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Structurally characterized homo-trinuclear $Zn^{II DOI: 10.1039/CSNJ00014C}$ hetero-pentanuclear [$Zn^{II}_4Ln^{III}$] complexes constructed from a octadentate bis(Salamo)-based ligand: Hirshfeld surfaces, fluorescent and catalytic properties

Xiao-Yan Li, Quan-Peng Kang, Chang Liu, Yang Zhang, Wen-Kui Dong*

One homo-trinuclear 3d and five novel windmill-type hetero-pentanuclear 3d-4f complexes $[Zn_3(L)(OAc)_2(H_2O)] \cdot CH_2Cl_2$ (1), $[Zn_4(L)_2Sm(NO_3)_2(EtOH)_2]NO_3 \cdot H_2O \cdot 2CHCl_3$ (2), $[Zn_4(L)_2Eu(NO_3)_2(EtOH)_2]NO_3 \cdot C_2H_5OH \cdot 2CHCl_3$ (3), $[Zn_4(L)_2Gd(NO_3)_2(EtOH)_2]NO_3 \cdot C_2H_5OH \cdot 2CHCl_3$ (4), $[Zn_4(L)_2Tb(NO_3)_2(EtOH)_2]NO_3 \cdot C_2H_5OH$ (5) and $[Zn_4(L)_2Dy(NO_3)_2(EtOH)_2]NO_3 \cdot C_2H_5OH \cdot 2CHCl_3$ (6) were synthesized by the reactions of a new bis(Salamo)-based tetraoxime ligand (H₄L) with Zn(OAc)₂·2H₂O and $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Sm, Eu, Gd, Tb and Dy), respectively. The structures of complexes 1-6 were characterized via elemental analyses, FT-IR, UV-Vis spectroscopy and single crystal X-ray crystallography, and their fluorescence properties, catalytic activities and Hirshfeld surface analysis were studied.

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Introduction

Salen-based ligands (R–CH=N–(CH₂)_n–N=CH–R) and their metal complexes have been extensively investigated in modern coordination chemistry for several decades.^{1–} ⁶ A number of homo- and heterometallic complexes have been derived from salen and its analogous ligands.^{7–9} Their metal complexes are used as catalysts,^{10,11} non-linear

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[†] CCDC: numbers 1875819-1875824 for complexes 1-6.

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59 60 optical materials,^{12,13} molecular recognitions,^{14–16} supramolecular architectures,^{12,13} molecular recognitions,^{14–16} supramolecular architectures,^{12,13} biological fields^{19,20} and so forth. Numerous studies on 3d-4f heterometallic complexes have been conducted and extensively studied because some of them exhibit interesting magnetic,^{21–23} luminescent²⁴ and catalytic properties.^{25,26} In particular, the zinc-lanthanide complexes are of interest because of the visible and near-infrared luminescence resulting from lanthanide f-f transitions.^{27,28} The luminescence applications of lanthanides are a consequence of their narrow emission bands, negligible environmental influences, large Stokes shifts and relatively long luminescence lifetimes.^{29,30} However, 3d-4f hetero-nuclear metal complexes with Salamo-like ligands have rarely been reported.^{31,24}

Herein, we designed and synthesized one homotrinuclear Zn^{II} and five novel windmill-type heteropentanuclear $[Zn^{II}_4Ln^{III}]$ (Ln = Sm, Eu, Gd, Tb and Dy) complexes of a new octadentate bis(Salamo)-based tetraoxime ligand (H₄L). In order to increase the fluorescence intensities of its corresponding complexes, two naphthaldehyde groups are introduced into the ligand H₄L. About the proportioning of ligand : metal ion, it is mainly determined by the types of ligands, and different ligands determined the ratio of ligand : metal. Compared with the 3-alkoxy Salamo ligand reported previously, the structures of the 3d-4f complexes formed by the ligand H₄L are not 1:2 ((L)²⁻ :Mⁿ⁺ (n=2, 3)).⁸ Compared with the 3-alkoxy bis(Salamo)-based ligand, the ligand H_4L has no O_6 recognition site. When a small radius 3d metal(II) atom is introduced into the ligand H₄L, the structure of the formed complex does not change. However, when a 4f metal(III) atom having a larger radius is introduced, since there is no 3-alkoxy group in the new ligand H₄L, in order to satisfy the coordination of the 4f metal(III) atom, novel 2 : 5 ((L)⁴⁻ : M^{n+} (n = 2, 3)) windmill-type hetero-pentanuclear 3d-4f metal complexes were formed (Chart 1), instead of common 1 : 3 ((L)⁴⁻ : M^{n+} (n = 2, 3))) complexes²⁴. Fluorescence properties, catalytic activities of these novel 2 : 5 ((L)⁴⁻ : M^{n+} (n = 2, 3)) 3d-4f metal complexes were studied. Hirshfeld surface analysis of complex 1 was discussed.

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Salen-based complexes have been widely used in catalytic fields, and functions of //Canada Condition a lot of important chemical reactions such as reduction, oxidation and polymerization.³¹⁻³³ However, there are few studies on the catalytic activities of Salamo-based metal(II/III) complexes, only the catalytic activities of Cu^{II 34} and Co^{II} ^{10,11} complexes have been studied untill now. The study on catalytic activity of Salamo-based Zn^{II} or [Zn^{II}Ln^{III}] complex has not been reported up to now, which provide a new idea for the application of Salamo-based Zn^{II} and [Zn^{II}Ln^{III}] complexes.



Chart 1 The structural contrast of 3d-4f complexes based on 3-alkoxy Salamo, 3-alkoxy bis(Salamo) and above-mentioned bis(Salamo) ligand H₄L.

Experimental Section

General details.

2-hydroxy-1-naphthaldehyde (99%), 1,2-dibromoethane, 1,2-dimethoxybenzene, TMEDA, n-butyllithium and boron tribromide were purchased from Alfa Aesar and used without further purification. Other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. Elemental analyses for C, H and N were detected with a GmbH VariuoEL V3.00 automatic elemental analysis instrument (Berlin, Germany). Zn^{II}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III} and Dy^{III} were obtained using an IRIS ER/S-WP-1 ICP atomic emission spectrometer (Berlin, Germany). Melting points

were obtained by a microscopic melting point apparatus made by Beijing¹¹Taike^{7/C9NJ00014C} Instrument Company Limited. IR spectra (400–4000 cm⁻¹) were determined by a Vertex 70 FT-IR spectrophotometer (Bruker, Billerica, MA, USA), with samples prepared as KBr pellets. UV-vis absorption spectra were recorded on a Shimadzu UV-3900 spectrometer (Shimadzu, Japan). ¹H NMR spectra were determined by German Bruker AVANCE DRX-400/600 spectroscopy. MS spectrum was obtained on a Bruker Daltonics APEX-II 47e spectrometer. The powder X-ray diffractions (PXRD) were recorded by a RIGAKU-DMAX2500 X-ray diffractometer using Cu K α radiation (λ = 0.154 nm) at a scanning rate of 5° / min for 20 ranging from 5° to 50°. X-ray single crystal structure determinations for complexes **1-6** were carried out on a Bruker APEX-II CCD. Fluorescence spectra were recorded on a F-7000 FL spectrophotometer.

X-ray crystallographic analysis.

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X-ray single crystal diffraction data of complexes **1-6** were recorded using a Bruker APEX-II CCD diffractometer with a monochromatic Mo-K α radiation ($\lambda = 0.71073$ Å) source at 173(2), 153(2), 153(2), 153(2), 153(2) and 296(2) K, respectively. The LP factor and semi-empirical absorption were using SADABS. The single crystal structures were solved via the direct methods (SHELXS-2016),³⁵ and all the hydrogen atoms were included at the calculated positions and constrained to ride on their parent atoms. All non-hydrogen atoms were refined anisotropically via a full-matrix least-squares procedure on F^2 with SHELXL-2016.³⁶ Data collection and refinements of these complexes were listed in Table 1.

Complex	1	2	3
Empirical formula	$C_{39}H_{36}Zn_{3}N_{4}O_{13}Cl_{2} \\$	$C_{74}H_{68}SmZn_4N_{11}O_{28}Cl_6$	$C_{76}H_{72}EuZn_4N_{11}O_{28}Cl_6$
Formula weight	1035.73	2183.92	2213.58
T (K)	173(2)	153(2)	153(2)
Wavelength (Å)	0.71073	0.71073	0.71073

Table 1 X-ray crystallographic data for complexes 1-6.

Crystal system	Triclinic	Monoclinic	View Article Onlin Monoclinic DOI: 10.1039/C9NJ000140
Space group	P-1	C12/c1	C12/c1
<i>a</i> (Å)	15.7572(9)	16.8229(9)	16.8834(9)
<i>b</i> (Å)	16.4079(9)	23.2495(12)	23.1409(12)
<i>c</i> (Å)	16.4852(9)	24.2036(14)	24.3047(12)
α (°)	90.038(2)	90	90
β (°)	104.887(2)	108.673(2)	108.679(2)
γ (°)	97.172(2)	90	90
V (Å ³)	4084.5(4)	8968.3(9)	8995.6(8)
Ζ	4	4	4
$D_{\text{calc}}(g \cdot \text{cm}^{-3})$	1.684	1.617	1.634
Absorption coefficient (mm ⁻¹)	1.950	1.959	1.999
F (000)	2104	4388	4456
Crystal size (mm)	0.220 x 0.190 x 0.180	$0.260\times0.250\times0.220$	$0.260\times0.220\times0.190$
θ Range (°)	2.542 to 25.009	2.604-27.582	2.020-27.691
Index ranges	$-18 \le h \le 14$	$-21 \le h \le 21$	$-20 \le h \le 21$
	$-19 \le k \le 19$	$-30 \le k \le 30$	$-30 \le k \le 20$
	$-19 \le l \le 19$	$-31 \le l \le 27$	$-31 \le l \le 31$
Reflections collected/unique	30142/14368	38065/10314	40357/10453
	$[R_{int} = 0.0402]$	$[R_{int} = 0.0445]$	$[R_{int} = 0.0646]$
Completeness to θ	99.6% (<i>θ</i> = 25.010)	99.6% (<i>θ</i> = 25.242)	99.8% (<i>θ</i> = 25.242)
Data/restraints/parameters	14368 / 25 / 1112	10314 / 149 / 671	10453 / 101 / 675
GOF	1.016	1.066	1.053
Final R ₁ , wR ₂ indices	0.0483, 0.1233	0.0501, 0.1291	0.0528, 0.1213
R ₁ , wR ₂ indices (all data)	0.0691, 0.1347	0.0714, 0.1411	0.0837, 0.1342
Largest diff. peak and hole	1.319 and -1.222 e.Å ⁻³	1.453 and -0.872 e.Å $^{-3}$	$1.065 \text{ and } -0.635 \text{ e.}\text{Å}^{-3}$

Complex	4	5	6
Empirical formula	$C_{76}H_{72}GdZn_4N_{11}O_{28}Cl_6$	$C_{74}H_{70}TbZn_4N_{11}O_{28}$	$C_{76}H_{72}DyZn_4N_{11}O_{28}Cl_6$
Formula weight	2218.87	1981.81	2224.12
T (K)	153(2)	153(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C12/c1	P121/c1	C12/c1
<i>a</i> (Å)	16.9752(18)	13.542(3)	16.9466(9)
<i>b</i> (Å)	23.090(2)	28.886(7)	23.0127(12)
<i>c</i> (Å)	24.837(3)	19.183(4)	24.9394(15)
α (°)	90	90	90
β (°)	111.300(2)	96.675(4)	111.278(2)
γ (°)	90	90	90
V (Å ³)	9069.8(16)	7453(3)	9063.0(9)
Ζ	4	4	4

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$D_{\text{calc}}(\mathbf{g}\cdot\mathbf{cm}^{-3})$	1.625	1.766	View Article Online 1.630 DOI: 10.1039/C9NJ000140
Absorption coefficient (mm ⁻¹)	2.022	2.300	2.116
F (000)	4460	4000	4468
Crystal size (mm)	$0.220\times0.190\times0.180$	$0.250\times0.190\times0.180$	$0.260\times0.220\times0.190$
θ Range (°)	2.492 to 27.642	1.280-25.000	2.491 to 27.656
Index ranges	$-20 \le h \le 22$	$-16 \le h \le 16$	$-21 \le h \le 22$
	$-30 \le k \le 30$	$-24 \le k \le 34$	$-29 \le k \le 30$
	$-32 \le l \le 20$	$-22 \le l \le 22$	$-32 \le l \le 27$
Reflections collected/unique	34092/10510	33737/12830	40263/10506
	$[R_{int} = 0.0786]$	$[R_{int} = 0.0783]$	$[R_{int} = 0.0564]$
Completeness to θ	99.8% (<i>θ</i> = 25.242)	97.8% (θ = 25.000)	99.8% (<i>θ</i> = 25.242)
Data/restraints/parameters	10510 / 287 / 733	12830 / 72 / 1090	10506 / 189 / 733
GOF	1.115	1.059	1.049
Final R ₁ , wR ₂ indices	0.0846, 0.1698	0.0877, 0.2247	0.0492, 0.1196
R ₁ , wR ₂ indices (all data)	0.1328, 0.192	0.1249, 0.2660	0.0744, 0.1298
Largest diff. peak and hole	$1.425 \text{ and } -1.198 \text{ e.Å}^{-3}$	$1.635 \text{ and } -1.483 \text{ e.Å}^{-3}$	1.138 and -0.559 e.Å $^{-3}$

Synthesis of the bis(Salamo) ligand (H₄L).

The reaction steps of the bis(Salamo)-based tetraoxime ligand (H_4L) can be seen from Scheme 1. 2,3-Dihydroxybenzene-1,4-dicarbaldehyde, 1,2-bis(aminooxy)ethane and 2-[O-(1-ethyloxyamide)]oxime-2-naphthol were prepared according to a similar method.^{37,38}



Scheme 1 Synthetic route to the bis(salamo)-based tetraoxime ligand H₄L.

To an ethanol solution (20 mL) of 2,3-dihydroxybenzene-1,4-dicarbaldehyde (332.3 mg, 2.0 mmol) was added to an ethanol solution (30 mL) of 2-[O-(1-ethyloxyamide)]oxime-2-naphthol (985.1 mg, 4 mmol). The solution was stirred at 55 °C for 8 h, cooling to room temperature, the precipitation was filtered and

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59 60 washed with n-hexane to obtained yellow powder. Yield: 1083.4 mg, 87%. mpp: $\pm 98^{\frac{1}{2}}/(\frac{1}{2})$ 200 °C. Anal. Calc. for C₃₄H₃₀N₄O₈: C, 65.59; H, 4.86; N, 9.00%. Found: C, 65.65; H, 4.94; N, 8.92%. ¹H NMR (400 MHz, CDCl₃) δ 10.82 (s, 2H), 9.70 (s, 2H), 9.17 (s, 2H), 8.25 (d, *J* = 2.5 Hz, 2H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.80 – 7.72 (m, 4H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 9.0 Hz, 2H), 6.75 (s, 2H), 4.56 (s, 8H). Mass Spectrometry (MS) *m/z*: 621.18 [H₄L - H]⁻. (Fig. S1). IR (KBr, cm⁻¹): 3435 (m), 2995 (m), 2833 (m), 1603 (m), 1239 (m), 1173 (m). UV-vis (CHCl₃/CH₃CH₂OH 1:1 *v/v*): λ_{max} (ε_{max}): 302, 313, 341 and 355 nm.

Preparation of complexes 1-6.

Complex 1 was synthesized by the reaction of H_4L with $Zn(OAc)_2$. Complexes 2-6 were synthesized by the reactions of H_4L with $Zn(OAc)_2$ and $Ln(NO_3)_3$ ($Ln^{III} = Sm^{III}$, Eu^{III} , Gd^{III} , Tb^{III} and Dy^{III}), respectively (Scheme 2).



Scheme 2 Syntheses of complexes 1–6.

 $[Zn_3(L)(OAc)_2(H_2O)] \cdot CH_2Cl_2$ (1) A solution of 6.58 mg (0.03 mmol) of $Zn(OAc)_2 \cdot 2H_2O$ in CH_3CH_2OH (3.0 mL) was added to the solution of H_4L (6.23 mg, 0.01 mmol) in CH_2Cl_2 (4 mL) and stirred for 15 min, then filtered the solution. Three

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weeks later, diffraction quality yellow acicular crystals were obtained **OP**: 1910; View Article Online evaporation of the solution in open atmosphere.

 $[Zn_4(L)_2Sm(NO_3)_2(EtOH)_2]NO_3 H_2O 2CHCl_3$ (2) A solution of 8.77 mg (0.04 mmol) of $Zn(OAc)_2 H_2O$ in CH_3CH_2OH (2.0 mL) was added to a solution of 12.45 mg (0.02mmol) of H_4L in CHCl_3 (4 mL), The color of the mixed solution instantly changes from light yellow to dark yellow, a solution of 4.44 mg (0.01 mmol) $Sm(NO_3)_3 H_2O$ in CH_3CH_2OH (2 mL) was then added. The mixture was stirred for 15 minutes and then filtered at room temperature. Two weeks later, some yellow block crystals suitable for X-ray diffraction were formed and filtered carefully. Complexes **3**, **4**, **5** and **6** were prepared by a similar procedure as for complex **2**.

Complex 1, yellow acicular crystals. Yield: 5.70 mg, 55%. Anal. calc. for $C_{39}H_{36}Zn_3N_4O_{13}Cl_2$: C, 45.22; H, 3.50; N, 5.41; Zn, 18.94%. Found: C, 45.28; H, 3.56; N, 5.32; Zn, 19.02%. IR (KBr, cm⁻¹): 2996 (m), 2837 (m), 1600 (m), 1184 (m), 1247 (m), 1184 (m). UV-Vis (CHCl₃/CH₃CH₂OH 1:1 ν/ν), λ_{max} (nm) (ε_{max}): 318 and 385 nm.

Complex **2**, yellow block crystals. Yield: 11.56 mg, 62%. Anal. calc. for $C_{74}H_{68}SmZn_4N_{11}O_{28}Cl_6$: C, 40.70; H, 3.14; N, 7.05; Zn, 11.98; Sm, 6.88%. Found: C, 40.78; H, 3.21; N, 6.97; Zn, 12.02; Sm, 6.91%. IR (KBr, cm⁻¹): 3341 (m), 2996 (m), 2836 (m), 1612 (m), 1393 (m), 1184 (m), 1244 (m), 1175 (m). UV-Vis (CHCl₃/CH₃CH₂OH 1:1 ν/ν), λ_{max} (nm) (ε_{max}): 326 and 381 nm.

Complex **3**, yellow block crystals. Yield: 10.82 mg, 58%. Anal. calc. for $C_{76}H_{72}EuZn_4N_{11}O_{28}Cl_6$: C, 41.24; H, 3.28; N, 6.96; Zn, 11.81; Eu, 6.86%. Found: C, 41.29; H, 3.32; N, 7.03; Zn, 11.86; Eu, 6.92%. IR (KBr, cm⁻¹): 3442 (m), 2990 (m), 2834 (m), 1613 (m), 1394 (m), 1241 (m), 1179 (m). UV-Vis (CHCl₃/CH₃CH₂OH 1:1 ν/ν), λ_{max} (nm) (ε_{max}): 325 and 382 nm.

Complex **4**, yellow block crystals. Yield: 9.17 mg, 49%. Anal. calc. for C₇₆H₇₂GdZn₄N₁₁O₂₈Cl₆: C, 41.14; H, 3.27; N, 6.94; Zn, 11.78; Gd, 7.09%. Found: C, 41.21; H, 3.31; N, 6.87; Zn, 11.84; Gd, 7.12%. IR (KBr, cm⁻¹): 3442 (m), 2994 (m),

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Complex **5**, yellow block crystals. Yield: 12.68 mg, 66%. Anal. calc. for $C_{74}H_{70}TbZn_4N_{11}O_{28}$: C, 44.85; H, 3.56; N, 7.77; Zn, 13.20; Tb, 8.02%. Found: C, 44.92; H, 3.62; N, 7.71; Zn, 13.26; Tb, 8.08%. IR (KBr, cm⁻¹): 3439 (m), 2996 (m), 2835 (m), 1609 (m), 1395 (m), 1244 (m), 1177 (m). UV-Vis (CHCl₃/CH₃CH₂OH 1:1 ν/ν), λ_{max} (nm) (ε_{max}): 322 and 382 nm.

Complex **6**, yellow block crystals. Yield: 11.63 mg, 62%. Anal. calc. for $C_{76}H_{72}DyZn_4N_{11}O_{28}Cl_6$: C, 41.04; H, 3.26; N, 6.93; Zn, 11.76; Dy, 7.31%. Found: C, 41.09; H, 3.32; N, 6.87; Zn, 11.81; Dy, 7.38%. IR (KBr, cm⁻¹): 3439 (m), 2994 (m), 2834 (m), 1612 (m), 1399 (m), 1243 (m), 1179 (m). UV-Vis (CHCl₃/CH₃CH₂OH 1:1 ν/ν), λ_{max} (nm) (ε_{max}): 319 and 382 nm.

Results and discussion

IR spectra.

The binding modes were determined by comparing several intense bands of the ligand H_4L and its complexes in the IR spectra (Fig. 1). The stretching band of the free ligand H_4L is observed at 1603 cm⁻¹ correspond to the stretching vibrations of the C=N bonds while complexes **1-6** are observed at 1609-1617 cm⁻¹. The spectral changes of complexes **1-6** shows that H_4L has coordinated with Zn^{II} atoms.^{39,40} In addition, the band at 1239 cm⁻¹ in the spectrum of the free ligand H_4L can be assigned to a typical Ar–O stretching band. In complexes **1-6**, the bands shifted to lower frequencies by *ca*. 5-10 cm⁻¹, indicating that the M-O bonds are formed between the metal(II/III) atoms and oxygen atoms of phenolic groups.⁴¹ The O–H stretching band of the free ligand H_4L was observed at *ca*. 3435 cm⁻¹ that belongs to the phenolic hydroxyl group, whereas complexes **2-6** shows a stretching band at *ca*. 3441, 3442, 3442, 3439 and 3439 cm⁻¹ that belongs to coordinated methanol molecules or ethanol molecules.⁴² Meanwhile, these bands at 1393, 1394, 1396, 1395 and 1399 cm⁻¹ of complexes **2-6** can be assigned to nitrate ions, indicating the nitrates are contained in

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Fig. 1 IR spectra of H_4L and its corresponding complexes 1–6.

UV-vis spectra.

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The UV–Vis absorption spectra of H₄L with its complexes **1-6** in chloroform/ethanol solutions (v:v = 1:1) are shown in Fig. 2.

In the UV-vis titration experiment of complex 1, the color of a solution of H_4L $(1.0 \times 10^{-5} \text{ M})$ gradually changed from colorless to light yellow upon addition of a solution of Zn^{II} acetate (1.0 × 10⁻³ M). The absorption spectrum of H₄L mainly shows four relatively strong absorption peaks at ca. 302, 313, 341 and 355 nm. The absorption peaks at *ca*. 302 and 313 nm can be assigned to the π - π * transitions of the naphthalene rings.⁴⁴ The other two absorption peaks at *ca*. 341 and 355 nm can be assigned to the intra-ligand π - π * transition of the oxime group.⁴⁵ Compared with the free ligand H_4L , the gradual addition of Zn^{II} ions brought changes to the absorption peaks, these peaks gradually disappeared with the emergence of new peaks at ca. 318 and 385 nm, which indicating the coordination of Zn^{II} atoms with the (L)⁴⁻ units.⁴⁶ However, when the added amount of the Zn^{II} ions reached 3.0 equiv, the absorbance of the solution became stable, keep addition of the Zn^{II}, the absorbance of the solution was not changed, which indicates 1:3 reaction stoichiometry between Zn^{II} and H₄L.

In the UV-vis titration experiment of complex 2, the spectrum of complex 1 showed absorption peaks at 318 and 385 nm. However, upon addition of 1 equiv of

 Sm^{III} ions, these peaks gradually disappeared with the emergence of new peaks at $gg_{9/C9NJ00014C}^{View Article Online}$ 326 and 381 nm, which indicating the coordination of Sm^{III} atoms with the $[Zn_3(L)]^{2+}$ units.⁴⁷ The titration curves also clearly indicated that the stoichiometry between Sm^{III} and $[Zn_3(L)]^{2+}$ was 1:2. As the UV–Vis absorption spectra of complexes **3–6** are alike, which obtain the same results.





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Fig. 2 (a) UV-Vis spectra of the changes in the H_4L upon addition of $Zn(OAc)_2 \cdot 2H_2O$; (b) UV-Vis spectra of the changes in complex 1 upon addition of (b) $Sm(NO_3)_3 \cdot 6H_2O$; (c) $Eu(NO_3)_3 \cdot 6H_2O$; (d) $Gd(NO_3)_3 \cdot 6H_2O$; (e) $Tb(NO_3)_3 \cdot 6H_2O$; (f) $Dy(NO_3)_3 \cdot 6H_2O$.

Description of the crystal structure.

The structures of complexes 1–6 were determined by single-crystal X-ray diffractions. Selected bond lengths and angles are given in Tables S1–2.

Crystal structure description of complex 1.

Complex 1 crystallizes in the triclinic crystal system, space group P-1, and each unit cell comprises two crystallographically independent and chemically equivalent homo-trinuclear complexes (Fig. 3). Complex 1 consists of three Zn^{II} atoms, one (L)^{4–} unit, two coordinated water molecules and two μ -acetato ions. Meanwhile, Zn1 and Zn2 atoms are situated in the N₂O₂ coordination cavities, Zn3 is respectively bridged by Zn1 and Zn2 through two deprotonated phenoxo donors O17 and O18 and two syn-syn bridging acetate ions in a μ_2 - η^1 : η^1 fashion.⁴⁸ Zn1 and Zn2 atoms presenting a ZnN₂O₃ coordination sphere, and assumed distorted trigonal bipyramidal coordination

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 geometries ($\tau_1 = 0.82$ and $\tau_2 = 0.74$).⁴⁹ However, Zn3 atom presenting Pal: ZnO₃/C9NJ00014C coordination sphere, and assumed distorted square-pyramidal geometry ($\tau_3 = 0.046$).⁴⁹

In the crystal structure of complex **1**, there are seven intramolecular hydrogen bonds (O13–H13D···O4, O13–H13C···O10, O23–H23B···O24, O23–H23A···O14, C12–H12B···O5, C23–H23C···O8 and C50–H50B···O20).^{50,51} In addition, complex **1** molecule formed a 2D supramolecular structure by intermolecular hydrogen bonds (C16–H16···O16, C51–H51A···O10 and C54–H54···O12) and C22-H22B··· π interactions (C22-H22B···Cg1 (Cg1=C63-C64-C69-C70-C71-C72)) (Fig. 4).⁵²



Fig. 3 (a) Molecule structure of complex **1** (hydrogen atoms and solvent molecules are omitted for clarity). (b) Coordination polyhedrons for Zn^{II} atoms of complex **1**.



Fig. 4 (a) View of the intramolecular hydrogen bonding interactions of complex 1. (b) View of an infinite 2D supramolecular structure of complex 1.

Crystal structures description of windmill-type complexes 2, 3, 4 and 6.

As depicted in Fig. 5, the X-ray structure of complex 2 revealed a hetero-pentanuclear structure, crystallizing in the monoclinic system, space group C12/c1. The corresponding hydrogen bonds of complexes 1–6 are summarized in Table S2.





Fig. 5 (a) Molecule structure of complex 2 (hydrogen atoms and solvent molecules are omitted for clarity). (b) Coordination polyhedrons for Zn^{II} and Sm^{III} atoms of complex 2. (c) View of the dihedral angles between the basal planes Zn1-O4-Sm1 and Zn2-O8-Sm1 of complex 2.

Complex 2 consists of four Zn^{II} atoms, one Sm^{III} atom, two (L)⁴⁻ units, two coordinated ethanol molecules and two nitrate groups, one crystalling water molecule, two trichloromethane molecules and one nitrate group. The Zn^{II} atoms presenting ZnN₂O₃ coordination sphere. The Zn1 and Zn2 (Zn1^{#1} and Zn2^{#1}) atoms are all made of the N₂O₂ sites of the salamo moieties and one coordinated nitrate group, which assumed a distorted trigonal bipyramidal coordination geometry ($\tau_1 = 0.66$ and $\tau_2 =$ 0.71).⁴⁹ The Sm^{III} atom exhibits a SmO₈ coordination sphere, which is made of eight phenoxo donors (O1, O4, O5, O8, O1^{#1}, O4^{#1}, O5^{#1} and O8^{#1}) of two completely deprotonated (L)4- units, while the central SmIII atom is octa-coordinated with a distorted square antiprism geometry.⁵³ Within complex 2, the distances between the metallic centers are $Zn1\cdots Sm1 = 3.564$ and $Zn2\cdots Sm1 = 3.578$ Å. Meanwhile, the

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 angle between the plane Zn1-O4-Sm1 and the plane Zn2-O8-Sm1 is $89.887(3)^{\circ}$ (Fig.)/C9NJ00014C 5 (c)). Complex 2 forms a novel 2 : 5 ((L) : M) windmill-type hetero-pentanuclear 3d-4f complex, which is completely different from the structures of 1 : 2, 1 : 3 ((L) : M) reported earlier in the Salamo-type 3d-4f complexes.^{8,24}



Fig. 6 (a) View of the intramolecular hydrogen bonding interactions of complex **2**. (b) View of an infinite 2D supramolecular structure of complex **2**.

In complex **2**, there are four pairs of significant intramolecular hydrogen bonds (C13–H13A···O11, C24–H24···O7, C33–H33···O10 and C36–H36C···O9) (Fig. 6 (a)).^{50,51} In addition, complex **2** molecules formed a 2D supramolecular structure by intermolecular hydrogen bonds (Fig. 6 (b)).⁵²

Complexes 2, 3, 4 and 6 are isostructural, therefore only the crystal structure of complex 2 was described. The crystal structures of complexes 3, 4 and 6 are shown in Figs. 7, 9 and 11, respectively. As shown in Figs. 8, 10 and 12, there are some intramolecular hydrogen bonds interactions, and the infinite 2D supramolecular networks are formed by intermolecular C–H…O hydrogen bond interactions in complexes 2, 3, 4 and 6.5^{52}





Fig. 7 (a) Molecule structure of complex 3 (hydrogen atoms and solvent molecules are omitted for clarity). (b) Coordination polyhedrons for Zn^{II} and Eu^{III} atoms of complex 3.





Fig. 8 (a) View of the intramolecular hydrogen bonding interactions of complex **3**. (b) View of an infinite 2D supramolecular structure of complex **3**.



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Fig. 9 (a) Molecule structure of complex **4** (hydrogen atoms and solvent molecules are omitted for clarity). (b) Coordination polyhedrons for Zn^{II} and Gd^{III} atoms of complex **4**.







Fig. 10 (a) View of the intramolecular hydrogen bonding interactions of complex 4.(b) View of an infinite 2D supramolecular structure of complex 4.





Fig. 11 (a) Molecule structure of complex 6 (hydrogen atoms and solvent molecules are omitted for clarity). (b) Coordination polyhedrons for Zn^{II} and Dy^{III} atoms of complex 6.





Fig. 12 (a) View of the intramolecular hydrogen bonding interactions of complex 6. (b) View of an infinite 2D supramolecular structure of complex 6.

Crystal structure description of windmill-type complex 5.

Complex 5 crystallizes in the monoclinic crystal system, space group $P12_1/c1$. X-ray crystallography clearly shows the formation of complex 5. Different from complexes 1, 2, 3, 4 and 6, it consists of four Zn^{II} atoms, one Tb^{III} atom, two (L)⁴⁻ units, two coordinated ethanol molecules, two nitrate groups and one crystalling ethanol molecule, one nitrate group (Fig. 13).

The Zn^{II} atoms are also located in the N₂O₂ sites, and four Zn^{II} atoms are also penta-coordinated. Zn1 and Zn2 atoms assumed distorted square-pyramidal geometries ($\tau_1 = 0.37$ and $\tau_2 = 0.44$). Zn3 and Zn4 atoms assumed distorted trigonal bipyramidal coordination geometries ($\tau_3 = 0.62$ and $\tau_4 = 0.56$). The Tb^{III} atom is also located in the O8 site that consists of eight phenoxy oxygen atoms, forming the geometry of a distorted square antiprism.

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N4

Zn4

(a)





Fig. 13 (a) Molecule structure of complex 5 (hydrogen atoms and solvent molecules are omitted for clarity). (b) Coordination polyhedrons for ZnII and TbIII atoms of complex 5.





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Fig. 14 (a) View of the intramolecular hydrogen bonding interactions of complex 5.(b) View of an infinite 2D supramolecular structure of complex 5.

The main interactions in complex **5** are listed in Table S2, some of intramolecular hydrogen bonds (C2–H2···O13, C2–H2···O20, C22–H22A···O26, C33–H33···O12, C33–H33···O17, C45–H45···O2, C47–H47A···O22, C56–H56A···O18, C56–

H56A…N3, C57–H57A…N4, C58–H58…O7, C69–H69A…O8, O27–H27A…O2^{thew Article Online} and O26–H26B…O19) are formed.^{50,51} Besides, four intermolecular hydrogen bonds (C55–H55…O25, C39–H39…O17, C46–H46B…O22 and C55–H55…O25) in complex **5**, which adopts a 2D supramolecular structure (Fig. 14).⁵²

Hirshfeld surface analysis.

 The Hirshfeld surface analysis⁵⁴ provides a three-dimensional picture of close contacts in a crystal, and these contacts can be given in a fingerprint plot. The Hirshfeld surface of complex 1 has been mapped over (a) d_{norm} , (b) *shape index* and (c) *curvedness* in Fig. 15. Other complexes did not undergo Hirshfeld surfaces analyses due to the presence of rare earth ions.

2D fingerprint plots are important intermolecular interactions appear as distinct spikes.⁵⁵ The O···H/H···O intermolecular interactions are distinct spikes in Fig. 16. The O···H interactions are expressed by a spike in the bottom left (donor) area of the fingerprint plot, the H···O interactions are expressed by a spike in the bottom right (acceptor) region of the fingerprint plot. The contribution of different interactions to the Hirshfeld surface has been given in Fig. 16. The proportion of C···H/H···C, Cl···H/H···Cl, O···H/H···O, and H···H interactions comprises 16.0%, 11.7%, 19.2% and 41.6% of the total Hirshfeld surfaces for each molecule of complex **1**, respectively. The main intermolecular interactions of total Hirshfeld surface is belonged to H···H interaction.



Fig. 15 Hirshfeld surface mapped with (a) d_{norm} ; (b) *Shape index*; (c) *Curvedness* for complex 1.

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Fig. 16 Fingerprint plot of complex 1: full and resolved into full and resolved into $C \cdots H$, $C I \cdots H$, $O \cdots H$ and $H \cdots H$ contacts showing the percentages of contacts contributed to the total Hirshfeld surface area of molecule.

Fluorescent properties.

The ligand (H₄L) and its corresponding complexes **1-6** were excited at 385 nm (λ_{ex}) respectively (Fig. 17). The emission spectrum of the ligand exhibits a broad emission band, and the emission maximum at 454 nm, which can be assigned to the π - π * electronic transitions in the ligand.⁵⁶ Compared with H₄L, the absorption peaks of complexes 1 and 3-6 are bathochromically-shifted, which is may originate from the ligand-to-metal-charge transfer (LMCT) emission,57 The order of fluorescence intensity is $H_4L > [Zn^{II}] > [Zn^{II}_4Gd^{III}] > [Zn^{II}_4Dy^{III}] > [Zn^{II}_4Eu^{III}] > [Zn^{II}_4Tb^{III}]$. The fluorescence intensity of Zn^{II} complex is stronger than that of $[Zn^{II}_4Ln^{III}]$ (Ln = Eu, Gd, Tb and Dy) complexes, which may be due to the decrease of conjugate plane due to the coordination of Ln (Sm, Eu, Gd, Tb and Dy) atoms. In addition, one can observe several visible emission bands from complex 2 containing Sm^{III} as lanthanide ion at 562, 598 and 645 nm (Fig. 17). These peaks correspond to the ${}^{4}G_{5/2}$ - ${}^{6}H_{5/2}$, ${}^{4}G_{5/2}$ - ${}^{6}H_{7/2}$ and ${}^{4}G_{5/2}$ - ${}^{6}H_{9/2}$ transitions, respectively. The transition at ${}^{4}G_{5/2}$ - ${}^{6}H_{7/2}$ belongs to the magnetic dipole transition, and the much stronger intensity of ${}^{4}G_{5/2}$ ⁶H_{9/2} is assigned to the electric dipole transition.^{58,59} Meanwhile, a broad band at 439 nm upon excitation at 385 nm, which is assigned to the π - π * transitions of the ligand H₄L. The Sm^{III} ion emission was sensitized by the $[Zn_3(L)]^{2+}$ unit and ligand-to-metal energy transfer (LMET) occurred efficiently in complex 2.60 In other words, the appearance of the characteristic emission bands reveals that the ligand H₄L could act as an antenna group, sensitizing Sm^{III}-based luminescence.⁶¹ Complexes **3-6** does not

show any sharp bands from lanthanides. The energy transfer processes of complex $2^{\text{View Article Online}}_{3/CPNJ00014C}$ the energy levels of the relevant electronic states of the ligand H₄L were investigated (Fig. 18). H₄L is transited from the ground state to the singlet excited state (S1) via absorbing energy, and the energy of the (S1) excited state is transferred to its triplet level (T1) through intersystem crossing (ISC), then to the lowest excited state ${}^{4}G_{5/2}$ of the Sm^{III} ion. The final energy is transferred to the ground state of the Sm^{III} ion in the form of fluorescence released, resulting in the characteristic fluorescence emission of the Sm^{III} ion.





Fig. 17 Emission spectra of the free ligand H_4L and its corresponding complexes in CH₃CN. ((a) Complexes 1, 3, 4, 5 and 6. (b) Complex 2.)



Fig. 18 Energy transfer processes for complex 2.

Catechol oxidase studies and kinetics.

The PXRD data at room temperature on the samples of complexes **1–6** well matched the calculated results from single crystal data (Fig. S2). Catecholamine activities of

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View Article Online complexes and 2 were studied. The most commonly substrate9/C9NJ00014C 1 3,5-di-tert-butylcatechol (3,5-DTBC) was used as substrate because of the low reduction potential for the quinone-catechol couple, which makes it easy to be oxidized into 3,5-di-tert-butylquinone (3,5-DTBQ).⁶² Besides, the reason being that its oxidized product, 3,5-ditert-butylquinone (3,5-DTBO), has a characteristic absorption band at around 405 nm ($\varepsilon = 1900 \text{ M}^{-1} \cdot \text{cm}^{-1}$) in MeCN (Scheme 3).^{10,63} The catechol oxidation reaction of complexes 1 and 2 with 3,5-DTBCH₂ were evaluated by means of UV-vis spectroscopy. Kinetic studies of the catecholase activities of the catalysts were determined by treating 2.5×10^{-5} M solutions of complexes and monitoring the increase of the concentration of 3,5-DTBC, ranging from 2.5×10^{-3} M to 2.5×10^{-2} M.



Fig. 19 Changes observed in UV-vis spectra of **1** in MeCN (conc. 2.5×10^{-5} M) upon addition of 100-fold 3,5-DTBC (2.5×10^{-3} M). The inset shows the plot of the difference in absorbance (ΔA) versus time to evaluate the initial rate of the catalytic oxidation of 3,5-DTBC by **1** in MeCN.

Solution of complexes 1 and 2 (2.5×10^{-5} M) were treated with 100 equivalents of 3,5-DTBCH₂ (2.5×10^{-3} M) under aerobic conditions in MeCN, with the mixture measured at 5 min interval (Fig.s 19 and 20). Upon addition of 3,5-DTBC the spectral

run done immediately exhibits increment of the absorbance nearly above that band^{fiew Article Online} Since it is well established that 3,5-DTBQ shows band maxima at 405 nm in MeCN, the experiment unequivocally proves oxidation of 3,5-DTBC to 3,5-DTBQ catalyzed by complexes **1** and **2**. The kinetics of the 3,5-DTBC oxidation was determined by monitoring the increase of the product 3,5-DTBQ. To investigate the reaction rate between 3,5-DTBC and complex **1** (or **2**), the difference in absorbance $\triangle A$ at 405 nm was plotted as time to obtain an initial value.



Scheme 3 Catalytic oxidation of 3,5-DTBC to 3,5-DTBQ in air-staturated CH₃CN solvent.



Fig. 20 Changes observed in UV-vis spectra of **2** in MeCN (conc. 2.5×10^{-5} M) upon addition of 100-fold 3,5-DTBC (2.5×10^{-3} M). The inset shows the plot of the difference in absorbance (ΔA) versus time to evaluate the initial rate of the catalytic oxidation of 3,5-DTBC by **2** in MeCN.

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Based on the Michielis-Menten dynamic model, the relationship between Miew Article Online Doi: 10.1039/C9NJ00014C substrate rate and concentration of substrate were analyzed (Fig. 21),⁶⁴ and the Lineweaver-Burk (double reciprocal) plot were obtained (Fig. 22). Meanwhile, the values of the Michaelis binding constant (K_m) , maximum velocity (V_{max}) , and rate constant for dissociation of substrates (turnover number or k_{cat}) were calculated (Table 2). The values of k_{cat} are 3.52×10^2 and 4.54×10^2 h⁻¹ for complexes 1 and 2, respectively. Compared with the previously reported Salamo-based complexes, the catalytic properties of complexes 1 and 2 are better.^{10,11} The catecholase model complexes have been reported to relate to several factors such as lability of exogenous ligands, metal-metal distance, electrochemical properties and coordination configuration.⁶⁵ A probable explanation for the catecholase catalytic reactivity of complexes 1, 2 and previously reported Salamo-based complexes was mainly related to its coordination configuration and environment. The five-coordinated Zn^{II} atom, eight-coordinated Sm^{III} atom and five-coordinated Co^{II} atom^{10,11} have saturated vacancies and can bind to catechol matrix. At the same time, the coordination environment of Zn^{II}, Sm^{III} and Co^{II 10,11} atoms may also be a factor affecting the catalytic ability.



Fig. 21 Plot of initial rates versus substrate concentration for the oxidation reaction catalyzed by complexes 1 and 2 in MeCN.

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Fig. 22 Lineweaver-Burk oxidation reaction plot for complexes 1 and 2 in MeCN.

 Table 2 Kinetic parameters for the oxidation of 3,5-DTBC catalyzed by complexes 1

 and 2.

Complex	$V_{\rm max} \left({ m M} \cdot { m s}^{-1} ight)$	$K_{\mathrm{M}}\left(\mathrm{M} ight)$	$K_{\rm cat}$ (h ⁻¹)	
1	9.49×10 ⁻⁵	3.93×10 ⁻³	3.52×10 ²	
2	1.20×10^{-4}	5.51×10 ⁻³	4.54×10^{2}	

Conclusion

One homo-trinuclear 3d and five novel windmill-type hetero-pentanuclear 3d-4f complexes with a flexible bis(Salamo)-type ligand H₄L have been prepared and structurally characterized. In complex 1, Zn1 and Zn2 atoms presenting a ZnN_2O_3 coordination sphere, and assumed distorted trigonal bipyramidal coordination geometries ($\tau_1 = 0.82$ and $\tau_2 = 0.74$). However, Zn3 atom presenting a ZnO₅ coordination sphere, and assumed a distorted square-pyramidal geometry ($\tau_3 = 0.046$). In complexes 2–6, The Ln^{III} atom exhibits a LnO₈ coordination sphere, and assumed a distorted square antiprism geometry. The fluorescence spectrum of complex 2 displayed three typical emission peaks at ca. 562, 598 and 645 nm upon excitation at ca. 385 nm and the Sm^{III} ion emission was sensitized by the $[Zn_3(L)]^{2+}$ unit. The catecholase activities of complexes 1 and 2 were examined using

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3,5-di-tert-butylcatechol (3,5-DTBC) in acetonitrile solution under completely aerobie/C9NJ00014C conditions. The catalytic reaction follows Michaelis–Menten enzymatic reaction kinetics, and the values of k_{cat} are 3.52×10^2 and 4.54×10^2 h⁻¹ for complexes 1 and 2, respectively. The study on catalytic activities of Salamo-based Zn^{II} or [Zn^{II}Ln^{III}] complex has not been reported up to now. In addition, the intermolecular interactions presented in complex 1 were discussed by Hirshfeld surface analysis in form of decomposed fingerprint plots.

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Graphical Abstract:

One homo-trinuclear 3d and five novel windmill-type hetero-pentanuclear 3d–4f complexes were synthesized by the reactions of a bis(Salamo)-based tetraoxime ligand (H₄L) with $Zn(OAc)_2 \cdot 2H_2O$ and $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Sm, Eu, Gd, Tb and Dy), respectively. The structures of complexes **1-6** were characterized via elemental analyses, FT-IR, UV-Vis spectroscopy and single crystal X-ray crystallography, and their fluorescence properties, catalytic activities and Hirshfeld surface analysis were studied.

