Two Dinuclear Lanthanide Coordination Er(III), Yb(III) Complexes: Structure and Near-Infrared Luminescence

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Abstract:- **Two lanthanide complexes based on phenoxy bridged dinuclear complexes, [$Ln_2(HL)_2(NO_3)_4$].3CH_3CN.CH_3OH(Ln = Er(1),Yb(2)), Constructed structurally by salicylamide Salen-like ligand, H_3L= 2-hydroxy-N-(2-(((3-hydroxynaphthalen-2-yl)methylene)amino)-ethyl)benzamide, were prepared and structurally characterized, Signal-crystal X-ray diffraction revealed by analysis is dinuclear complexes. Coordinated by two phenoxys bridged LnIII, two doubly deprotonated HL- ligand, two bidenates nitrate oxygen atom, the luminescent properties indicate this complexes display near-infrared emission of the corresponding Ln^{3+} ion.**

***Keywords—** Saliylamide salen-like ligand; dinuclear complex; Crystal structure; NIR Luminescence properties.*

I. INTRODUCTION

Most of the studies in the field of luminescent lanthanide ions have been consecrate to Eu(III) and Tb(III), which emit in the visible spectral region, but recently many researchers much attention has been paid to near-infrared (NIR) luminescence of trivalent lanthanide Ln(III) ions, such as Yb(III), Er(III), due to their potential applications as biomolecule labels in luminescent bioassays, as functional materials for optical telecommunication networks and laser systems[1,4]. For instance, the relative transparency of human tissue at around 1000 nm suggests that in vivo luminescent probes operating at this wavelength (Yb-based emission) could have diagnostic value. NIR luminescence from (Er-based emission) it proved very useful when employed in telecommunication network optical signal amplifiers [5, 7].

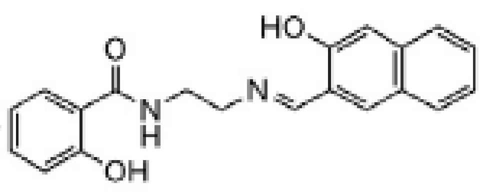
However, the f-f transitions of lanthanide ions (Ln^{3+}) are usually laporte forbidden, which results in low absorption cross section and poor luminescence efficiency which limits their efficient application[8]. To circumvent this problem, often we introduce coordinate organic ligand to assemble lanthanide coordination complexes to obtain highly efficient lanthanide luminescence via so called Antenna effect [9]. In which, the organic ligands that high efficiently absorb the light like an antenna, followed by energy transfer to the excited states of lanthanide ions [10]. When the lanthanide ions return to the ground state via radiative transitions, characteristic fluorescence of the lanthanide is produced [11, 12].

Lanthanide ions have not only high coordination number and flexible coordination geometry but also the affinity for organic ligands containing hard donor atoms. So we proceeded the study of Coordination behavior of the salicylamide salen-like ligand (Scheme.1.) 2-hydroxy-N-(2-(((3-hydroxynaphthalen-2-yl)-methylene)amino)ethyl)benzamide (H_3L) as the following considerations: (I) H_3L possesses two phenolic hydroxyl group and one NH group that may be completely or partially deprotonated. (II) It is a flexible ligand which can allow the rotation of two aromatic rings around the C–C single bond [13]. To construct lanthanide (Ln^{3+}) complexes and in aid of excellent phenoxy atom bridging ability, we succeeded synthetized two novels of the dinuclear complexes formula:[$Ln_2(HL)_2(NO_3)_4$].3CH_3CN.CH_3OH(Ln = Er(1),Yb(2)) Are obtained, Their structures were determined by single-crystal X-ray diffraction analyses, FT-IR spectroscopy, and near-infrared emission.

II. EXPERIMENTAL

A. Materials and instrumentation

All operations were performed in an open atmosphere. Solvents and other chemicals were obtained from commercial sources and used without further purification. The synthesis of ligand H_3L was prepared according to the literature [14] using N-(2-aminoethyl)-2-hydroxybenzamide instead. Melting points were determined on a Kofler apparatus. IR spectra were recorded in the range (4000–400 cm^{-1}) on a Perkin-Elmer FTIR spectrometer using KBr sdiscs on a Nicolet FT-170SX instrument in the wavenumber range of 4000–400 cm^{-1} with an average of 128 scans and 4 cm^{-1} of spectral resolution. Near-IR photophysical data were obtained on a Jobin Y von-Horiba flourolog-3 spectrometer fitted with a Hamamatsu R5509-73 detector.



Scheme. 1. The molecular structure of H_3L

B. General Synthetic Procedure for Complexes 1 and 2

0.1 mmol (0.0334g) of ligand H_3L was added to 20 ml of an acetonitrile solution, 27 uL (0.2 mmol) of triethylamine was added to make a clear solution, stirring for 30min, then 0.1 mmol of $Ln(NO_3)_3$.6H_2O was added as a solid, and the solution was Stirring at room temperature for another 4 h produces a large amount of precipitation, then adding 5 ml of anhydrous methanol to obtain clear solution which was filtered into a sealed 10–20 mL glass vial for crystallization at room temperature. After about two weeks, pale yellow single crystals like tetrahedron shape. Suitable for crystal analysis were obtained and collected by filtration, washed with cold methanol, and dried in the air.

$[Er_2(HL)_2(NO_3)_4].3CH_3CN.CH_3OH$(1)The empirical formula: $C_{42}\ H_{35}\ N_9\ O_{18}\ Er_2$, Yield: 34.2 mg, 48% based on $Er(NO_3)_3.6H_2O$. Analytical data (%), calculated: C, 39.16; H, 2.71; N, 9.79 found: C, 39.26; H, 2.69; N, 9.84%; IR (KBr, υ, cm-1): 3482 (m), 1624 (s), 1542 (s), 1480 (m), 1335 (m), 1266 (m), 1053 (w), 1028 (m) 976 (w), 851 (s), 756 (s), 625 (m), 486 (s).

$[Yb_2(HL)_2(NO_3)_4].3CH_3CN.CH_3OH$**(2)** The empirical formula: $C_{47}\ H_{47}\ N_{11}\ O_{19}\ Yb_2$, Yield: 37 mg, 57% based on $Yb(NO_3)_3.6H_2O$. Analytical data (%), calculated: C, 39.85; H, 3.32; N, 10.88 found: C, 39.87; H, 3.31; N, 10.89%; IR (KBr, υ, cm-1): 3482 (m), 1624 (s), 1542 (w), 1480 (m), 1347 (m), 1266 (w), 1159 (w), 1028 (m), 982 (w), 851 (s), 750 (s), 631 (m), 486 (s).

C. X-ray crystallographic analysis

Single-crystal X-ray diffraction analysis of complexes were carried out on a Bruker SMART Apex CCD area detector diffractometer (Mo Kα, λ = 0.71073 Å) at 293K. Data processing was accomplished with the SAINT processing program [15]. Multiscan absorption corrections were applied by using the program SADABS [16].The structures were solved with direct methods and refined with full-matrix least squares on F^2 using the SHELXL-97 program package [17]. All non-hydrogen atoms were subjected to anisotropic refinement, and all hydrogen atoms were added in idealized positions and refined isotropically. The R1 values are defined as $R1=\Sigma\|Fo|-|Fc\|/\Sigma|Fo|$ and $wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$. Crystallographic diagrams were drawn using the DIAMOND software package [18]. A summary of the relevant crystallographic data and the final refinement details are given in Table. 1, important bond lengths (Å) and angles (°) are presented in Table. 2.

Table. 1. Crystallographic data and structure refinement parameters for complexes 1and 2

Empirical formula	***$C_{42}\ H_{35}\ Er_2\ N_9\ O_{18}$***	***$C_{47}\ H_{47}\ Yb_2\ N_{11}\ O_{19}$***
Formula weight	1288.31 g/mol	1416.03 g/mol
T (k)	1288.31 g/mol	1416.03 g/mol
Dcalcd (g/cm3)	1.64098	1.79699
Crystal system	Monoclinic,	Monoclinic,
Space group	P 1 21/c1	P 1 21/c1
a(Å)	a=20.7546(19)	a=20.7521(2)
b(Å)	b=19.2955(11)	b=19.3342(2)
c(Å)	c=13.6681(10)	c=13.6296(10)
α(°)	90	90
β(°)	107.707(9)	106.8520(10)
γ(°)	90	90
V /Å^3, Z	5214.4(7), 2	5233.70(9), 4
μ / mm^{-1}	7.271	3.638
F(000)	3610	2792
Theta range for data collection.	3.351 to 25.242	1.914 to 25.595
Completeness	99.6%	98.1%
Limiting indices	27≤h≤25 -25≤k≤25 -6≤I≤18	-24≤h≤25 -22≤k≤23 -12≤I≤16
Reflections collected/ unique	22472/11897	23087/9581
Data/restraints/params	11897/0/703	9581/1.078/820
Goodness-of-fit on F^2	1.084	1.078
Final R indices [I>2sigma(I)]	R1= 0.0676, wR2 = 0.1287	R1= 0.0361, wR2 = 0.1103
R indices (all data)	R1 = 0.1485, wR1 = 0.1725	R1 = 0.0381, wR1 = 0.1124

Table. 2. Selected bond lengths (Å) and angles (◦) for Er(III) and Yb(III) complexes

$[Er_2(HL)_2(NO_3)_4].3CH_3CN.CH_3OH$
Er1-O4 2.275(6) Er1-O5 2.278(6) Er1-O6 2.231(5) Er1-O7 2.432(7) Er1-O8 2.388(6) Er1-O10 2.436(6) Er1-O11 2.403(6) Er1-O1 2.323(5) O1-Er1-O7 84.6(2) O1-Er1-O8 137.9(288) O1-Er1-O10 122.4(2) O1-Er1-O11 84.1(2) O4-Er1-O1 72.0(2) O4-Er1-O5 76.18(19) O4-Er1-O7 156.5(2) O4-Er1-O8 149.0(2) O4-Er1-O10 78.9(2) O4-Er1-O11 98.7(2) O5-Er1-O1 138.0(2) O5-Er1-O7 125.1(2) O5-Er1-O8 80.0(2) O5-Er1-O10 75.9(2) O5-Er1-O11 127.8(2) O6-Er1-O1 86.1(2) O6-Er1-O4 98.8(2) O6-Er1-O5 72.4(2) O6-Er1-O7 80.8(2) O6-Er1-O8 92.5(2) O6-Er1-O10 147.8(2) O6-Er1-O11 156.1(2)O7-Er1-O10 113.9(2) O8-Er1-O7 53.9(2) O8-Er1-O10 76.4(2) O8-Er1-O11 80.6(2) O11-Er1-O7 76.7(2) O11-Er1-O10 52.5(2)
$[Yb_2(HL)_2(NO_3)_4].3CH_3CN.CH_3OH$
O10-Yb1 2.392(3) O8-Yb1 2.372(4) O1-Yb1 2.230(3) O2-Yb1 2.250(3) O3-Yb1 2.259(3) O6-Yb1 2.277(3) O11-Yb1 2.394(3) O7-Yb1 2.402(3) O1-Yb1-O2 73.5(1) O1-Yb1-O3 98.73(11) O2-Yb1-O3 76.58(10) O1-Yb1-O6 85.71(10) O2-Yb1-O6 139.84(1) O3-Yb1-O6 73.06(10) O1-Yb1-O8 159.78(1) O2-Yb1-O8 126.71(1) O3-Yb1-O8 86.88(14) O6-Yb1-O8 77.32(12) O1-Yb1-O10 83.12(13) O2-Yb1-O10 127.55(1) O3-Yb1-O10 154.52(1) O6-Yb1-O10 81.79(11) O8-Yb1-O10 83.64(15) O1-Yb1-O11 80.22(11) O2-Yb1-O11 76.37(10) O3-Yb1-O11 152.04(1) O6-Yb1- O11 134.15(1) O8-Yb1-O11 103.79(1) O10-Yb1-O11 53.43(11) O1-Yb1-O 146.42(1) O2-Yb1-O7 74.91(12) O3-Yb1-O78 4.70(11) O6-Yb1-O7 126.64(1) O8-Yb1-O7 53.10(13) O10-Yb1-O7 107.84(1) O11-Yb1-O7 81.58(11)

III. RESULTS AND DISCUSSION

D. synthesis and characterization

The reaction between H_3L with Ln $(NO_3)_3.6H_2O$ and NEt_3 in 1:1:2 molar ratio in methanol and acetonitrile mixture (v:v =1:4) at room temperature. Which volatilized to obtain the desired complexes as analytically pure solids, the two compounds which were found to be rather insoluble in most solvents other than methanol, DMSO and DMF. In the infrared spectra of H_3L, the characteristic band of carbonyl group of free ligand in IR spectra at band 1644 cm^{-1} Upon coordination appearance new band presented at ca.1624 cm^{-1} of the complexes sifted 20 from (1644 to 1624) compared to free ligands, indicates the complete coordination of the ligand as shown in (fig .1). The absorption bands assigned to the coordinated nitrates were observed as two group bands at about 1480 cm $^{-1}$ (ν_1) and 1335 cm $^{-1}$ (ν_4) for the complexes. The differences between the strongest absorption band ν_1 and ν_4 of nitrate group ca.145 cm$^{-\ 1}$, indicating that coordinated nitrate groups in the complexes are bidentate anions.

E. Crystal structure descriptions

Signal-crystal X-ray diffraction analysis revealed that as synthesized of The crystals structural $[Ln_2(HL)_2(NO_3)_4].3CH_3CN.CH_3OH$ containing complexes 1 and 2 dinuclear complexes and crystallizes in the monoclinic system, space group P 1 21/c1. The Er(III), Yb(III) complexes are isostructural, so here we select complex 2 to describe their structure features in detail. A view of the molecular structure, organized with its numbering scheme, is depicted in (Fig. 2a). The ytterbium atom is in a distorted dodecahedron coordination geometry (Fig. 2b), of which the coordination sphere for YbIII is defined by, one amide oxygen atom(O2), two phenolic oxygen atom (O1, O3) from the same partly deprotonated HL^{2-} ligand, one phenolic oxygen(O6) bridging another partly deprotonated HL^{2-} ligand and the remaining four oxygen atoms from two bidentate nitrates (O7, O8, O11, O10).as shown in (Fig. 2c) two crystallographically equivalent YbIII ions are bridged by phenoxy ocygen atom to give a dinuclear building block.

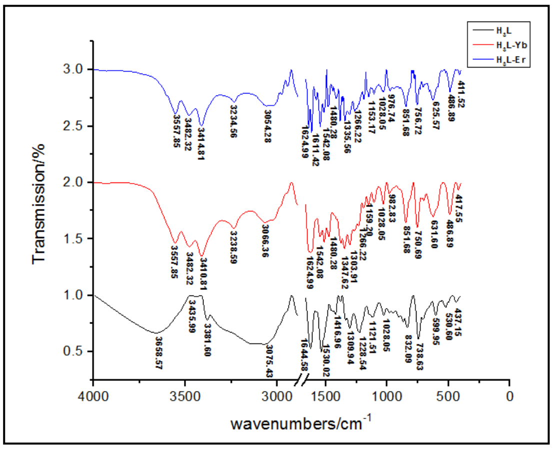
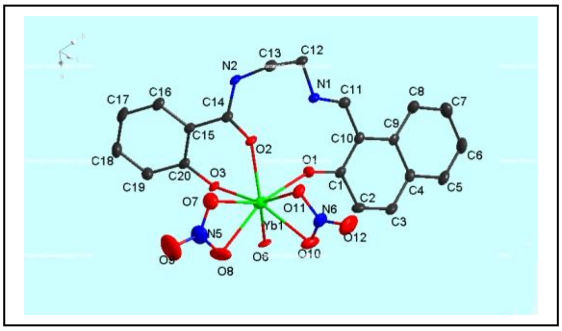
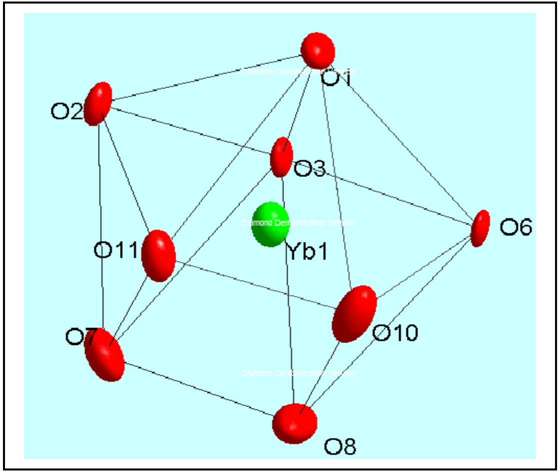


Fig. 1. IR Spectra of ligand H_3L and lanthanide complexes

(a)



(b)



(c)

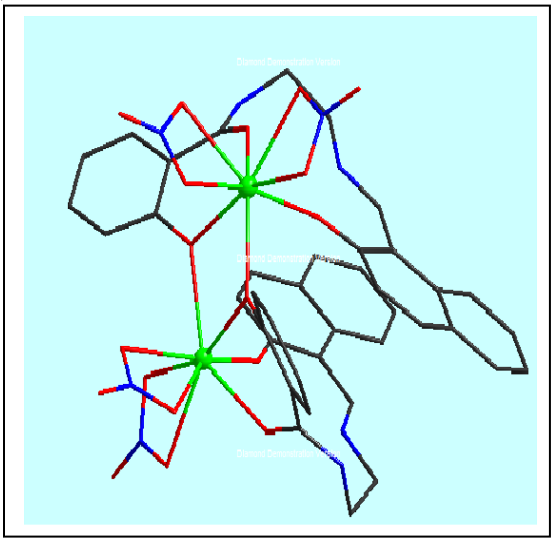


Fig. 2. a) The coordination environment of YbIII ion in compound 2 with thermal ellipsoids at 30% probability (All hydrogen atoms are omitted for clarity).color code: Yb, green; O, red; N, blue; C, black.(b) Coordination polyhedron of Yb(III) in compound 2 (c) the dinuclear structure of compound 2 with a Yb–O–Yb–O four-membered ring

F. NIR luminescence properties

We have studied herein the NIR luminescence properties of complexes 1, 2 in the solid state. Upon excitation, at 470 nm (in fig.3) characteristic Er(III) ion emissions were observed. The ErIII ion emits spectra cover a broad spectral range 1200–1600 nm. With the emission sharp peak maxima centered at1530 nm. The emission obtained is attributed to the typical $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of the Er^{3+} ion. Actually, Er-doped materials with high bandwidth and optical gain were of great interest in optical communications technology because the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition around 1540 nm matches one of the fiber low-loss windows [19]. For Yb(III) ion When excited at 368 nm (in Fig. 4), the typical emission band of the Yb(III) ion in the complex is a single sharp transition in which well-split NIR emission peaks are observed. The Yb^{3+} ion emits in the range 870‑1200 nm. The emission sharp peak centered at 978 nm was assigned to the transition of $^2F_{5/2} \rightarrow {}^2F_{7/2}$. The Yb^{3+} ion plays an important role in laser emission because of its (a) very simple f–f energy level structure. (b)There is no excited-state absorption on reducing the effective laser cross section, (c) no up-conversion, (d) no concentration quenching, (e) no absorption in the visible range [20]. Moreover, upon excitation of the ligand–centered absorption band in NIR region, noticeable is very weak NIR emission and strong emission for 1, 2 complexes respectively.these indications in fact that the ligand–center has absorbed and transferred energy to lanthanide ions as a type of organic antenna. The weak emission of 1 complex may be due to the fact Er(III) NIR emission can be quenched by C-H vibrations of the ligand.

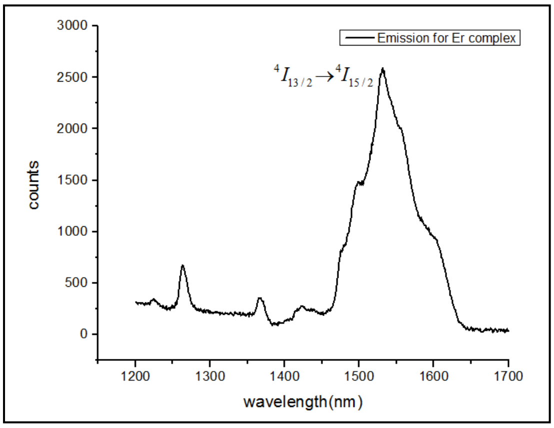


Fig. 3. The NIR emission spectra of 1 (λ_{ex} = 470 nm) in solid state

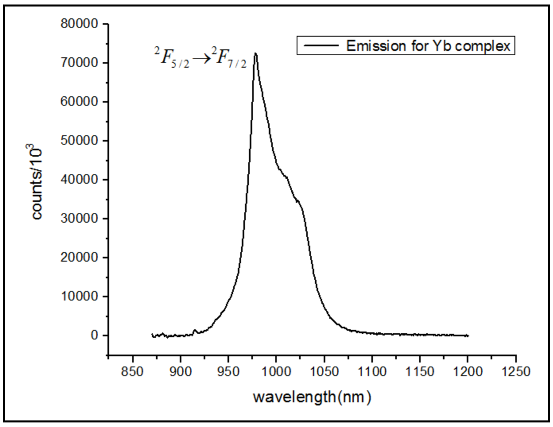


Fig. 4. The NIR emission spectra of 2 (λ_{ex} = 368 nm) in solid state

Appendix Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 1012481 and 1012485. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

CONCLUSION

Finally, two dinuclear complexes have been prepared under similar reaction conditions. By the salicylamide Salen-like ligand H_3L with lanthanide (III) nitrate. The structures of the 1,2 complexes have been determined by single-crystal X-ray diffraction revels bridged by phenoxy dinuclear Ln(III) ions complexes all of the emission spectra of the complexes in the solid state are characteristic NIR luminescence of the corresponding Ln^{3+} ions. This is ascribed to efficient energy transfer from the ligands to the Ln^{3+} ion (the so-called “antenna effect”).

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