

Synthesis, crystal structures and characterization of a pair of Tb^{III}-based enantiomers

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Abstract: A pair of novel Tb^{III}-based enantiomers, [Tb(dbm)₃·L_{SS}] (**1**) and [Tb(dbm)₃·L_{RR}] (**2**) (where L_{SS}=(+)-4,5-pinene bipyridine, L_{RR}=(−)-4,5-pinene bipyridine, dbm=dibenzoylmethanate), were synthesized and characterized based on single crystal X-ray diffraction, elemental analysis, FT-IR, TG and CD spectra. X-ray diffraction analysis showed that both the complexes crystallized in monoclinic crystal system with *P*₂₁ chiral space group. The Tb^{III} ion was eight-coordinated by six O atoms of three dbm ligands and two N atoms from one chiral ligand L_{SS} or L_{RR}. The CD spectra revealed that complexes **1** and **2** were enantiomers. Thermogravimetric analysis results indicated that **1** and **2** were thermally stable up to 246 °C.

Keywords: enantiomers; chirality; rare earths; terbium complex

In the field of coordination chemistry, chiral ligands play a key role in the design of functional complexes. Many metal complexes with chiral ligands have been successfully employed in asymmetric catalysis, enantiomer-selective extraction, chirality sensing, biomimetic modeling and so on^[1–3]. Additionally, many physical properties such as ferroelectricity, piezoelectricity, magneto-chiral dichroism (MCD) and second harmonic generation (SHG), etc.^[4,5], are only based on the noncentrosymmetric crystal lattices that can be effectively and facily realized by the introduction of chiral motifs in a molecule. Furthermore, chiral lanthanide complexes have attracted considerable interest because of their use as chiral shift reagents for resolving NMR spectra and enantiomer-selective catalysts^[6]. Based on our previous work^[7–9], a pair of chiral bipyridine derivative ligands [L_{SS}=(+)-4,5-pinene bipyridine, L_{RR}=(−)-4,5-pinene bipyridine (Scheme 1)] were to react with Tb(dbm)₃·2H₂O (dbm=dibenzoylmethanate) respectively, and a new pair of Tb^{III}-based enantiomers [Tb(dbm)₃·L] (L=L_{SS} **1** or L_{RR} **2**) were obtained. Herein, the synthesis, crystal structures, CD spectra and thermal properties of complexes **1** and **2** were reported.



Scheme 1 L_{SS} (+)-4,5-pinene bipyridine (left) and L_{RR} (−)-4,5-pinene bipyridine (right)

1 Experimental

1.1 Materials and measurements

All chemicals and reagents were of analytical grade from commercial sources and used as received. The L_{SS} and L_{RR} ligands were synthesized according to reported procedure^[10,11], and Tb(dbm)₃·2H₂O was prepared according to a literature method^[12]. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. IR spectra were acquired on a Vector22 Bruker spectrophotometer using the KBr pellet technique in the 400–4000 cm^{−1} region. The circular dichroism spectra were recorded on a JASCO J-810 spectropolarimeter in THF (THF=tetrahydrofuran).

1.2 Preparation of complexes **1** and **2**

A solution of L_{SS} (25 mg, 0.1 mmol) in acetone (5 ml) was added to a solution of Tb(dbm)₃·2H₂O (42.6 mg, 0.1 mmol) in ethanol (5 ml). The mixture was gently stirred for 10 min and allowed to stand for three weeks. Yellow block crystals of **1** were obtained in 70% yield. Elemental analysis (%) calcd. for **1** (C₆₂H₅₁N₂O₆Tb): C 68.95, H 4.73, N 2.59; Found: C 66.87, H 5.12, N 2.86. IR (KBr, cm^{−1}): ν 1601 s (C=O stretching), ν 1552 s (C=N stretching).

Complex **2** [Tb(dbm)₃·L_{RR}] was obtained with the procedure similar to that of complex **1** using L_{RR} (25 mg, 0.1 mmol) instead of L_{SS} to react with Tb(dbm)₃·2H₂O. Yield: 65%. Elemental analyses (%) calcd. for **2** (C₆₂H₅₁N₂O₆Tb):

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C 68.95, H 4.73, N 2.59; Found: C 67.37, H 4.96, N 2.74. IR (KBr, cm⁻¹): ν 1601 s (C=O stretching), ν 1552 s (C=N stretching).

1.3 X-ray data collection and structure determination

The crystal structures of complexes **1** and **2** were measured on a Bruker SMART CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda=0.071073$ nm) at room temperature. Cell refinement and data reduction were made with the Bruker SAINT program. The structures were solved by directed method and refined on F^2 by using full-matrix least-squares methods with SHELXTL-97. All non-hydrogen atoms were refined by using anisotropic displacement parameters. H atoms were introduced in the calculations using the riding model. Detailed information about the structure data for complexes **1** and **2** are summarized in Table 1, while their selected atomic distances and bond angles are given in Table 2.

2 Results and discussion

2.1 Description of the crystal structure

The structure of complex **2** has been reported elsewhere^[13], so only the structure of **1** is depicted here. Due to the introduction of the chiral 2,2'-bipyridine derivative ligands, both complexes crystallize in the chiral space group $P2_1$. As shown in Fig. 1, the mononuclear Tb^{III}-based complexes are eight-coordinated with six O atoms, O1–O6, from β -diketonate ligands and two N atoms of chiral 2,2'-bipyridine derivative. The O–Tb distances range from 0.2312 to 0.2391 nm, and the bond angles of O–Tb–O range from 72.39° to

Table 1 Crystal data and structure refinement parameters for complexes **1** and **2**

Complex	1	2
Chemical formula	C ₆₂ H ₅₁ N ₂ O ₆ Tb	C ₆₂ H ₅₁ N ₂ O ₆ Tb
Formula weight	1078.97	1078.97
Space group	$P2_1(1)$	$P2_1(1)$
a/nm	0.9533(9)	0.9517(2)
b/nm	2.0769(2)	2.0726(5)
c/nm	1.2752(12)	1.2729(3)
$\beta/^\circ$	92.162(2)	92.300(5)
V/nm^3	2.5231(4)	2.5087(10)
Z	2	2
$D_{\text{calc}}/(\text{g}/\text{cm}^3)$	1.420	1.428
μ (Mo K α)/(mm ⁻¹)	1.457	1.465
Data/restraints/parameters	9498/1/642	8601/1/642
θ Range/ $^\circ$	1.60–26.00	1.60–26.00
R_{int} (on F^2)	0.0269	0.0355
Goodness of fit on F^2	1.114	1.137
R_1 [$I > 2 \sigma(I)$] ^a	0.0573	0.0502
wR_2 (all data) ^b	0.1335	0.1064
Flack	0.040(14)	0.032(13)

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)|^2 / \sum w(|F_o|^2)]^{1/2}$

Table 2 Selected bond lengths (10⁻¹ nm) and angles ($^\circ$) for complexes **1** and **2**

Complex 1			
N(1)–Tb(1)	2.549(6)	O(3)–Tb(1)	2.350(4)
N(2)–Tb(1)	2.596(6)	O(4)–Tb(1)	2.325(5)
O(1)–Tb(1)	2.346(5)	O(5)–Tb(1)	2.331(5)
O(2)–Tb(1)	2.312(7)	O(6)–Tb(1)	2.391(6)
O(2)–Tb(1)–O(1)	70.5(2)	O(4)–Tb(1)–O(3)	72.39(17)
O(5)–Tb(1)–O(6)	72.9(2)	N(1)–Tb(1)–N(2)	61.9(2)
O(3)–Tb(1)–O(6)	80.3(3)	O(2)–Tb(1)–O(4)	81.0(2)
O(5)–Tb(1)–N(1)	79.3(2)	O(6)–Tb(1)–N(1)	76.2(2)
O(5)–Tb(1)–O(1)	75.81(18)	O(3)–Tb(1)–N(2)	80.03(18)
O(6)–Tb(1)–N(2)	71.5(3)	O(2)–Tb(1)–O(3)	76.4(3)
Complex 2			
N(1)–Tb(1)	2.572(6)	O(3)–Tb(1)	2.342(4)
N(2)–Tb(1)	2.579(5)	O(4)–Tb(1)	2.297(5)
O(1)–Tb(1)	2.309(6)	O(5)–Tb(1)	2.335(6)
O(2)–Tb(1)	2.317(7)	O(6)–Tb(1)	2.352(7)
O(1)–Tb(1)–O(2)	71.6(2)	O(4)–Tb(1)–O(3)	72.10(17)
O(5)–Tb(1)–O(6)	72.5(2)	N(1)–Tb(1)–N(2)	62.4(2)
O(4)–Tb(1)–O(2)	82.6(2)	O(1)–Tb(1)–O(5)	75.94(18)
O(3)–Tb(1)–O(6)	79.9(3)	O(6)–Tb(1)–N(1)	76.7(2)
O(2)–Tb(1)–O(3)	76.0(3)	O(5)–Tb(1)–N(1)	78.8(2)
O(6)–Tb(1)–N(2)	72.0(3)	O(3)–Tb(1)–N(2)	79.81(16)

143.61°. The two N–Tb distances are 0.2549 and 0.2596 nm, respectively. The N–Tb–N bond angle is 61.9°. Eight bonds with different lengths give rise to a strongly distorted square antiprism environment around the Tb^{III} cation. The two square planes are defined by O3–O4–O5–O6 (bottom plane) and O1–O2–N1–N2 (top plane) (see Fig.2) with the mean deviations of 0.0057 and 0.0092 nm from each plane, respectively. Their dihedral angle is 1.81°.

2.2 The CD absorption spectra

The circular dichroism (CD) spectra of complexes **1** and **2** are shown in Fig. 3. Complex **1** shows positive Cotton effects at $\lambda=250$ and 280 nm with a negative one at $\lambda=220$ nm, while complex **2** exhibits Cotton effects with opposite sign at the same wavelength. They are mirror images in the observed CD spectra. The sign patterns of the CD spectra of complexes **1** and **2** suggest the intrinsic chiral nature of the ligands L_{SS} and L_{RR}, because the ligands L_{SS} and L_{RR} are enantiomers. Their CD spectra are also mirror images (see Fig. 3).

2.3 Thermogravimetric analysis

Since the complexes **1** and **2** are enantiomers, they exhibit the same thermal properties. Only the thermogravimetric analysis of **1** is described in detail (Fig. 4). The thermal behaviour of the complex **1** exhibits two stage decomposition pattern. The initial stage of the decomposition occurs at 420 °C with mass loss 63.8% (calcd. 64.6%), which is attributed to the release of the chiral bipyridine derivative ligand

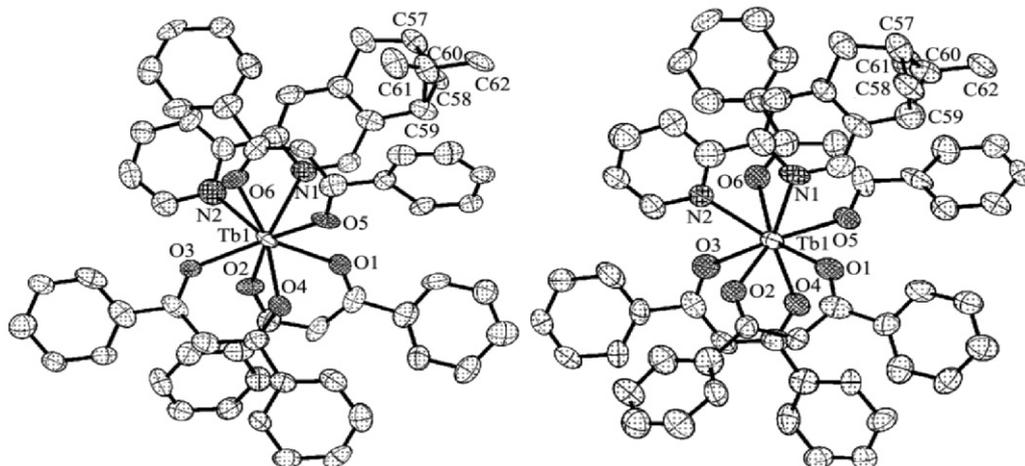


Fig. 1 Structures of **1** (left) and **2** (right) showing 50% probability displacement ellipsoids and the atom-numbering schemes (H atoms are omitted for clarity)

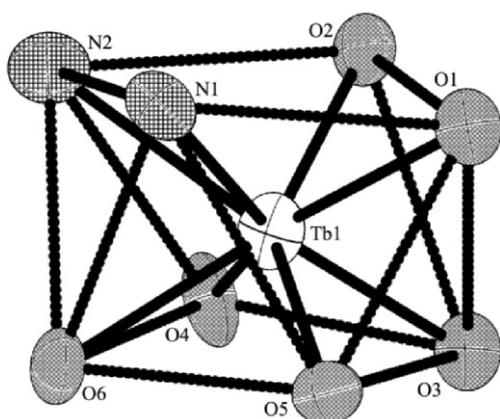


Fig. 2 Coordination polyhedron of **1** around Tb^{III} ion

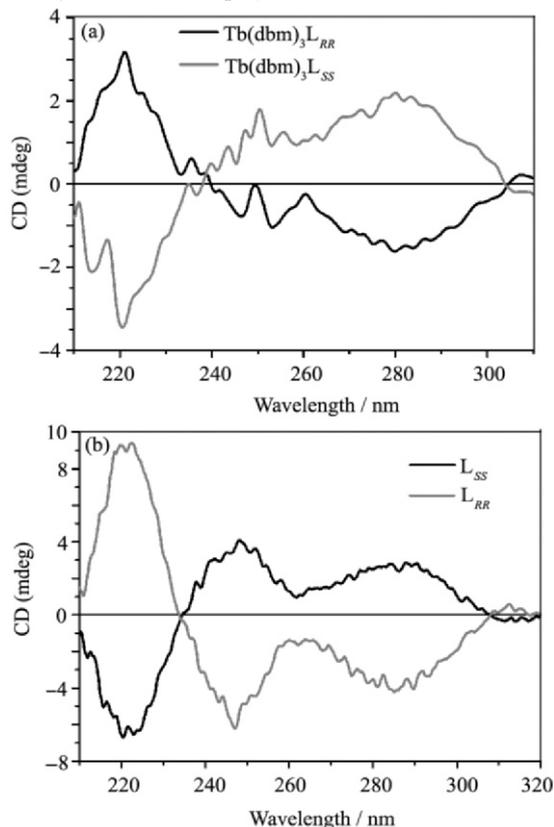


Fig. 3 CD spectra of complexes **1** (grey), **2** (black) and chiral ligands in THF at room temperature

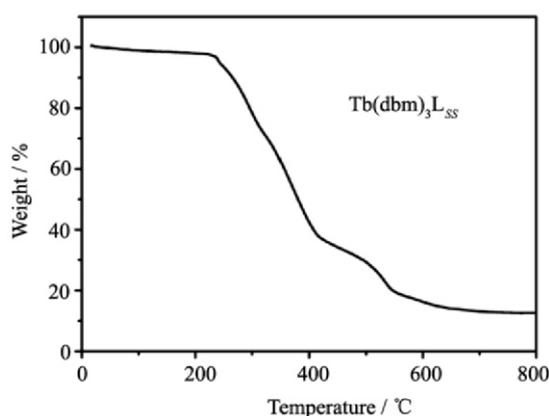


Fig. 4 Chart of TG for complex **1**

and two dibenzoylmethanate (dbm) ligands. The second stage of decomposition occurs between 420 and 550 °C with mass loss of 18.81% (calcd. 20.7%) related to the loss of the last one dibenzoylmethanate ligand. The total observed mass loss at 640 °C is 83.6%, and the final residuals are not characterized.

3 Conclusions

We synthesized a pair of Tb^{III}-based enantiomers with chiral ligands and their structures were established by single crystal X-ray diffraction. The CD spectra reflected that the two complexes showed promising chirality. The thermogravimetric analysis implied that they exhibited a relatively high thermal stability.

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