



# Synthesis, crystal structure and luminescence properties of homodinuclear lanthanide complexes with a new tetrapodal thenylsalicylamide ligand



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## ABSTRACT

Five new homodinuclear lanthanide(III) complexes with a new tetrapodal thenylsalicylamide ligand (L), of formulae  $[\text{Nd}_2\text{L}_2(\text{NO}_3)_6(\text{CH}_3\text{OH})_2] \cdot 2\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$  (**1**), and  $[\text{Ln}_2\text{L}_2(\text{NO}_3)_6(\text{CH}_3\text{OH})_2] \cdot 4\text{CH}_3\text{OH}$ , Ln = Sm (**2**), Eu (**3**), Gd (**4**), Tb (**5**)) have been synthesized and characterized by single-crystal X-ray diffraction, elemental analysis, IR spectroscopy and molar conductance analysis. The two arms of L ligand arranged in a complementary head to head fashion to bind two lanthanide to form a cage-like coordination dimer with the other two uncoordinated arms constructing interesting three dimensional supramolecular structures. The europium and terbium containing compounds both exhibit luminescence of the referring trivalent lanthanide ions, giving a red luminescence for Eu(III) and a green luminescence for Tb(III) triggered by an efficient antenna effect of the thenylsalicylamide group.

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## 1. Introduction

The excellent photoactive properties of trivalent lanthanide ion, such as sharp emission spectra for high color purity, broad emission bands covering the ultraviolet - Vis (UV) near infrared (NIR) region, a wide range of lifetimes from the microseconds to seconds level, and high luminescence quantum efficiencies, have attracted much attention for a wide variety of applications in the fields of lighting devices (television and computer displays, optical fibers, optical amplifiers, lasers), and biomedical analysis (medical diagnosis and cell imaging) [1–11]. Not surprisingly, there have been numerous examples of luminescent Ln(III) complexes reported in the literature, with emission spanning from the visible [12–14] to near-infrared (NIR) regions [15,16]. As is known, a common feature of these systems is the use of an organic chromophore, which incorporates a donor atom (or atoms) capable of forming coordination bonds to the lanthanide cations resulting in thermodynamically stable complexes. This chromophore then functions as an ‘antenna’ [17], absorbing incident photons and transferring to the metal, which is necessary since the  $4f \rightarrow 4f$  absorptions of Ln(III) cations are Laporte forbidden.

In order to gain high luminescence, the ligands used in the construction of lanthanide complexes should be able to efficiently transfer the energy absorbed by chromophores to the lanthanide ions. In addition, the non-radiation processes of the centre ion's excited state should be reduced by protecting the ion from O–H oscill-

lators. Of the many antennae, salicylamide ligands are widely used in the construction of lanthanide complexes possessing strong luminescence properties as well as diverse interesting structures [18] because the modification of both the backbone and the terminal group can tune the structure as well as luminescent properties effectively, which prompts us to synthesize and investigate analogues of the extensive series of these ligands. Therefore the new member of salicylamide derivatives namely, 1,1,1,1-tetrakis[(2'-(2-thenylaminoformyl))phenoxy]methylmethane (L) (Scheme 1) and the resulting lanthanide complexes were prepared to extend our systematic research. As a result, five new homo-dinuclear complexes with interesting supramolecular properties were isolated. These compounds, namely,  $[\text{Nd}_2\text{L}_2(\text{NO}_3)_6(\text{CH}_3\text{OH})] \cdot 2\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$  (**1**),  $[\text{Sm}_2\text{L}_2(\text{NO}_3)_6(\text{CH}_3\text{OH})] \cdot 4\text{CH}_3\text{OH}$  (**2**),  $[\text{Eu}_2\text{L}_2(\text{NO}_3)_6(\text{CH}_3\text{OH})] \cdot 4\text{CH}_3\text{OH}$  (**3**),  $[\text{Gd}_2\text{L}_2(\text{NO}_3)_6(\text{CH}_3\text{OH})] \cdot 4\text{CH}_3\text{OH}$  (**4**),  $[\text{Tb}_2\text{L}_2(\text{NO}_3)_6(\text{CH}_3\text{OH})] \cdot 4\text{CH}_3\text{OH}$  (**5**) were synthesized by the solution evaporation method and characterized via single-crystal X-ray diffraction analysis, IR, elemental and molar conductance analysis. The luminescence properties of the resulting complexes formed with ions used in fluoroimmunoassays (Ln = Eu, Tb) are also studied in detail.

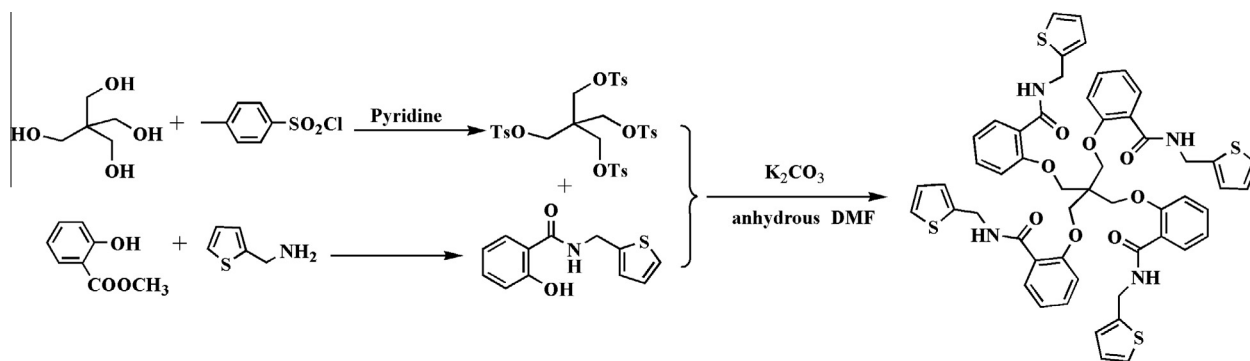
## 2. Experimental

### 2.1. Materials and instrumentation

Thenylamine and anhydrous N,N-dimethylformamide (DMF) were obtained from Alfa Aesar Co. Other commercially available chemicals were of analytical grade and were used without further

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**Scheme 1.** The synthetic route of the ligand L.

purification. The lanthanide nitrates [19] were prepared according to the literature method.

The metal ions analyses were determined by EDTA titration using xylenol orange as indicator. Carbon, nitrogen, sulfur and hydrogen analyses were performed using an EL elemental analyzer. Conductivity measurements were carried out with a DDS-307-type conductivity bridge using  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> solutions in methanol at 25 °C. Powder X-ray diffraction patterns (PXRD) were determined with Rigaku-D/Max-II X-ray diffractometer with graphite-monochromatized Cu K $\alpha$  radiation. Melting points were determined on a Kofler apparatus. Infrared spectra (4000–400 cm<sup>-1</sup>) were obtained with KBr discs on a Thermo Mattson FTIR spectrometer. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> solution at room temperature on a Bruker 400 instrument operating at a frequency of 400 MHz and referenced to tetramethylsilane (0.00 ppm) as an internal standard. Chemical shift multiplicities are reported as s = singlet, d = doublet, t = triplet and m = multiplet. The emission spectra of the sample was collected by two lenses in a monochromator (WDG30), detected by a photomultiplier and processed by a Boxcar Average (EGG model 162) in line with a microcomputer. Quantum yields were determined by an absolute method [20] using an integrating sphere on FLS920 of Edinburgh Instrument. The luminescence decays were recorded using a pumped dye laser (Lambda Physics model FL2002) as the excitation source. The nominal pulse width and the line width of the dye-laser output were 10 ns and 0.18 cm<sup>-1</sup>, respectively. Reported quantum yields and luminescence lifetimes are averages of at least three independent determinations. The estimated errors for quantum yields and luminescence lifetimes are 10%. The 77 K solution-state phosphorescence spectra of the Gd(III) complex was recorded with solution samples (a 1:1 Ethyl acetate–MeOH (v/v) mixture) loaded in a quartz tube inside a quartz-walled optical Dewar flask filled with liquid nitrogen in the phosphorescence mode [21].

## 2.2. Synthesis of the ligand

The synthetic route for the ligand (L) is shown in Scheme 1. 2-Thenylsalicylamide was prepared according to the literature procedure with minor modifications [22] and pentaerythritol benzenesulfonate [23] were prepared according to the literature.

To a solution of pentaerythritol benzenesulfonate (2.32 g, 3.3 mmol) in anhydrous N,N-dimethylformamide (DMF) was added dried K<sub>2</sub>CO<sub>3</sub> (2.07 g, 15 mmol) and the mixture was stirred for 30 min at room temperature, 2-thenylsalicylamide 3.50 g (15 mmol) in 20 ml of anhydrous DMF was added dropwise in 30 min and the resulting solution was stirred and heated to reflux for 48 h. After cooling down, inorganic salts were separated by filtration and the solvent removed from the filtrate under reduced pressure. The crude product was purified by chromatography on

silica, gradient elution from petroleum to 1:1 petroleum–ethyl acetate to give a white solid. 2.55 g, Yield 76.2%. m.p. 121–122 °C. *Anal.*, Calc. for C<sub>53</sub>H<sub>48</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub>: C, 63.83; H, 4.85; N, 5.62; S, 12.86; Found: C, 63.67; H, 4.74; N, 5.76%. IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3375 (s), 2912 (m), 2886 (w), 1650 (s, C=O), 1597 (m), 1532 (s), 1481 (m), 1293 (s), 1226 (s, Ar–O), 752 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$ : 3.892 (s, 8H, OCH<sub>2</sub>), 4.688 (d, 8H, NHCH<sub>2</sub>,  $J$  = 5.2 Hz), 6.697 (m, 12H, ArH), 6.913 (m, 4H, ArH), 7.069 (t, 4H, NH), 7.156 (t, 4H, ArH), 7.530 (m, 4H, ArH), 8.009 (t, 4H, ArH).

## 2.3. Synthesis of the complexes

One millimole of ligand and 1 equiv (1 mmol) of the lanthanide nitrates were dissolved in a hot methanol + ethyl acetate (v/v = 1:10) solution to make a concentrated solution. Then the flask was cooled, and the mixture was filtered into a sealed 10–20 mL glass vial for crystallization at room temperature. After about three weeks crystals suitable for analysis were obtained. IR, molar conductance and elemental analysis data for all complexes are summarized in Tables 1 and 2 respectively.

## 2.4. X-ray single-crystal diffraction analysis

The single crystal was carefully selected under a microscope and glued at the tip of a thin glass fiber with cyanoacrylate adhesive. Diffraction data were collected at 296 K on a computer controlled Bruker SMART Apex CCD area detector diffractometer which equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) operating at 50 kV and 30 mA. The crystal structures were solved by direct methods and refined with full-matrix least squares on  $F^2$  using the SHELXT-97 program package [24]. All the non-hydrogen atoms were located from the difference maps and refined with anisotropic thermal parameters. The H atoms of the organic ligand were placed theoretically, while the H atoms of water were located from the difference maps. All the hydrogen atoms were isotropically refined using the riding model. Further details of the X-ray structural analysis are given in Table 1 and representative bond lengths (Å) are presented in Table 2.

## 3. Results and discussion

### 3.1. Physical measurements

Analytical data for the newly synthesized lanthanide complexes, listed in Table 3, conforms to a 1:1 metal-to-L stoichiometry. All complexes are soluble in DMF, DMSO, ethanol, methanol and slightly soluble in ethyl acetate. The molar conductance of the complexes in methanol (Table 3) indicate that all complexes act as non-electrolytes.

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