable attentions, such as optical sensors [14,15], catalyses [16,17], luminescence properties [18–24], supra-molecular buildings [25–33], electrochemistries [34,35], magnetic materials [36–41], biological systems [42–51] and nonlinear optical materials [52], and so forth. In recent years, Salen-type complexes have attracted considerable attention from the viewpoint of the integration effect of multiple functional units. In the meantime, a class of salen-based supramolecules is the self-assembled salen metal complexes which may be obtained by the metal-assisted self-assembly of multiple salen units [5].

More recently, Salamo, a better class of N_2O_2 -donor ligands, has been exploited, using $[-CH=N-O-(CH_2)_n-O-N=CH-]$ instead of $[-CH=N-(CH_2)_n-N=CH-]$ group. The studies showed that Salamo-type ligands are relatively stable than Salen-type ligands [53]. So far, lots of reports have been documented concerning the preparation of homo-, or hetero-multinuclear metallic complexes possessing Salamo-type ligands [54–63]. Currently, hetero-multimetallic 3d-4f complexes pose an extreme yet attractive challenge in the field of coordination chemistry. This is due to



the fact that stable high-nuclear and structurally novel 3d-4f metallic complexes exhibit good luminescence properties. With the expectation of obtaining novel structures and interesting properties, a bis(salamo)-type ligand H₄L containing O₆ coordination sphere was already prepared earlier to obtain a series of homo-, hetero-nuclear Zn^{II}-M^{II}, Co^{II}-M^{II} (M = Ca, Sr and Ba) and Zn^{II}-Ln^{III} (Ln = La, Ce and Dy) complexes. In addition, the crystal structures and properties of complexes have been discussed in detail [57,64,65]. Therefore, these compounds are considered to be heterotrinuclear bis(salamo)-type complexes. Owing to the bis(salamo)-type ligand H₄L bearing an O₆ coordination sphere, it can form homotrinuclear bis(salamo)-type complexes. The transition metal atom located in the O₆ coordination sphere can be replaced by rare earth atoms with a larger atomic radius. Herein, as an extension of our previous studies, two new hetero-trinuclear 3d-4f complexes [Zn₂(L)Ho(μ_2 -OAc)₂(OAc)(MeOH)]·CH₂Cl₂ (1) and [Zn₂(L)Er(μ_2 -OAc)₂]OAc (2), constructed from the bis(salamo)-type ligand H₄L, were prepared and characterized structurally. In addition, the fluorescence properties of complexes 1 and 2 were studied in detail.

2. Experimental

2.1. Materials and Methods

2-Hydroxy-3-methoxybenzaldehyde (99%), methyl trioctyl ammonium chloride (90%), borontribromide (99.9%) and pyridinium chlorochromate (98%) were bought from Alfa Aesar (New York, NY, USA). Hydrobromic acid 33wt % solution in acetic acid was purchased from J & K Scientific Ltd. (Beijing, China). Other chemicals were obtained from Tianjin Chemical Reagent Factory (Tianjin, China). Elemental C, H and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument (Elementar, Berlin, Germany). Elemental analyses for metal atoms were performed on an IRIS ER/S-WP-ICP atomic emission spectrometer (Elementar, Berlin, Germany). Melting points were determined on a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company (Beijing, China) and were uncorrected. IR spectra were measured on a VERTEX70 FT-IR spectrophotometer (Bruker, Billerica, MA, USA), with samples prepared as KBr (500–4000 cm⁻¹) pellets. UV-Vis spectra in the 250–550 nm range were measured by a Hitachi UV-3900 spectrometer (Shimadzu, Tokyo, Japan). Fluorescent spectra were determined on a Hitachi F-7000 spectrophotometer (Hitachi, Tokyo, Japan). Single crystal X-ray structure determinations were performed on a SuperNova Dual, Cu at zero, Eos four-circle diffractometer.

2.2. Synthesis of H_4L

2,3-Dihydroxynaphthalene-1,4-dicarbaldehydeand 2-[O-(1-ethyloxyamide)] oxime-6-methoxyphenol were prepared according to the early reported methods [64,66]. The synthesis of H₄L and its complexes is depicted in Scheme 1.



Scheme 1. Cont.



Scheme 1. Synthetic routes to H₄L and its complexes.

The ligand H₄L was synthesized according to the previously reported method [57,64,65]. Yield, 54.1%. m.p. 171–172 °C. Anal. Calcd. for $C_{32}H_{32}N_4O_{10}$ (%): C, 60.75; H, 5.10; N, 8.86; Found: C, 60.93; H, 5.22; N 8.70. ¹H NMR (400 MHz, CDCl₃) 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).

2.3. Synthesis of complex 1

The ligand H₄L (9.42 mg, 0.015 mmol) was dissolved in dichloromethane (2 mL). To stirring solution of Zn(OAc)₂ (12.67 mg, 0.03 mmol) in methanol (2 mL) and Ho(OAc)₃ (2.24 mg, 0.015 mmol) in methanol (2 mL) was added in drops solution of H₄L in dichloromethane (2 mL) at room temperature. After about 15 min, the resulting solution turned clear. The mixed solution was filtered, and the filtrate was placed at room temperature for slow evaporation. Clear light colourless crystals were collected and washed with n-hexane. Finally, complex **1** was dried and collected. Yield: 51.3%. Anal. Calcd. for $C_{40}H_{43}Cl_2Zn_2HoN_4O_{17}$ (%): C, 39.43; H, 3.56; N, 4.60; Zn, 10.73; Ho, 13.54; Found: C, 39.62; H, 3.71; N, 4.45; Zn, 10.54; Ho, 13.39.

2.4. Synthesis of complex 2

To stirring solution of Zn(OAc)₂ (4.51 mg, 0.02 mmol) in methanol (2 mL) and Er(OAc)₃ (1.28 mg, 0.01 mmol) in methanol (2 mL) was added solution of H₄L in methanol (2 mL) in a dropwise manner at room temperature. After about 15 min, the resulting solution turned clear. The mixed solution was filtered and stayed for ca. two weeks, after which clear light colorless crystals were gained. Yield: 50.4%. Anal. Calcd. for $C_{38}H_{37}Zn_2ErN_4O_{16}$ (%): C, 41.35; H, 3.38; N, 5.08; Zn, 11.85; Er, 15.15; Found: C, 41.59; H, 3.42; N, 5.02; Zn, 12.15; Er, 15.46.

2.5. X-ray Structure Determinations for complexes 1 and 2

Intensity data of complexes **1** and **2** were collected on a SuperNova Dual, Cu at zero, Eos diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293.78(10) and 293.18(10) K, respectively. Multiscan absorption corrections were applied. The structures were solved by Direct Methods and refined anisotropically using full-matrix least-squares methods on F² with the SHELX-2014 program package. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and isotropically fixed in the final refinement. Contributions to scattering due to these very large solvent accessible VOID(S) in structure were removed using the SQUEEZE routine of PLATON, the structures were then refined again using the data generated. The crystallographic and refinement parameter data including the structural determinations are listed in Table 1. Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Centre (CCDC Nos. 1825954 and 1825953 for complexes **1** and **2**) and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

Complex	1	2
Formula	C40H43Cl2Zn2H0N4O17	C ₃₈ H ₃₇ Zn ₂ ErN ₄ O ₁₆
Formula weight	1218.35	1103.71
Temperature (K)	293.78(10)	293.18(10)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ /c	I2/c
Unit cell dimensions		
a (Å)	12.6372(2)	7.8033(4)
b (Å)	13.68094(19)	30.0645(18)
<i>c</i> (Å)	26.7692(5)	20.5938(10)
α (°)	90	90
β (°)	103.494(2)	93.545(4)
γ (°)	90	90
$V(Å^3)$	4500.33(14)	4822.1(4)
Z	4	4
$D_c ({\rm g}{\rm cm}^{-3})$	1.798	1.520
μ (mm ⁻¹)	2.995	2.777
F (000)	2432	2196
Crystal size (mm)	0.31 imes 0.32 imes 0.35	0.20 imes 0.22 imes 0.24
θ Range (°)	3.7820-28.1060	1.199-28.8430
	$-15 \le h \le 14$	$-10 \le h \le 10$
Index ranges	$-16 \le k \le 16$	$-40 \le k \le 35$
	$-33 \le l \le 32$	$-25 \le l \le 25$
Reflections collected	26,900	19,152
Independent reflections	8584	5715
R _{int}	0.035	0.019
Completeness	96.06%	99.70%
Data/restraints/parameters	8584/3/604	4642/4/296
GOF	1.040	1.017
Final R_1 , wR_2 indices	0.0337, 0.0746	0.0309, 0.0927
R_1 , wR_2 indices (all data)	0.0455, 0.0814	0.0398, 0.0945
Largest differences peak and hole (e $Å^{-3}$)	0.809/-0.854	1.330/-0.960

Table 1. Crystal and refinement parameter data for complexes 1 and 2.

3. Results and Discussion

Complexes **1** and **2** derived from a bis(salamo) ligand H₄L were prepared and characterized by UV-Vis, IR, X-ray crystallography and fluorescence spectra.

3.1. IR Spectra

The main FT-IR spectral data for H_4L and its corresponding metallic complexes 1 and 2 in the 500–4000 cm⁻¹ region are delineated in Table 2.

Compound	$\nu_{(O-H)}$	$v_{(C=N)}$	$v_{(Ar-O)}$	$v_{(C=C)}$
H ₄ L	3167	1628	1253	1374
Complex 1	3389	1601	1220	1316
Complex 2	-	1604	1217	1314

Table 2. Main FT-IR spectral data of H_4L and its complexes 1 and 2 (cm⁻¹).

In the FT-IR spectra, the phenolic O–H vibration band for H₄L exhibited a strong characteristic absorption at 3167 cm⁻¹. Nevertheless, this band disappeared, and a new O–H vibration band of methanol molecule was displayed at 3389 cm⁻¹ in complex **1**, which is in agreement with the result of the elementary analyses. However, this band disappeared in complex **2**, indicating that the hydroxyl groups of phenolic and naphthalenediol of H₄L are completely deprotonated and coordinated with the metal atoms, and the methanol solvent used is not involved in the coordination. A typical C=N stretching vibration band of H₄L was detected at 1628 cm⁻¹. Upon complexation, the C=N bands of complexes **1** and **2** appeared at 1601 and 1604 cm⁻¹, respectively, which are both shifted to low

frequencies, demonstrating the coordination of the C=N nitrogen atoms of the N₂O₂ binding sites with Zn^{II} atoms [65]. The IR spectrum of H₄L exhibited one absorption band at ca. 1253 cm⁻¹, assignable to the Ar–O absorption band. Compared with H₄L, the typical Ar–O stretching frequencies of complexes **1** and **2** occurred at 1220 and 1217 cm⁻¹, respectively. This phenomenon can be explained by the formation of M–O bonds [67]. The results mentioned above show consistence with single crystal X-ray diffraction.

3.2. UV-Vis Spectra

In many studies, UV–Vis absorption spectra have been utilized to study the lanthanides complexes. In this study, the UV–Vis spectrum of H₄L in CH₃OH:CHCl₃ (1:1) (1.0×10^{-5} mol L⁻¹) with its corresponding complexes **1** and **2** in methanol/H₂O (10:1) (1.0×10^{-3} mol L⁻¹) were determined in the range of 250–550 nm. According to the previously reported results, the free ligand H₄L has absorption peaks at about 269, 340, 360 and 374 nm. The former peak at 269 nm could be attributed to the π - π * transition of the benzene rings while the other peaks could be appointed to those of the oxime groups [65].

In the UV–Vis titration test, gradual addition of $Zn(OAc)_2$ to H_4L solution resulted in solution changes from yellow to colorless. In contrast to H_4L , the peaks are bathochromically shifted. This phenomenon is owing to the reaction of H_4L with Zn^{II} ions. When Zn^{II} ions were added in excess of 3 equiv, the absorbance no longer changed. The spectroscopic titration of H_4L and $Zn(OAc)_2$ obviously showed a 1:3 homo-trinuclear complex was formed which is shown in Figure 1a.

Then, upon the addition of 1 equiv of Ho^{III} ions, the absorbance changed and showed two isoabsorptive points at about 298 and 380 nm. The titration test obviously showed that the stoichiometry ratio of the replacement reaction is 1:1 (inset of Figure 1b). Similar change was observed in complex **2**, giving the same results and is shown in Figure 2.



Figure 1. Cont.



Figure 1. (a) UV-Vis spectral changes of H_4L (1.0×10^{-5} M) upon the addition of Zn^{II} (1.0×10^{-3} M) ions; (b) UV-Vis spectral changes of $[LZn_3]^{2+}$ upon the addition of Ho^{III} (1.0×10^{-3} M) ions.



Figure 2. Cont.



Figure 2. (a) UV–Vis spectral changes of H_4L (1.0×10^{-5} M) upon the addition of Zn^{II} (1.0×10^{-3} M) ions; (b) UV–Vis spectral changes of $[LZn_3]^{2+}$ upon the addition of Er^{III} (1.0×10^{-3} M) ions.

3.3. Crystal Structure Description of complex 1

The determined crystal structure of complex **1** is depicted in Figure 3. From the Figure 3, complex **1** crystallizes in monoclinic system, consisting of two Zn^{II} atoms, one Ho^{III} atom, one deprotonated $(L)^{4-}$ unit, two μ_2 -acetate anions, one monodentate coordinated acetate anion, one coordinated methanol and one crystallizing dichloromethane molecules.



Figure 3. (a) View of the crystal structure of complex 1; (b) Coordination polyhedrons for Zn^{II} and Ho^{III} atoms.

The X-ray diffraction analysis revealed that the Zn1 atom is surrounded by a N₂O₂ donor environment and is bonded to two nitrogen atoms (Zn1-N1, 2.140(4) Å and Zn1-N2, 2.157(4) Å) of the oxime groups, two oxygen (Zn1-O2, 2.154(3) Å and Zn1-O5, 2.053(3) Å) atoms of the phenolic groups, one oxygen atom of the μ_2 -acetate anion (Zn1-O12, 2.061(3) Å) and one oxygen atom (Zn1-O16, 2.088(3) Å) of the monodentate coordinated acetate anion (Table 3). Therefore, the Zn1 is six-coordinated and has octahedral coordination geometry [68]. The Zn1-O/N bond lengths are in the range of 1.950(3)–2.157(4) Å. Zn2 atom is five-coordinated and has a tetragonal pyramid geometry, which being calculated by τ value was estimated to be $\tau = 0.19$ [64,65,68]. The Zn2 atom is linked by two nitrogen atoms (Zn2-N3, 2.100(3) Å and Zn2-N4, 2.054(3) Å) of the oxime groups, two oxygen (Zn2-O6, 1.991(3) Å and Zn2-O9, 2.045(3) Å) atoms of the phenolic group and the μ_2 -acetate anion (Zn2-O14, 1.986(3) Å). The Zn2-O/N bond lengths are in range of 1.986(3)–2.100(3) Å.

Bond Lengths					
Zn1-O2	2.154(3)	Zn1-O5	1.950(3)	Zn1-O12	2.061(3)
Zn1-O16	2.088(3)	Zn1-N1	2.140(4)	Zn1-N2	2.157(4)
Zn2-06	1.991(3)	Zn2-O9	2.045(3)	Zn2-O14	1.986(3)
Zn2-N3	2.100(3)	Zn2-N4	2.054(3)	Ho1-O1	2.587(3)
Ho1-O2	2.308(3)	Ho1-O5	2.327(3)	Ho1-O6	2.341(3)
Ho1-O9	2.356(3)	Ho1-O10	2.634(3)	Ho1-O11	2.394(3)
Ho1-O13	2.373(4)	Ho1-O15	2.460(3)		
Bond Angles					
O1-Ho1-O2	63.07(9)	O1-Ho1-O5	129.30(9)	O1-Ho1-O6	144.05(9)
O1-Ho1-O9	111.59(9)	O1-Ho1-O10	65.13(9)	O1-Ho1-O11	117.67(9)
O1-Ho1-O13	68.67(9)	O1-Ho1-O15	72.96(10)	O2-Ho1-O5	73.40(9)
O2-Ho1-O6	138.15(9)	O2-Ho1-O9	148.88(9)	O1-Ho1-O10	90.44(9)
O2-Ho1-O11	75.84(9)	O2-Ho1-O13	125.83(10)	O2-Ho1-O15	74.04(11)
O5-Ho1-O6	65.45(9)	O5-Ho1-O9	119.11(10)	O5-Ho1-O10	142.08(9)
O5-Ho1-O11	71.99(9)	O5-Ho1-O13	126.72(10)	O5-Ho1-O15	71.10(11)
O6-Ho1-O9	65.39(9)	O6-Ho1-O10	127.09(9)	O6-Ho1-O11	97.72(10)
O6-Ho1-O13	77.01(10)	O6-Ho1-O15	85.55(11)	O9-Ho1-O10	61.88(9)
O9-Ho1-O11	81.36(9)	O9-Ho1-O13	71.93(10)	O9-Ho1-O15	135.89(11)
O10-Ho1-O11	70.84(9)	O10-Ho1-O13	90.68(9)	O10-Ho1-O15	137.86(11)
O11-Ho1-O13	152.58(10)	O11-Ho1-O15	137.49(11)	O13-Ho1-O15	69.55(12)

Table 3. Selected bond lengths (Å) and angles (°) for complex **1**.

Meanwhile, the Ho^{III} atom is nine-coordinated and has a mono-capped square antiprism coordination geometry. The Ho^{III} atom located in O₉ coordination sphere is coordinated with six oxygen atoms (Ho1-O1, 2.587(3) Å; Ho1-O2, 2.308(3) Å; Ho1-O5, 2.327(3) Å; Ho1-O6, 2.341(3) Å; Ho1-O9, 2.356(3) Å and Ho1-O10, 2.634(3) Å) from the phenolic oxygen and methoxy groups, two μ_2 -acetate oxygen atoms (Ho1-O11, 2.394(3) Å and Ho1-O13, 2.373(4) Å) and one oxygen atom (Ho1-O15, 2.460(3) Å) of the coordinated methanol molecule.

The hydrogen bonding and C-H··· π interactions are summarized in Table 4. In the structure of complex 1, there are four pairs of intra-molecular O15-H15····O16, C8-H8B···O12, C9-H9B···O17 and C22-H22A···O14 hydrogen bonding in Figure 4 [69–74]. As illustrated in Figure 5, a 2D supra-molecular structure is interlinked via two significant intermolecular C15-H15A···O17 and C24-H24···O11 hydrogen bonding interactions are constructed. In addition, one significant C-H··· π interaction (C8-H8A···Cg1 (C25-C30)) is built in Figure 6 [75–78].

Table 4. Hydrogen bonding (Å, °) and C-H $\cdots\pi$ interactions for complex **1**.

D-H···A	D····A	Н…А	D-H···A
O15-H15…O16	2.603(5)	1.80(3)	152
C8-H8BO12	3.250(6)	2.40	146
C9-H9B…O17	3.469(7)	2.50	178
C22-H22A…O14	3.297(6)	2.37	160

Table 4. Cont.	
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D-H····A	D····A	Н…А	D-H···A
C15-H15A…O17	3.478(7)	2.56	169
C24-H24…O11	3.278(5)	2.38	162
D-X···A	D-A	X····A	D-X···A
C8-H8A…Cg1	3.727(6)	2.79	163

Note: Cg1 = C25–C26–C27–C28–C29–C30.



Figure 4. Intra-molecular O-H…O and C-H…O hydrogen bonding of complex 1.



Figure 5. View of 2D supra-molecular structure of complex **1** by the intermolecular O-H…O and C-H…O hydrogen bonding interactions.



Figure 6. View of 1D supra-molecular structure via C-H··· π interactions in complex **1**.

3.4. Crystal Structure Description of complex 2

The structure of complex **2** is illustrated in Figure 7. It crystallizes in monoclinic system. The asymmetric trinuclear structure is similar to complex **1** and contains two Zn^{II} atoms, one Er^{III} atom, one deprotonated (L)⁴⁻ unit, two μ_2 -acetate anions and one crystallizing acetate anions. The Zn^{II} atom (Zn1 or Zn1ⁱ) is five-coordinated with two oxime nitrogen (Zn1-N1, 2.084(3) Å and Zn1-N2, 2.057(3) Å) atoms, two phenol oxygen (Zn1-O2, 2.029(3) Å and Zn1-O5, 2.012(2) Å) atoms and one oxygen (Zn1-O6, 1.984(2) Å) atom of the μ_2 -acetate anion (Table 5) [68]. So, the Zn^{II} atoms (Zn1 and Zn1ⁱ) possess tetragonal pyramid geometries, which calculated by τ values were estimated to be τ (Zn1 and Zn1ⁱ) = 0.14 [68]. The Er^{III} atom located in O₈ coordination sphere is coordinated with six oxygen atoms (Er1-O1, 2.484(3) Å; Er1-O1ⁱ, 2.484(3) Å; Er1-O2, 2.318(2) Å; Er1-O2ⁱ, 2.318(2) Å; Er1-O5, 2.288(2) Å and Er1-O5ⁱ, 2.288(2) Å) from one deprotonated (L)⁴⁻ moiety and two μ_2 -acetate oxygen atoms (Er1-O7, 2.281(2) Å) atom Er1-O7ⁱ, 2.281(2) Å). Therefore, the Er^{III} atom is eight-coordinated and has the geometry of square antiprism. The distances between Er1 atom and the phenolic oxygen (O2, O5, O2ⁱ and O5ⁱ) atoms of the (L)⁴⁻ unit are ranged from 2.288(2) to 2.318(2) Å, which are clearly shorter than those of the methoxy groups (Er1-O1, 2.484(3) Å and Er1-O1ⁱ, 2.484(3) Å).



Figure 7. (a) The crystal structure of complex 2; (b) Coordination polyhedrons for Zn^{II} and Er^{III} atoms.

The hydrogen bonding and $\pi \cdots \pi$ interactions are summarized in Table 6. In the structure of complex **2**, there is one pairs of intra-molecular C9-H9A····O6 hydrogen bonding and one significant intermolecular C10-H10B····O9 hydrogen bonding interactions in Figure 8. As illustrated in Figure 9, the space skeleton of complex **2** adopts a 3D supra-molecular structure by the hydrogen bonding and $\pi \cdots \pi$ stacking interactions [71–73].

Bond Lengths					
Zn1-O2	2.029(3)	Zn1-O5	2.012(2)	Zn1-O6	1.984(2)
Zn1-N1	2.084(3)	Zn1-N2	2.057(3)	Er1-O1	2.484(3)
Er1-O2	2.318(2)	Er1-O5	2.288(2)	Er1-O7	2.281(2)
Bond Angles					
O1-Er1-O2	64.33(9)	O1-Er1-O5	120.36(9)	O1-Er1-O7	122.83(10)
O1-Er1-O1 ⁱ	67.20(10)	O1-Er1-O2 ⁱ	97.15(9)	O1-Er1-O5 ⁱ	151.02(9)
O1-Er1-O7 ⁱ	74.67(10)	O2-Er1-O5	66.80(9)	O2-Er1-O7	80.66(9)
O1 ⁱ -Er1-O2	97.15(9)	O2-Er1-O2 ⁱ	158.64(10)	O2-Er1-O5 ⁱ	134.51(9)
O2-Er1-O7 ⁱ	102.95(9)	O5-Er1-O7	78.84(9)	O1 ⁱ -Er1-O5	151.02(9)
O5-Er1-O5 ⁱ	68.10(9)	O5-Er1-O7 ⁱ	85.26(9)	O7-Er1-O7 ⁱ	160.81(10)

Table 5. Selected bond lengths (Å) and angles (°) for complex **2**.

Symmetry code: ⁱ: 1 - x, y, 3/2 - z.



Figure 8. View of 1D supra-molecular structure of complex 2 by the hydrogen bonding interactions.



Figure 9. View of 3D supra-molecular structure of complex **2** by the hydrogen bonding and $\pi \cdots \pi$ stacking interactions.

D-H···A	D····A	Н…А	D-Н…А
С9-Н9А…О6	3.553(5)	2.60	162
C10-H10B····O9	3.171(6)	2.33	142
Ring1 Ring2	DCC(Å)	CgI-perp(Å)	CgJ-perp(Å)
Cg1 Cg2	4.289(2)	3.7112(15)	-3.7033(17)

Table 6. Hydrogen bonding (Å, °) and $\pi \cdots \pi$ stacking interactions for complex **2**.

Note: $Cg1 = C12-C13-C13^{i}-C12^{i}-C14^{i}-C14$; $Cg2 = C14-C15-C16-C16^{i}-C15^{i}-C14^{i}$; DCC = distance between ring centroids; CgI-perp = perpendicular distance of Cg(I) from ring J; CgJ-perp = perpendicular distance of Cg(J) from **Ring 1**.

3.5. Fluorescence Properties

Recently, some Salamo-type lanthanide complexes have been reported to perform excellent fluorescence properties [21,24,32]. Zn^{II} components have been applied as lanthanide fluorescence sensitizers.

The emission spectra of H₄L in CH₃OH:CHCl₃ (v/v = 1:1) solution and its corresponding metallic complexes **1** and **2** in methanol solution were measured in detail. As shown in Figure 10, H₄L exhibited an emission peak at ca. 442 nm upon excitation at ca. 350 nm, which could be attributed to the intra-ligand π - π * transition [59]. Whereas, upon excitation at ca. 350 nm, complexes **1** and **2** showed relatively strong emission peaks at about 447 and 448 nm, respectively. These relatively intense emission peaks are bathochromically shifted, which could be assigned to ligand-to-metal charge transfer (LMCT) transitions [62,65].



Figure 10. Emission spectra of H₄L and its complexes 1 and 2.

4. Conclusions

In summary, two new hetero-trinuclear complexes, Zn^{II} -Ho^{III} (1) and Zn^{II} -Er^{III} (2) derived from a bis(salamo) C-shape ligand H₄L were prepared and characterized. Using a controlled design and introduction of methanol molecules, the UV–Vis titration test of complexes **1** and **2** showed that the stoichiometric ratio of ligand to Zn^{II} and Ln^{III} (Ln = Ho and Er) ions are both 1:2:1. Complex **1** has 1D supra-molecular structure formed by the C-H… π stacking interactions, and 2D supra-molecular structure by the hydrogen bonding interactions. Meanwhile, a large 3D supra-molecular structure of complex **2** is also built by hydrogen bonding and $\pi \cdots \pi$ stacking interactions. In addition, the fluorescence spectra of complexes **1** and **2** showed relatively strong emission peaks, and exhibited bathochromic shifts compared to ligand H₄L, respectively.

Author Contributions: W.-K.D. supervised the project and contributed materials/reagents/analysis tools; X.-Y.D., Q.-P.K. and X.-Y.L. performed the experiments.

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