



A Nd^{III} enantiomeric pair: Synthesis, crystal structures and near-infrared luminescent properties



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ABSTRACT

Based on enantiopure bis-bidentate N-donor ligands (-)/(+)-2,5-bis(4,5-pinene-2-pyridyl)pyrazine (L_R/L_S), a new pair of Nd^{III} enantiomers with the formula Nd(dbm)₃L_{R/S}·2H₂O (**R-1** and **S-1** being the isomers containing the L_R and L_S ligands, respectively, and dbm = dibenzoylmethanate) have been isolated and characterized by X-ray crystallography and spectroscopic methods. Notably, unlike our previously reported homodinuclear Eu^{III} and Dy^{III} complexes based on the identical ligands (L_R and L_S), the dinuclear Nd^{III} congener have not been obtained by controlling the ligand-to-metal ratio as expected, the reason of which was elucidated in this work. The crystal structure analyses of **R-1** and **S-1** reveal that they are mononuclear Nd^{III} complexes and crystallize in chiral space group *P*2₁2₁ of the orthorhombic system. Circular dichroic (CD) spectra confirmed their chiroptical activities and enantiomeric nature. The photoluminescence investigations showed that they display characteristic near-infrared (NIR) emissions of the Nd^{III} ions with notable emitting lifetime value.

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1. Introduction

The design and construction of luminescent lanthanide (Ln) complexes has received considerable attention over the past decades not only due to the peculiar photophysical properties such as element-specific emitting, long lifetime, large Stokes shift and sharp emission bands [1,2], but also to their practical and potential applications in display devices, tunable lasers, luminescent probes in biology and efficient photo-conversion molecular devices [3–6]. However, the f–f transitions of Ln^{III} ions are Laporte-forbidden, resulting in very low molar absorption coefficients. For the observation of intensive emissions in Ln^{III} complexes, it is necessary to use organic chromophores which act as “antenna” of light harvesting to excite the emitting of Ln^{III} ions indirectly. β-diketones are the most common “antenna” ligands for the emitting of Ln^{III} ions due to the fact that they can not only form stable adducts with Ln^{III} ions but also possess strong absorption within a large wavelength range, which favors to transfer efficiently the energy to Ln^{III} centers [7–10]. Among the reported Ln^{III} β-diketonate complexes, of the type Ln^{III} tris(β-diketonate) species are most investigated. These complexes are electrically neutral and usually contain one or two

water molecules in the inner coordination sphere. However, water molecule can quench emissions of Ln^{III} ions because of the presence of the O–H oscillators. So, another neutral N-donor ligand is adopted usually to displace the water molecules for the intensive emitting of resulting Ln^{III} complex. The typical N-donor ligands include 2,2'-bipyridine, 1,10-phenanthroline, 2,2':6',2''-terpyridine and their derivatives [11–15]. They not only provide N-donor atoms to chelate Ln^{III} ion so as to prevent the coordination of solvent molecules but also function as β-diketone, so called “synergistic effect”.

Traditionally, the Eu^{III}, Tb^{III}, Sm^{III} and Dy^{III} complexes usually exhibiting emissions in the visible range are exploited intensively. However, the Nd^{III}, Er^{III} and Yb^{III} species showing near-infrared (NIR) luminescent properties are less developed [16]. Recently, considerable efforts have been devoted to the investigations on the NIR emission properties of Ln^{III} β-diketonate complexes because of their promising applications in laser systems, fluoroimmunoassay, optical amplification and telecommunication networks [17–25]. In particular, the Nd^{III}-containing complexes (emitting at 890, 1060 and 1330 nm) have been applied to laser systems and biological tissues owing to the fact that the light with the wavelength of 0.9–1.5 μm has less interference with biomaterials [26].

In addition to their excellent luminescence features, Ln^{III} β-diketonate complexes with chirality may display other interesting properties such as circularly polarized luminescence (CPL), second

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harmonic generation (SHG), triboluminescence, chirality sensing and ferroelectricity which only correlate to the chiral molecule structures or noncentrosymmetric molecule arrays [27–30]. Based on aforementioned facts and as a continuous work of our researches related to the chiral Ln^{III} functional complexes [24,31–35], we chose enantiopure bis-bidentate ligands (–)/(+)-2,5-bis(4,5-pinenene-2-pyridyl)pyrazine (L_R/L_S, Scheme 1) as N-donor ligands to replace the H₂O molecule of Nd(dbm)₃H₂O. Subsequently, a new pair of enantiomers with the formula Nd(dbm)₃L_{R/S}·2H₂O (**R-1** and **S-1** being the isomers containing the L_R and L_S ligands, respectively, and dbm = dibenzoylmethanate) were synthesized and structurally characterized. The NIR luminescent properties and enantiomeric nature of **R-1** and **S-1** were also investigated.

2. Experimental

2.1. Material and physical measurements

All of the chemicals are commercially available and used without further purification. Nd(dbm)₃H₂O was prepared according to reference's method [36]. (–)/(+)-2,5-bis(4,5-pinenene-2-pyridyl)pyrazine (L_R/L_S) were synthesized according to previously reported procedures [37]. Elemental analyses for C, H and N were performed on a Vario EL III Elemental analyzer. IR spectra were registered on a TENSOR27 Bruker Spectrophotometer from KBr pellets in the region of 4000–400 cm⁻¹. Excitation and emission spectra along with luminescent lifetimes were measured with an Edinburgh FLS920 fluorescence spectrophotometer at room temperature. The solid state CD spectra were performed on a JASCO J-810 spectropolarimeter from KCl pellets (1% wt.) at room temperature.

2.2. Synthesis

2.2.1. Synthesis of Nd(dbm)₃L_R·2H₂O (**R-1**)

A solution of Nd(dbm)₃H₂O (83 mg, 0.1 mmol) in ethanol (10 mL) was added to a solution of (–)-2,5-bis(4,5-pinenene-2-pyridyl)pyrazine (L_R) (42 mg, 0.1 mmol) in acetone (8 mL) with gentle stirring for 20 min at room temperature. Subsequently, the mixture was placed undisturbed for two weeks. Pale yellow crystals of **R-1** were obtained in 63% yield (based on Nd). Elemental analysis (%) calcd. for **R-1** (C₇₃H₆₇N₄NdO₈): C, 68.90; H, 5.30; N, 4.40. Found:

C, 68.76; H, 5.17; N, 4.37. IR (KBr pellet, cm⁻¹): 1605 (s, ν_{C=O} stretching), 1552 (s, ν_{C=N} stretching).

2.2.2. Synthesis of Nd(dbm)₃L_S·2H₂O (**S-1**)

S-1 was prepared as pale yellow crystals by a method similar to that of **R-1** using (+)-2,5-bis(4,5-pinenene-2-pyridyl)pyrazine (L_S) instead of (–)-2,5-bis(4,5-pinenene-2-pyridyl)pyrazine (L_R). Yield: 67% (based on Nd). Elemental analysis (%) calcd for **S-1** (C₇₃H₆₇N₄NdO₈): 68.90; H, 5.30; N, 4.40. Found: C, 68.72; H, 5.21; N, 4.35. IR (KBr pellet, cm⁻¹): 1602 (s, ν_{C=O} stretching), 1557 (s, ν_{C=N} stretching).

Notably, unlike our previously reported homodinuclear Eu^{III} and Dy^{III} complexes based on the identical ligands (L_R and L_S) [32,33], the reaction of two equivalents of Nd(dbm)₃H₂O with one equivalent of (+)/(–)-2,5-bis(4,5-pinenene-2-pyridyl)pyrazine (L_{R/S}) still resulted in mononuclear complexes Nd(dbm)₃L_{R/S} under the same reaction conditions. Since ionic radius of Nd^{III} ion is bigger than those of Dy^{III} and Eu^{III} ions, we believe that the effect of the lanthanide contraction possesses a considerable influence on the nuclearity and structure of resulting complex, which also was observed in other reported lanthanide complexes [38–40].

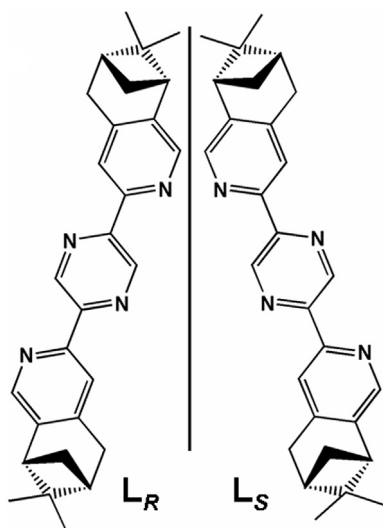
2.3. X-ray data collection and structure determination

The X-ray single crystal data of **R-1** and **S-1** were collected on a Bruker SMART APEX CCD area detector equipped with graphite monochromated Mo–Kα radiation (λ = 0.71073 Å) at room temperature using both Φ- and ω-scan modes. The structures were obtained by direct methods and refined on F² by full matrix least square using SHELXTL-97 crystallographic software package with anisotropic displacement parameters for all non-hydrogen atoms. H atoms bonded to O atoms were located on difference Fourier maps and their coordinates were included as parameters in the refinement. All other H atoms were introduced in calculations using the riding model. Detailed crystallographic data and structures refinement parameters, and selected bond lengths and angles for enantiomeric pair **R-1** and **S-1** are listed in Table 1 and Table 2, respectively.

3. Results and discussion

3.1. Structural descriptions of **R-1/S-1**

X-ray single crystal analyses revealed that **R-1** and **S-1** are a pair of enantiomers and crystallize in the chiral space group P2₁2₁2₁ with the Flack parameters of 0.007(15) and 0.009(18) for **R-1** and **S-1**.



Scheme 1. The chemical structures of enantiopure bis-bidentate ligands L_R and L_S.

Table 1
Crystallographic data and structure refinement parameters for **R-1/S-1**.

	R-1	S-1
Chemical formula	C ₇₃ H ₆₇ N ₄ NdO ₈	C ₇₃ H ₆₇ N ₄ NdO
Formula	1272.55	1272.55
Crystal system	Orthorhombic	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
a (Å)	17.3450(9)	17.3645(4)
b (Å)	17.5383(10)	17.7590(4)
c (Å)	21.9571(13)	21.9020(5)
α = β = γ (°)	90	90
V (Å ³)	6679.4(6)	6754.1(3)
Z	4	4
D _c (g/cm ³)	1.265	1.251
μ/mm ⁻¹	0.834	0.824
GOF	1.006	1.006
R ₁ ^a /ωR ₂ ^b	0.0548/0.1465	0.0543/0.1465
Flack parameter	0.007(15)	0.009(18)

^aR₁ = Σ||F_o| - |F_c||/Σ|F_o|. ^bωR₂ = [Σw(F_o² - F_c²)²/Σw(F_o²)²]^{1/2}.

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