Crystal Structure, and Magnetic and Fluorescence Properties of a New Terbium(III) Complex, [Tb(L)$_3$(2,2′-bipy)(DMF)]·(2,2′-bipy)

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A new Tb(III) complex, [Tb(L)$_3$(2,2′-bipy)(DMF)]·(2,2′-bipy) (**1**), has been synthesized with 2-benzoylbenzoic acid (HL) and 2,2′-bipyridine (2,2′-bipy) as ligands. In **1**, the Tb(III) ion is coordinated by nine atoms to give a distorted tri-capped trigonal-prismatic geometry. The magnetic and fluorescence properties of **1** are discussed. Compound **1** is paramagnetic in the temperature range of 300 – 24 K, and when the temperature decreases from 22 to 2 K, it exhibits weak ferromagnetism. The compound shows four intense fluorescence emission bands arising from the transitions of Tb^{3+}: $^5D_4 \rightarrow {}^7F_6$ (492 nm), $^5D_4 \rightarrow {}^7F_5$ (546 nm), $^5D_4 \rightarrow {}^7F_4$ (590 nm) and $^5D_4 \rightarrow {}^7F_3$ (622 nm) with an excitation wavelength of 315 nm.

Key words: Terbium(III) Complex, Crystal Structure, Magnetic and Fluorescence Properties

Introduction

In the domain of rare earth chemistry, there is a great deal of interest in the design and construction of complexes with organic ligands due to their intriguing structural topologies and potential application in many fields such as luminescence labeling, magnetic molecular materials, catalysis, adsorption, and selective extraction of lanthanide ions [1 – 7]. Nowadays, in this field, much attention has been focused on Tb(III) complexes because the Tb(III) ion is one of the most important optical centers for application in the production of plastic membranes, lighting and ornament materials [8 – 15]. In the past few years, we have also carried out some work to prepare functional Tb(III) complexes. For example, we have synthesized the Tb(III) complexes [Tb$_2$(ClC$_6$H$_4$COO)$_6$(2,2′-bipy)$_2$]·(ClC$_6$H$_4$COOH)·(H$_2$O) [16] and {[Tb(*p*-MBA)$_2$(H$_2$O)$_2$]$_2$·(4,4′-bipy)$_2$}$_n$ [17], and studied their properties.

It is noteworthy to point out that 2-benzoylbenzoate acid is a rigid organic ligand of extensive use. It is an important raw material for anthraquinone dyes intermediates used in manufacturing anthraquinone and 1-aminoanthraquinone. The complex [Pr(BYBA)$_3$(H$_2$O)$_2$]·[Pr(BYBA)$_3$(H$_2$O)] has been synthesized with this ligand [18]. Rare earth complexes with its derivatives, such as 2,5-bis(4-methylbenzoyl)terephthalate and 4,6-bis(4-methylbenzoyl)isophthalate, have also been reported in the literature [19].

As an extension of our continuous research, in this paper, we report the synthesis and crystal structure of a new Tb(III) complex [Tb(L)$_3$(2,2′-bipy)(DMF)]·(2,2′-bipy) (**1**) based on 2-benzoylbenzoate (HL) as a ligand through solvothermal reaction. The magnetic and fluorescence properties of **1** are also discussed.

Results and Discussion

Structure description

Fig. 1 shows the molecular structure of **1**. Fig. 2 displays the coordination polyhedron for the Tb(III) ion. Details of the crystal parameters, data collection and refinement are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

As shown in Fig. 1, complex **1** consists of one central Tb(III) ion, three L$^-$ anions, two 2,2′-bipy molecules and one *N,N*-dimethylformamide (DMF) molecule. The coordination mode of the L$^-$ anions is bidentate chelating. Each Tb(III) ion is coordinated by seven oxygen atoms and two nitrogen atoms. The Tb(III) ion adopts a distorted tricapped trigonal-prismatic geometry (Fig. 2), where the three cap positions are occupied by O7, N1 and O1. The bond an-
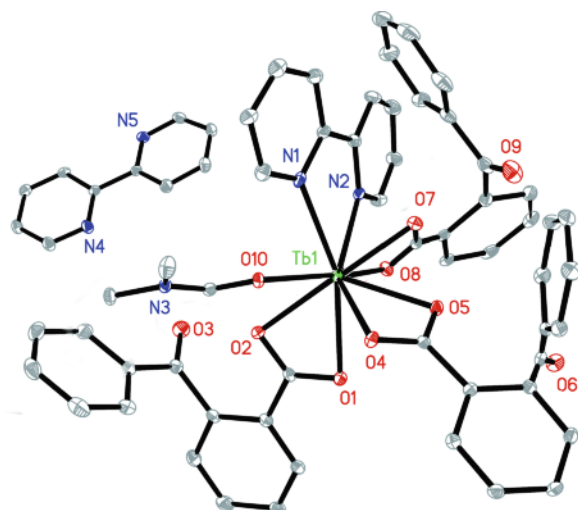
Fig. 1 (color online). Molecular structure of **1** (all hydrogen atoms are omitted for clarity).
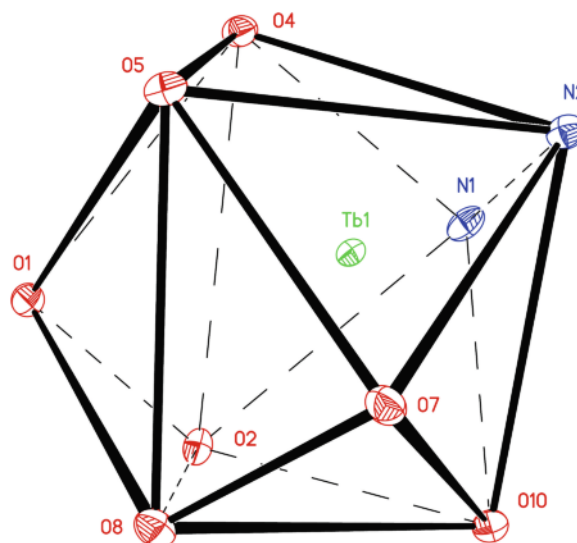

Fig. 2 (color online). Coordination geometry of the tricapped triangular prism of the Tb(III) ion of **1**.

Table 1. Crystal structure data for **1**.

Empirical formula	$C_{65} H_{50} N_5 O_{10}$ Tb
M_r	1220.02
Crystal size, mm³	$0.15 \times 0.14 \times 0.13$
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	27.8929(17)
b, Å	9.5819(6)
c, Å	20.4704(12)
β, deg	102.0030(10)
V, Å³	5351.4(6)
Z	4
$D_{calcd.}$, g cm⁻³	1.51
μ (MoK_α), cm⁻¹	13.9
$F(000)$, e	2480
hkl range	$-33 \rightarrow +31, \pm 11, -14 \rightarrow +24$,
$((\sin\theta)/\lambda)_{max}$, Å⁻¹	0.645
Refl. measured / unique / R_{int}	27 045 / 9429 / 0.0280
Param. refined	732
$R(F)$ / $wR(F^2)^{a,b}$ (all refls.)	0.0304 / 0.0580
A / B values for weighting scheme^b	0.0184 / 6.4642
GoF $(F^2)^c$	1.084
$\Delta\rho_{fin}$ (max / min), e Å⁻³	0.65 / −0.82

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^{b} $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^{c} GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses.

Tb1–O10	2.3892(17)	Tb1–O4	2.4783(17)
Tb1–O5	2.3969(17)	Tb1–O1	2.5038(18)
Tb1–O8	2.4169(17)	Tb1–N2	2.509(2)
Tb1–O2	2.4342(18)	Tb1–N1	2.547(2)
Tb1–O7	2.4651(18)	O1–C24	1.258(3)
O10–Tb1–O5	151.76(6)	O2–Tb1–O1	52.81(6)
O10–Tb1–O8	80.97(6)	O7–Tb1–O1	119.65(6)
O5–Tb1–O8	86.81(6)	O4–Tb1–O1	71.44(6)
O10–Tb1–O2	75.80(6)	O10–Tb1–N2	86.63(6)
O5–Tb1–O2	127.35(6)	O5–Tb1–N2	81.90(6)
O8–Tb1–O2	80.95(6)	O8–Tb1–N2	130.02(6)
O10–Tb1–O7	76.70(6)	O2–Tb1–N2	141.73(6)
O5–Tb1–O7	75.56(6)	O7–Tb1–N2	76.52(6)
O8–Tb1–O7	53.53(6)	O4–Tb1–N2	74.72(6)
O2–Tb1–O7	129.61(6)	O1–Tb1–N2	145.84(6)
O10–Tb1–O4	146.06(6)	O10–Tb1–N1	76.41(6)
O5–Tb1–O4	53.74(6)	O5–Tb1–N1	120.28(6)
O8–Tb1–O4	132.62(6)	O8–Tb1–N1	152.50(7)
O2–Tb1–O4	101.62(6)	O2–Tb1–N1	78.52(7)
O7–Tb1–O4	124.09(6)	O7–Tb1–N1	133.14(7)
O10–Tb1–O1	124.97(6)	O4–Tb1–N1	70.01(6)
O5–Tb1–O1	74.58(6)	O1–Tb1–N1	107.21(7)
O8–Tb1–O1	73.57(6)	N2–Tb1–N1	64.27(7)

gles N1–Tb1–O1, O1–Tb1–O7 and O7–Tb1–N1 are 107.21(7), 119.65(6) and 133.14(7)°, respectively, and their sum is 360°, which is characteristic of this type of polyhedron. Atoms N2, O4 and O5 give the upper plane of the trigonal prism, and atoms O10, O2 and O8 determine the plane below. Their dihedral angle is 13.3°. Owing to the occupancy of O1 and N1 in capping positions, it is reasonable that the bonds Tb1–O1 (2.5038(18) Å) and Tb1–N1 (2.547(2) Å) are longer than the other Tb1–O and Tb1–N bonds.
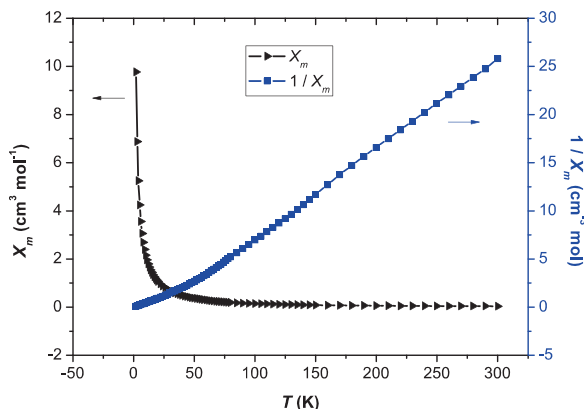
Fig. 3 (color online). Temperature dependence of the magnetic susceptibility of **1** in the form of χ_M and $1/\chi_M$ *vs. T*.

Fig. 4 (color online). Emission spectrum of **1** in a mixed solvent of DMF-H_2O (v/v; 4 : 1) at room temperature.

Magnetic properties

The magnetic susceptibility of **1** was measured in the temperature range of $300 - 2$ K with an applied magnetic field of 2 kOe. The temperature dependence of the molar magnetic susceptibility of **1** is presented in Fig. 3 in the form of χ_M and $1/\chi_M$ *vs. T*. The product of χ_M increases slowly from 0.039 cm^3 mol^{-1} at 300 K to 0.88 cm^3 mol^{-1} at 24 K, while when the temperature decreases from 22 to 2 K, χ_M increases quickly from 0.963 to 9.77 cm^3 mol^{-1}. The data in the temperature ranges of $300 - 24$ K and $22 - 2$ K are in linear relationships between $1/\chi_M$ *vs. T*, and the linear regression equations are $1/\chi_M = 0.0914T - 1.8583$ and $1/\chi_M = 0.0465T + 0.0016$, with correlation coefficients of 0.9983 and 0.9997, respectively. According to the Curie-Weiss law, $\chi_M = C/(T - \theta)$, the Weiss constant (θ) can be obtained; θ of the former is 20.3 K, and that of the latter is -0.0344 K. This magnetic behavior shows that **1** is a paramagnetic compound in the range of $300 \sim 24$ K, and when the temperature changes from 22 to 2 K, it exhibits weak ferromagnetism.

Fluorescence properties

The fluorescence properties of **1** were measured in a mixed solvent of DMF-H_2O (v/v; 4 : 1) at room temperature in the range of $300 - 700$ nm. The emission spectrum is shown in Fig. 4. For an excitation wavelength of 315 nm, **1** has four intense fluorescence emission bands at 492, 546, 590, and 622 nm. Under the same conditions, the emission spectrum of 2,2′-
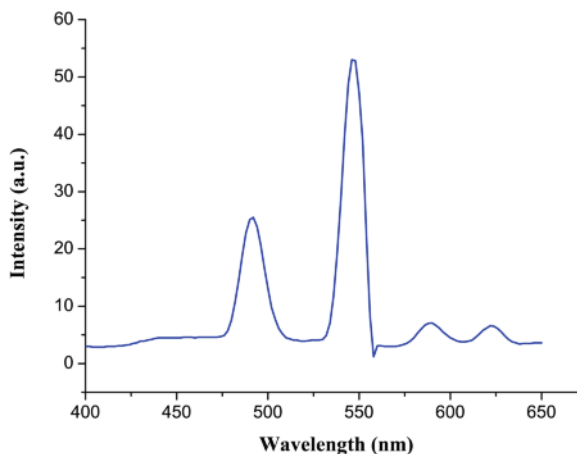
bipy and of HL was investigated with the same excitation wavelength. These ligands do not display similar fluorescence emission bands, which indicates that intraligand transitions do not cause the fluorescence emission of **1**. As in a similar Tb(III) complex [17], the photoluminescence bands of **1** probably arise from the transitions of Tb^{3+}: $^5D_4 \rightarrow {}^7F_6$ (492 nm), $^5D_4 \rightarrow {}^7F_5$ (546 nm), $^5D_4 \rightarrow {}^7F_4$ (590 nm) and $^5D_4 \rightarrow {}^7F_3$ (622 nm).

Experimental Section

The reagents were obtained from commercial sources and used without further purification. C, H, N analysis was conducted by means of a PE-2400(II) apparatus. Magnetic measurements in the range of $2 - 300$ K were performed on a MPMS-SQUID magnetometer at a field of 2 kOe on a crystalline sample in the temperature settle mode (1 kOe $= 7.96 \times 10^4$ A m^{-1}). The fluorescence spectra of samples in solution were obtained at room temperature on a WGY-10 fluorescence spectrophotometer.

*Preparation of [Tb(L)$_3$(2,2′-bipy)(DMF)]·(2,2′-bipy) (**1**)*

A mixture of terbium hydroxide (0.505 mmol, 0.106 g), HL (0.81 mmol, 0.183 g) and 2,2′-bipy (0.45 mmol, 0.070 g) was dissolved in 3 mL of the mixed solvent of DMF-H_2O (v/v; 2 : 1). The solution was poured into a 25 mL hydrothermal reaction autoclave and kept at 150 °C for 6 h. Then, the resulting solution was cooled to room temperature, and evaporated slowly. Colorless single crystals suitable for X-ray analysis were obtained after five weeks. Yield: 33 %. Anal.

for $[Tb(L)_3(2,2'\text{-bipy})(DMF)]\cdot(2,2'\text{-bipy})$: calcd. C 63.99, H 4.13, N 5.74; found C 63.93, H 4.12, N 5.73.

X-Ray structure determination

The single-crystal X-ray diffraction measurement for **1** was carried out on a Bruker Smart CCD area detector at 153(2) K by using graphite-monochromatized Mo K_α (λ = 0.71073 Å) radiation. The absorption correction was carried out by the program SADABS. The structure was solved by Direct Methods and refined by a full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs, respectively [20, 21]. All hydrogen atoms were generated geometrically and refined isotropically using the riding model.

CCDC 921634 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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