Four rare structurally characterized heteropentanuclear \([Zn_4Ln]\) bis(salamo)-type complexes: syntheses, crystal structures and spectroscopic properties†

Lu-Mei Pu,†a Lan Wang,†b Xiao-Yan Li,†b Yin-Xia Sun,†b Quan-Peng Kang,b Hai-Tao Long,a Wei-Bing Xu,a* and Wen-Kui Dong,a†b

Four new heteropentanuclear 3d--4f complexes \([Zn_4(L)La(NO_3)_2(OEt)(H_2O)]\) (1), \([Zn_4(L)Ce(NO_3)_2-(OMe)(MeOH)]\) (2), \([Zn_4(L)Pr(NO_3)_2(OEt)(EtOH)]\) (3) and \([Zn_4(L)Nd(NO_3)_2(OMe)(MeOH)]\) (4) were synthesized by the reactions of a newly synthesized octadentate bis(salamo)-based tetraoxime ligand \((H_4L)\) with \(Zn(OAc)_2\cdot2H_2O\) and \(Ln(NO_3)_3\cdot6H_2O\) \((Ln = La, Ce, Pr and Nd)\), respectively, and characterized via elemental analyses, FT-IR, UV-Vis spectroscopy and single crystal X-ray crystallography. The X-ray crystallographic investigation revealed that all \(Zn^{II}\) ions were located in \(N_2O_3\) coordination spheres, and possessed a trigonal bipyramidal coordination environment. The \(Ln^{III}\) ion lay in an \(O_6\) coordination sphere, and adopted a distorted square antiprismatic coordination environment. Furthermore, supramolecular interactions and fluorescence properties were investigated.

1 Introduction

Salen-type ligands and their analogues are very versatile chelating ligands in inorganic and organometallic chemistry.† Their complexes have considerable intrinsic value due to their wide applications in electrochemistry,7 building supramolecular structures,4 catalysis fields,4 magnetism,2 biological fields4 and so forth.

In recent years, a preferable class of salen-type compounds (salamo: \(R-CH=N-O-(CH_2)_n-O=N-CH-R\)) has been reported,7 and the large electronegativity of O atoms has expected to lead to different and novel structures and properties of the resulting complexes. The 3d--4f complexes have attracted much attention due to the visible and near-infrared luminescence produced by lanthanide f-f transitions.8 Luminescence applications of lanthanides are a consequence of their narrow emission bands, large Stokes shifts, negligible environmental influences and relatively long luminescence lifetimes. However, 3d--4f complexes with salamo-like ligands have been rarely reported.9

Herein, a series of rare heteropentanuclear \([Zn_4Ln]\) \((Ln = La, Ce, Pr and Nd)\) complexes containing octadentate bis(salamo)-based tetraoxime ligand \(H_4L\) were synthesized and structurally characterized. Meanwhile, the luminescence properties of complexes 1–4 were studied.

2 Experimental

2.1 Materials and methods

1,2-Dimethoxybenzene, 1,2-dibromoethane, TMEDA, n-butyl-lithium, boron tribromide and 2-hydroxy-1-naphthaldehyde (99%) 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 carbon, hydrogen and nitrogen were obtained using a GmbH VarianOL V3.00 automatic elemental analysis instrument (Berlin, Germany). LaIII, CeIII, PrIII and NdIII were gained using an IRIS ER-S-WP-1 ICP atomic emission spectrometer (Berlin, Germany). Melting points were obtained via a microscopic melting point apparatus made by Beijing Taike Instrument Company Limited. IR spectra (4000–400 cm⁻¹) were determined via a Vertex 70 FT-IR spectrophotometer (Bruker, Billerica, MA, USA), with samples prepared as KBr pellets. UV-Vis absorption spectra were determined using a Shimadzu UV-3900 spectrometer (Shimadzu, Japan). 1H NMR spectra were determined via German Bruker AVANCE DRX-400/600 spectroscopy. X-ray single crystal structure determinations for complexes 1, 2, 3 and 4 were carried out on a Bruker APEX-II CCD diffractometer. Fluorescence spectra were recorded on an F-7000 FL
spectrophotometer. Near infrared (NIR) spectra were determined through PTI QM4 spectrofluorometer with a PTI QM4 Near infrared InGaAs detector.

2.2. Synthesis of the H₄L

The reaction steps of the ligand (H₄L) can be seen from Scheme 1. 1,2-Bis(aminooxy)ethane, 2,3-dihydroxybenzene-1,4-dicarbal-
The synthesis methods of complexes 1–4

Table 1 Crystal data and the structure refinements for complexes 1–4

| Complex | 1 | 2 | 3 | 4 |
|---------|---|---|---|---|
| Empirical formula | C$_{70}$H$_{59}$LaZn$_4$N$_{10}$O$_{24}$ | C$_{70}$H$_{59}$CeZn$_4$N$_{10}$O$_{24}$ | C$_{72}$H$_{63}$PrZn$_4$N$_{10}$O$_{24}$ | C$_{70}$H$_{59}$NdZn$_4$N$_{10}$O$_{24}$ |
| Formula weight | 1824.66 | 1824.86 | 1854.71 | 1829.99 |
| T (K) | 296(2) | 173(2) | 173(2) | 173(2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Space group | C2/c | C2/c | Monoclinic | Monoclinic |
| Z | 8 | 4 | 4 | 4 |
| D$_{calc}$ (g cm$^{-3}$) | 1.440 | 3.33 | 1.369 | 1.336 |
| F (000) | 7344 | 3672 | 3744 | 3684 |
| Crystal size (mm) | 0.270 × 0.250 × 0.220 | 0.220 × 0.190 × 0.160 | 0.220 × 0.200 × 0.180 | 0.220 × 0.190 × 0.160 |
| θ Range (°) | 2.044–25.010 | 2.485–25.008 | 1.548–26.000 | 2.485–25.008 |
| Index ranges | −25 ≤ h ≤ 28 | −20 ≤ h ≤ 20 | −20 ≤ h ≤ 20 | −20 ≤ h ≤ 17 |
| | −18 ≤ k ≤ 18 | −22 ≤ k ≤ 27 | −27 ≤ k ≤ 28 | −27 ≤ k ≤ 27 |
| | −51 ≤ l ≤ 54 | −29 ≤ l ≤ 29 | −29 ≤ l ≤ 29 | −29 ≤ l ≤ 28 |
| Reflections collected/unique | 59 539/14 818 | 32 767/999 | 19 902/8832 | 32 970/8002 |
| Completeness to θ | 99.8% (θ = 25.010) | 99.8% (θ = 25.008) | 99.7% (θ = 25.242) | 99.8% (θ = 25.008) |
| | 99.8% (θ = 25.008) | 1.548–26.000 | 2.485–25.008 | 2.485–25.008 |
| | 14 818/1000 | 7999/493 | 8832/5/496 | 8002/6/487 |
| | 9.039/1009 | 9.039/1000 | 9.039/1000 | 9.039/1000 |
| | 0.963 | 1.049 | 1.043 | 1.030 |
| | 0.0399, 0.1006 | 0.0363, 0.1003 | 0.0315, 0.0971 | 0.0377, 0.0974 |
| | 0.0454, 0.1044 | 0.0448, 0.1059 | 0.0412, 0.1007 | 0.0465, 0.1020 |
| | 25.008 | 2.485–25.008 | 2.485–25.008 | 2.485–25.008 |
| | 1.492 and −1.009 | 1.563 and −0.981 | 1.048 and −0.805 | 1.814 and −0.783 |

Dehydration and 2-[(O-1-ethyloxyamide)oxime-2-naphthol were prepared according to analogous methods reported earlier. An ethanol solution (10 mL) of 2,3-dihydroxybenzene-1,4-di-carboxaldehyde (166.2 mg, 1.0 mmol) was added to an ethanol solution (20 mL) of 2-[O-1(ethyloxyamide)]oxime-2-naphthol (492.6 mg, 2 mmol). The mixed solution was stirred at 55°C for 8 h, cooling to room temperature, the precipitate was filtered and washed with n-hexane to obtain a yellow powder. Yield: 87%, mp.: 198–200°C. Anal. calc. for C$_{70}$H$_{59}$LaZn$_4$N$_{10}$O$_{24}$: C, 46.08; H, 3.26; N, 7.68; Zn, 14.33; La, 7.48. Found (%): C, 46.19; H, 3.38; N, 7.53; Zn, 14.41; La, 7.48.

2.3. General procedure for the preparation of complexes 1–4

The synthesis methods of complexes 2–4 are similar to that of complex 1 (Scheme 2). An ethanol solution (3 mL) of Zn(OAc)$_2$-2H$_2$O (13.155 mg, 0.065 mmol) was added to a chloroform solution (5 mL) of H$_4$L (18.675 mg, 0.03 mmol) under constant magnetic stirring, and an ethanol solution (3 mL) of La(NO$_3$)$_3$-6H$_2$O (4.33 mg, 0.015 mmol) was then added. The mixed solution was stirred for 15 minutes at room temperature and then filtered off, and the filtrate was transferred to a cillin bottle. Sealed the opening of the bottle with tinfoil and let it stand for two weeks, some block-like crystals suitable for X-ray diffraction were formed.

Complex 1, yellow block-like crystals. Yield: 52%. Elemental analysis: calc. for [Zn$_4$(L)$_2$La(NO$_3$)$_2$(OEt) (H$_2$O)] (C$_{70}$H$_{59}$LaZn$_4$N$_{10}$O$_{24}$) (%): C, 46.08; H, 3.26; N, 7.68; Zn, 14.33; La, 7.48. Found (%): C, 46.19; H, 3.38; N, 7.53; Zn, 14.41; La, 7.48.

Complex 2, yellow block-like crystals. Yield: 62%. Elemental analysis: calc. for [Zn$_4$(L)$_2$Ce(NO$_3$)$_2$(OMe)(MeOH)] (C$_{70}$H$_{59}$CeZn$_4$N$_{10}$O$_{24}$) (%): C, 46.05; H, 3.26; N, 7.67; Zn, 14.32; Ce, 7.67. Found (%): C, 46.12; H, 3.37; N, 7.56; Zn, 14.39; Ce, 7.81.

Complex 3, yellow block-like crystals. Yield: 69%. Elemental analysis: calc. for [Zn$_4$(L)$_2$Pr(NO$_3$)$_2$(OEt)(EtOH)] (C$_{70}$H$_{63}$PrZn$_4$N$_{10}$O$_{24}$) (%): C, 46.62; H, 3.42; N, 7.55; Zn, 14.10; Pr, 7.60. Found (%): C, 46.79; H, 3.48; N, 7.50; Zn, 14.15; Pr, 7.68.
Complex 4, yellow block-like crystals. Yield: 64%. Elemental analysis: anal. calc. for [Zn₄(L)₂Nd(NO₃)₂(OEt)(H₂O)] (C₇₀H₅₉NdZn₄N₁₀O₂₄) (%): C, 45.94; H, 3.25; N, 7.65; Zn, 14.29; Nd, 7.88. Found (%): C, 46.09; H, 3.38; N, 7.53; Zn, 14.38; Nd, 7.96.

2.4. X-ray crystallographic analysis
Crystal data for complexes 1–4 were collected on a Bruker APEX-II CCD area detector with Mo Kα radiation (λ = 0.71073 Å) at 296(2), 173(2), 173(2) and 173(2) K, respectively. Reflection data were corrected for LP factors semi-empirical absorption were
### Table 2  Selected bond lengths (Å) and angles (°) for complexes 1–4

#### Complex 1

| Bond     | Lengths | Bond     | Lengths | Bond     | Lengths |
|----------|---------|----------|---------|----------|---------|
| Zn1–O19  | 2.001(3)| Zn1–O20  | 2.085(3)| Zn1–O22  | 2.054(6)|
| Zn2–O1   | 2.051(2)| Zn2–O4   | 1.957(2)| Zn1–O22  | 2.019(4)|
| Zn3–O24  | 2.014(3)| Zn3–O5   | 1.975(2)| Zn3–O6   | 1.983(3)|
| Zn3–O7   | 2.081(2)| Zn4–O12  | 1.999(3)| Zn4–O13  | 2.057(3)|
| Zn4–O14  | 2.059(3)| Zn1–N3   | 2.149(3)| Zn1–N4   | 2.048(3)|
| Zn5–N2   | 2.011(3)| Zn2–N6   | 2.108(3)| Zn3–N1   | 2.127(3)|
| Zn5–N5   | 2.019(3)| Zn4–N7   | 2.038(4)| Zn4–N8   | 2.120(3)|
| La1–O5   | 2.491(2)| La1–O12  | 2.497(2)| La1–O19  | 2.500(2)|
| La1–O20  | 2.496(3)| La1–O4   | 2.505(2)| La1–O7   | 2.514(2)|
| La1–O1   | 2.534(3)| La1–O13  | 2.537(3)|          |         |

#### Complex 1

| Bond       | Angles | Bond       | Angles | Bond       | Angles |
|------------|--------|------------|--------|------------|--------|
| O19–Zn1–O22| 109.0(2)| N4–Zn1–O22| 123.2(2)| O19–Zn1–O20| 81.62(10)|
| O19–Zn1–O22 | 134.0(5)| O19–Zn1–N4| 124.08(12)| O22–Zn1–N4 | 101.9(4)|
| O22–Zn1–O20 | 105.3(4)| N4–Zn1–O20| 83.62(11)| O22–Zn1–O20| 85.79(17)|
| O19–Zn1–N3 | 86.56(12)| O22–Zn1–N3| 89.3(4)| N4–Zn1–N3 | 95.80(14)|
| O22–Zn1–N3 | 106.58(18)| O20–Zn1–N3| 165.20(13)| O4–Zn2–N2 | 129.50(12)|
| O4–Zn2–O24 | 109.62(13)| N2–Zn2–O24| 120.27(14)| O4–Zn2–O1 | 83.74(10)|
| N2–Zn2–O1 | 85.55(11)| O24–Zn2–O1| 93.95(12)| O4–Zn2–N6 | 89.59(11)|
| O5–Zn3–O6 | 95.24(12)| O24–Zn2–N6| 92.61(13)| O1–Zn2–N6 | 171.90(12)|
| O5–Zn3–O6 | 113.02(12)| O5–Zn3–N5| 128.10(12)| O6–Zn3–N5 | 117.44(14)|
| O5–Zn3–O7 | 83.24(10)| O6–Zn3–O7 | 90.74(12)| N5–Zn3–O7 | 84.77(11)|
| O5–Zn3–N1 | 87.25(11)| O6–Zn3–N1 | 97.52(14)| N5–Zn3–N1 | 97.33(13)|
| O7–Zn3–N1 | 169.29(12)| O12–Zn4–N7 | 124.57(13)| O12–Zn4–O13 | 82.80(10)|
| O7–Zn4–O13 | 84.94(12)| O12–Zn4–O14| 103.94(11)| N7–Zn4–O14 | 130.82(13)|
| O13–Zn4–O14 | 94.37(12)| O12–Zn4–N8 | 87.66(12)| N7–Zn4–N8 | 96.06(14)|
| O13–Zn4–N8 | 169.00(13)| O14–Zn4–N8 | 93.24(14)|          |         |
| O5–La1–O20 | 91.87(9)| O5–La1–O12| 129.19(8)| O20–La1–O12 | 126.29(8)|
| O5–La1–O19 | 148.96(9)| O20–La1–O19| 64.64(8)| O12–La1–O19 | 63.26(8)|
| O5–La1–O4 | 63.24(8)| O20–La1–O4 | 78.16(8)| O12–La1–O4 | 146.66(8)|
| O19–La1–O4 | 126.01(8)| O5–La1–O7 | 65.16(8)| O20–La1–O7 | 89.17(9)|
| O12–La1–O7 | 81.51(8)| O19–La1–O7 | 93.10(8)| O4–La1–O7 | 125.23(8)|
| O5–La1–O1 | 124.73(8)| O20–La1–O1| 90.06(9)| O12–La1–O1 | 91.02(8)|
| O19–La1–O1 | 77.66(8)| O4–La1–O1 | 64.15(8)| O7–La1–O1 | 170.10(8)|
| O5–La1–O13 | 77.97(8)| O20–La1–O13 | 169.01(8)| O12–La1–O13 | 64.41(8)|
| O19–La1–O13 | 126.35(8)| O4–La1–O13 | 93.23(9)| O7–La1–O13 | 90.31(9)|
| O1–La1–O13 | 92.31(9)|          |         |          |         |

#### Complex 2

| Bond       | Lengths | Bond       | Lengths | Bond       | Lengths |
|------------|---------|------------|---------|------------|---------|
| O12–Zn1   | 2.020(3)| O11–Zn1   | 2.043(2)| O10–Zn2   | 2.068(2)|
| O9–Zn2    | 2.026(3)| O4–Zn2    | 1.985(2)| O3–Zn1    | 1.972(2)|
| N4–Zn2    | 2.015(3)| N3–Zn2    | 2.137(3)| N2–Zn1    | 2.110(3)|
| N1–Zn1    | 2.019(3)|          |         |            |         |
| Ce1–O3    | 2.475(2)| Ce1–O10   | 2.475(2)| Ce1–O11   | 2.511(2)|
| Ce1–O3    | 2.475(2)| Ce1–O4    | 2.479(2)| Ce1–O11   | 2.511(2)|
| Ce1–O10   | 2.475(2)| Ce1–O4    | 2.479(2)|          |         |

#### Complex 2

| Bond       | Angles | Bond       | Angles | Bond       | Angles |
|------------|--------|------------|--------|------------|--------|
| O3–Zn1–O12 | 113.98(12)| O3–Zn1–N1 | 127.13(12)| O12–Zn1–N1 | 117.85(14)|
| O3–Zn1–O11 | 81.99(10)| O12–Zn1–O11| 93.03(11)| N1–Zn1–O11 | 85.67(12)|
| O3–Zn1–N2  | 88.94(11)| O12–Zn1–N2 | 95.64(12)| N1–Zn1–N2  | 95.67(13)|
| O11–Zn1–N2 | 169.37(12)| O4–Zn2–N4 | 122.97(12)| O4–Zn2–O9 | 109.03(11)|
| O4–Zn2–O9  | 127.60(13)| O4–Zn2–O10| 82.84(9)| N4–Zn2–O10 | 84.60(11)|
Table 2 (Contd.)

Complex 2

| Bond     | Angles | Bond          | Angles  | Bond          | Angles |
|----------|--------|---------------|---------|---------------|--------|
| O9-Zn2–O10 | 96.52(12) | O4–Zn2–N3    | 87.24(11) | N4–Zn2–N3    | 95.14(13) |
| O9-Zn2–N3  | 93.18(14) | O10–Zn2–N3   | 167.93(12) | O3–Ce1–O3   | 126.22(11) |
| O3–Ce1–O3–O2 | 126.22(11) | O3–Ce1–O10–O2 | 92.34(8)  | O3–Ce1–O10–O2 | 127.67(8) |
| O3–Ce1–O10–O2 | 127.67(8) | O3–Ce1–O10–O2 | 92.34(8)  | O3–Ce1–O10–O2 | 146.35(8) |
| O3–Ce1–O4–O2 | 146.35(8) | O4–Ce1–O4    | 130.09(11) | O3–Ce1–O11  | 63.72(8)  |
| O3–Ce1–O4–O2 | 63.21(8)  | O3–Ce1–O11–O2 | 80.04(8)  | O3–Ce1–O11–O2 | 126.67(8) |
| O10–Ce1–O4–O2 | 78.78(8)  | O3–Ce1–O11–O2 | 63.72(8)  | O10–Ce1–O11–O2 | 65.57(8)  |
| O10–Ce1–O4–O2 | 65.57(8)  | O4–Ce1–O11–O2 | 90.07(8)  | O10–Ce1–O11–O2 | 146.35(8) |
| O10–Ce1–O4–O2 | 78.78(8)  | O4–Ce1–O11–O2 | 125.03(8) | O10–Ce1–O11–O2 | 65.57(8)  |
| O10–Ce1–O4–O2 | 85.70(9)  | O4–Ce1–O11–O2 | 90.03(8)  | O10–Ce1–O11–O2 | 78.78(8)  |

Complex 3

| Bond     | Lengths  | Bond          | Lengths  | Bond          | Lengths |
|----------|----------|---------------|----------|---------------|---------|
| N1–Zn1   | 2.015[2] | N2–Zn1        | 2.015[2] | N3–Zn2        | 2.110(3) |
| N4–Zn2   | 2.018[3] | O1–Zn1        | 2.0699(19)| O5–Zn2        | 1.9785(19)|
| O8–Zn2   | 2.0372[19]| O12–Zn2     | 2.110(3) | O5–Pr1        | 2.4471(19)|
| O1–Pr1   | 2.4646(19)| O8–Pr1       | 2.5097(19)| O6–Pr1        | 2.4471(19)|
| O4–Pr1   | 2.4605(19)| O4–Pr1       | 2.4605(19)| O6–Pr1        | 2.4471(19)|
| O5–Pr1   | 2.4471(19)| O4–Pr1       | 2.4471(19)| O6–Pr1        | 2.4471(19)|

Complex 4

| Bond     | Lengths  | Bond          | Lengths  | Bond          | Lengths |
|----------|----------|---------------|----------|---------------|---------|
| N1–Zn1   | 2.020(3) | N2–Zn1        | 2.110(3) | N3–Zn2        | 2.133(3) |
| N4–Zn2   | 2.017[3] | O3–Zn1        | 1.968(3) | O4–Zn2        | 1.983(2) |
| O9–Zn2   | 2.023(3) | O10–Zn2       | 2.061(3) | O11–Zn1       | 2.046(3) |
| O12–Zn2  | 2.017(3) | O4–Zn2        | 2.450(2) | Nd1–O11        | 2.481(3) |
| Nd1–O4   | 2.449(2) | Nd1–O3        | 2.450(2) | Nd1–O11        | 2.481(3) |
| Nd1–O4²  | 2.449(2) | Nd1–O10       | 2.450(2) | Nd1–O11        | 2.481(3) |
| Nd1–O3²  | 2.450(2) | Nd1–O10       | 2.450(2) | Nd1–O11        | 2.481(3) |
Complex 4

| Bond     | Angles | Bond     | Angles | Bond     | Angles |
|----------|--------|----------|--------|----------|--------|
| O3–Zn1–O12 | 113.61(13) | O3–Zn1–N1 | 127.19(13) | O12–Zn1–N1 | 118.26(15) |
| O3–Zn1–O11 | 81.28(10)  | O12–Zn1–O11 | 93.77(12)  | N1–Zn1–O11 | 86.07(12)  |
| O3–Zn1–N2  | 89.29(12)  | O12–Zn1–N2 | 95.15(13)  | N1–Zn1–N2 | 95.29(14)  |
| O11–Zn1–N2 | 169.03(13) | O4–Zn2–N4 | 122.85(13) | N4–Zn2–O9 | 109.21(11) |
| N4–Zn2–O9 | 127.58(13) | O4–Zn2–O10 | 82.07(10)  | N4–Zn2–O10 | 85.26(12)  |
| O9–Zn2–O10 | 96.81(13)  | O4–Zn2–N3 | 87.26(12)  | N4–Zn2–N3 | 94.59(14)  |
| O9–Zn2–N3 | 93.47(14)  | O10–Zn2–N3 | 167.13(12) | O10–Zn2–N3 | 94.93(14)  |
| O4–Nd1–O174 | 129.32(12) | O4–Nd1–O170 | 78.43(9)  | O10–Nd1–O174 | 90.19(9)  |
| O4–Nd1–O3174 | 145.82(8)   | O4–Nd1–O170 | 65.72(8)  | O10–Nd1–O174 | 167.33(8) |
| O4–Nd1–O3174 | 63.98(8)    | O3–Nd1–O170 | 128.56(8) | O4–Nd1–O171 | 126.22(8) |
| O4–Nd1–O3174 | 63.98(8)    | O3–Nd1–O170 | 91.74(8)  | O4–Nd1–O172 | 89.50(8)  |
| O4–Nd1–O3174 | 145.82(8)   | O10–Nd1–O170 | 88.34(12) | O3–Nd1–O172 | 79.37(8)  |
| O3–Nd3–O3174 | 125.79(12)  | O3–Nd1–O170 | 89.50(8)  | O3–Nd1–O173 | 64.06(9)  |
| O4–Nd1–O170 | 65.72(8)    | O3–Nd1–O170 | 126.21(8) | O3–Nd1–O174 | 167.33(8) |
| O4–Nd1–O170 | 78.43(9)    | O3–Nd1–O170 | 64.06(8)  | O3–Nd1–O174 | 90.20(9)  |
| O3–Nd3–O170 | 91.73(8)    | O3–Nd1–O170 | 79.37(8)  | O3–Nd1–O174 | 93.93(12) |
| O3–Nd3–O170 | 128.56(8)   | O3–Nd1–O170 | 93.93(12) | O3–Nd1–O174 | 93.93(12) |

* Symmetry transformations used to generate equivalent atoms: $^\overrightarrow {2}$ $3/2 - x, -1/2 + y, 3/2 - z; ^\overrightarrow {2} - x + 1, y, -z + 1/2; ^\overrightarrow {3} - x, y, -z + 1/2; ^\overrightarrow {4} - x + 1, y, -z + 1/2.

The IR spectra of H$_4$L and its corresponding complexes 1–4 displayed various bands in the 4000–400 cm$^{-1}$ region (Fig. 1).

In the infrared spectrum of H$_4$L, a typical C=N stretching band appeared at ca. 1603 cm$^{-1}$, and C==N stretching bands of complexes 1–4 were observed at 1609–1614 cm$^{-1}$, indicating that H$_4$L has coordinated with Zn$^{II}$ ions. In addition, the free ligand H$_4$L exhibited a typical Ar–O stretching frequency at ca. 1239 cm$^{-1}$, while the Ar–O stretching frequencies in complexes 1–4 were observed at ca. 1232, 1235, 1231 and 1232 cm$^{-1}$, which are shifted to lower frequencies, indicating that the Zn–O or Ln–O bond is formed between the oxygen atoms of phenolic group and the metal ions. Meanwhile, the hydroxyl stretching band of H$_4$L was observed at ca. 3435 cm$^{-1}$ that belongs to the phenolic O–H groups. These absorption bands in complexes 1–4 were observed at ca. 3441–3443 cm$^{-1}$, indicating the existence of coordinated water, methanol or ethanol molecules.

The UV-Vis absorption spectra of H$_4$L and its complexes 1–4 in CHCl$_3$/CH$_3$CH$_2$OH solution (v/v = 1 : 1) are shown in Fig. 2. The absorption spectrum of H$_4$L (1.0 × 10$^{-5}$ M) showed four relatively strong absorption peaks at ca. 302, 313, 341 and 355 nm, the former two peaks can be assigned to the $\pi$–$\pi^*$ transitions of the naphthalene rings. The later two absorption peaks can be assigned to the intra-ligand $\pi$–$\pi^*$ transition of the oxime group.

3. Results and discussion

3.1. IR spectra

IR spectra of H$_4$L and its corresponding complexes 1–4 displayed various bands in the 4000–400 cm$^{-1}$ region (Fig. 1).

In the infrared spectrum of H$_4$L, a typical C=N stretching band appeared at ca. 1603 cm$^{-1}$, and C==N stretching bands of complexes 1–4 were observed at 1609–1614 cm$^{-1}$, indicating that H$_4$L has coordinated with Zn$^{II}$ ions. In addition, the free ligand H$_4$L exhibited a typical Ar–O stretching frequency at ca. 1239 cm$^{-1}$, while the Ar–O stretching frequencies in complexes 1–4 were observed at ca. 1232, 1235, 1231 and 1232 cm$^{-1}$, which are shifted to lower frequencies, indicating that the Zn–O or Ln–O bond is formed between the oxygen atoms of phenolic group and the metal ions. Meanwhile, the hydroxyl stretching band of H$_4$L was observed at ca. 3435 cm$^{-1}$ that belongs to the phenolic O–H groups. These absorption bands in complexes 1–4 were observed at ca. 3441–3443 cm$^{-1}$, indicating the existence of coordinated water, methanol or ethanol molecules.

3.3. Crystal structure descriptions

X-ray crystallographic analysis revealed the crystal structures of complexes 1–4. Selected bond lengths and angles are given in Table 1.

3.3.1. Crystal structure of complex 1. The crystallographic data revealed that complex 1 ([Zn$_4$(L)$_2$La(NO$_3$)$_3$(OEt)(H$_2$O)]) was a hetero-pentanuclear complex, crystallizes in the monoclinic system, space group C2/c, and consists of four Zn$^{II}$ ions, one La$^{III}$ ion, two (L)$^{1+}$ units, one coordinated ethoxy group, one coordinated water molecule and two nitrate groups (Fig. 3). N$_2$O$_5$ sites of the salamo moieties were occupied by four Zn$^{II}$ ions (Zn1, Zn2, Zn3 and Zn4), the Zn$^{II}$ ions were located in N2O3 units, one coordinated ethoxy group, one coordinated water molecule, two nitrate groups (Fig. 3), N$_2$O$_5$ sites of the salamo moieties were occupied by four Zn$^{II}$ ions (Zn1, Zn2, Zn3 and Zn4), the Zn$^{II}$ ions were located in N$_2$O$_3$ units, one coordinated ethoxy group, one coordinated water molecule, two nitrate groups (Fig. 3).
ion lay in an O₈ coordination sphere, and adopted a distorted square antiprismatic coordination environment. Finally, complex 1 formed a rare heteropentanuclear 3d–4f complex. The distances of Zn–La₁, Zn–N, Zn–O and La₁–O bonds are in the ranges of 3.6130(5)–3.6513(5), 2.011(3)–2.149(3), 1.957(2)–2.085(3) and 2.491(2)–2.537(3) Å, respectively.

The intramolecular and intermolecular hydrogen bonds for complex 3 are presented in Table 2. Each molecule formed five intramolecular hydrogen bonds (C23–H23A···O12 and C8–H8A···O10) as shown in Fig. 4. Meanwhile, a self-assembled infinite 2D supramolecular structure was formed by C12–H12A···O3 and C47–H47A···O15 hydrogen bond interactions (Fig. 4).

3.3.2. Crystal structure of complex 2. The crystallographic data revealed that complex 2 ([Zn₄(L)₂Ce(NO₃)₂(OMe)(MeOH)]) crystallizes in the monoclinic system, space group C2/c. Unlike complex 1, it consists of four Zn²⁺ ions, one Ce³⁺ ion, two ligand (L)⁻² units, one coordinated methoxo group, one coordinated...
methanol molecule and two monodentate nitrate groups (Fig. 5).

Zn1 and Zn2 ions were located in penta-coordinated spheres and adopted trigonal bipyramid coordination environments \((\tau_1 = 0.704 \text{ and } \tau_2 = 0.67)\). The coordination number of Ce\(^{III}\) ion is 8, consisting of eight phenolic oxygen atoms from two full deprotonated \((L)^4\) units and adopted a distorted square antiprismatic coordination environment (Fig. 5).

In the crystal structure of complex 2, there were many intramolecular hydrogen bonds \((\text{C}2-\text{H}2-\text{O}9-\text{O}11 \text{ and C}22-\text{H}22\text{A}-\text{O}7)\). As shown in Fig. 6. Moreover, the 2D supramolecular structure was formed by C12–H12A–O7 hydrogen bonding interactions in complex 2 (ref. 21) (Fig. 6).

3.3.3. Crystal structure of complex 3. Complex 3 \([\text{Zn}_4(L)_2\text{Pr(NO}_3)_2\text{[(OEt)[EtOH]]}]\) crystallizes in the monoclinic crystal system, space group C2/c. X-ray crystallography clearly showed the formation of complex 3. Different from complexes 1 and 2, it consists of four Zn\(^{II}\) ions, one Pr\(^{III}\) ion, two ligand \((L)^3\) units, one coordinated ethoxy group, one coordinated ethanol molecule and two monodentate nitrate groups (Fig. S2†).

The Zn\(^{II}\) ions also were located in the N\(_2\)O\(_3\) sites, and four Zn\(^{III}\) ions are also penta-coordinated. The Zn\(^{III}\) ions \((\text{Zn}1 \text{ and Zn}2)\) adopted trigonal bipyramidal coordination environment \((\tau_1 = 0.67 \text{ and } \tau_2 = 0.72)\). The Pr\(^{III}\) ion was also located in the O\(_8\) site that consists of eight phenoxy oxygen atoms, forming a distorted square antiprismatic coordination environment.

The main interactions in complex 3 are listed in Table 3, four pairs of intramolecular hydrogen bonds \((\text{C}13-\text{H}13\text{B}-\text{O}10, \text{C}24-\text{H}24-\text{O}7, \text{C}27-\text{H}27-\text{O}9 \text{ and C}35-\text{H}35\text{B}-\text{O}11)\) were formed. Besides, The O10 atom of nitrate group as acceptor formed a hydrogen bond with the donor \((\text{C}23\text{H}23\text{B})–\text{O}7, \text{C}27\text{H}27\text{B})\) in complex 3, which adopted a 2D supramolecular structure† (Fig. S3†).

3.3.4. Crystal structure of complex 4. As shown in Fig. S4† X-ray crystallographic analysis of complex 4 \([\text{Zn}_4(L)_2\text{Nd(NO}_3)_2\text{[(OMe)[MeOH]]}]\) revealed that crystallizes in the monoclinic system, space group C2/c. Similar to the structure of complex 2, it consists of four Zn\(^{II}\) ions, one Nd\(^{III}\) ion, two ligand \((L)^4\) units, one coordinated methoxy group, one coordinated methanol molecule and two monodentate nitrate groups.

All Zn\(^{II}\) ions lay in N\(_2\)O\(_3\) coordination spheres. The Zn1 and Zn2 \((\text{Zn}1^{14} \text{ and Zn}2^{14})\) ions were all made of the N\(_2\)O\(_3\) cavities and one coordinated nitrate group, which assumed trigonal bipyramidal coordination environments \((\tau_1 = 0.69 \text{ and } \tau_2 = 0.66)\). The Nd\(^{III}\) ion exhibited an O\(_8\) coordination sphere, which is made of eight phenoxy donors \((\text{O}3, \text{O}4, \text{O}10, \text{O}11, \text{O}3^{14}, \text{O}4^{14}, \text{O}10^{14} \text{ and O}11^{14})\) from two completely deprotonated \((L)^{14}\) units, while the central Nd\(^{III}\) ion is octacoordinated with a distorted square antiprismatic coordination environment.

In complex 4, three pairs of significant intramolecular hydrogen bonds \((\text{C}2-\text{H}2-\text{O}9-\text{O}11 \text{ and C}22-\text{H}22\text{A}-\text{O}7)\) were formed† (Fig. S5(a)†). Meanwhile, complex 4 molecules formed a 2D supramolecular structure by intermolecular hydrogen bonds \((\text{C}6-\text{H}6-\text{O}8 \text{ and C}12-\text{H}12\text{A}-\text{O}7)\) (Fig. S5(b)†).

3.4. Spectroscopic properties

The free ligand \(H_4L\) and its corresponding complexes 1–4 were excited at 385 nm \((\lambda_{ex})\) respectively (Fig. 7). The emission
Fig. 6  (a) View of the intramolecular hydrogen bonding interactions of complex 2. (b) View of an infinite 2D supramolecular structure of complex 2.
spectrum of H₄L exhibited a broad emission band, and the emission maximum at 454 nm, which can be assigned to the π–π* electronic transitions in the ligand. Compared to H₄L, the absorption peaks of complexes 1–3 are bathochromically-shifted, which is may originated from the LMCT emission.

Due to energy mismatch, complexes 1–3 have no NIR luminescence. The NIR luminescence spectrum of complex 4 excited at 385 nm showed the characteristic emitting peaks at ca. 871, 917, 1055 and 1324 nm (Fig. 7[b]). These emission peaks are typical peaks of Nd³⁺ ions, and correspond to ⁴F₃/₂ → ⁴I₁₁/₂, ⁴F₄/₂ → ⁴I₁₁/₂ and ⁴F₄/₂ → ⁴I₁₃/₂ transitions. The ligand (L)⁺ units could serve as sensitizing agent for Nd³⁺ luminescence in the NIR region.

4 Conclusions

In this work, four rare hetero-pentanuclear 3d–4f complexes of a bis(salamo)-type ligand (H₄L) have been synthesized and structurally characterized. In complexes 1–4, all four Zn²⁺ ions presented N₄O₂ coordination spheres. The Ln³⁺ ion exhibited an O₈ coordination sphere, and assumed a distorted square
antiprismatic coordination environment. In a conclusion, the studies demonstrated that incorporation of salamo-like ligand was an optimistic approach to build ZnII and LnIII complexes which can display excellent spectroscopic resting with the lanthanide ions used.

Conflicts of interest

There are no conflicts to declare.

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| Complex 1 | C7–H7A···O14 | 0.93 | 2.55 | 3.436(5) | 159 | \(1 - x, 1 - y, 1 - z\) |
| Complex 2 | C2–H2···O9  | 0.95 | 2.51 | 3.451(5) | 173 | \(1 - y, 1/2 + y, z\) |
| Complex 3 | C13–H13B···O10 | 0.99 | 2.53 | 3.516(4) | 173 | \(1/2 + x, 1/2 + y, z\) |
| Complex 4 | C2–H2A···O9  | 0.95 | 2.51 | 3.456(6) | 172 | \(1 - y, 1/2 - z\) |

Table 3 Hydrogen bonding distances (Å) and bond angles (°) for complexes 1–4
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