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ORIGINAL PAPER

Synthesis, Crystal Structure and Luminescent Property of Complex $[Tb_{0.1}Gd_{0.9}(TPTZ)(H_2O)_6]Cl_3{\cdot}3H_2O$

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Abstract The complex $[Tb_{0.1}Gd_{0.9}(TPTZ)(H_2O)_6]Cl_3{\cdot}3H_2O$ was prepared through the reaction of 2,4,6-tris-(2-pyridyl)-1,3,5-triazine (TPTZ) with $TbCl_3$:$GdCl_3$ (0.1:0.9) in absolute ethanol at room temperature. Single crystal X-ray diffraction revealed that the metal atom is nine-coordinated with three nitrogen atoms from one TPTZ ligand and six oxygen atoms from six water molecules. The complex emits intense green fluorescence under ultraviolet light. The luminescence peaks correspond to the characteristic emission $^5D_4 \rightarrow {}^7F_J$ (J=3–6) transitions of the Tb^{3+} ion.

Keywords 2,4,6-tris-(2-pyridyl)-1,3,5-triazine · Terbium complex · Luminescent property · Crystal structure

Introduction

We have been interested in developing new lanthanide complexes for potential applications in organic light-emitting devices [1–3]. The neutral ligands are important in modifying the properties of luminescent lanthanide complexes. One of the ligands is 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ, Fig. 1), a bulky aromatic compound featuring three 2-pyridyl rings fixed on a central 1,3,5-triazine platform [4]. This ligand has been studied previously for its application in actinide–lanthanide group separations in a synergistic extraction system [5]. There are a few structurally characterized lanthanide complexes in which TPTZ acts as a tridentate ligand [6–7]. TPTZ, by offering three coordinating atoms, protects the lanthanide ion from interacting with solvent molecules, and therefore, restrains solvent-based vibrational coupling and luminescence quenching [8]. Furthermore, the remaining nitrogen atoms allow further coordination to other metals, transition metals in particular. Thus, complicated heterometallic complexes structurally may be envisioned, for which novel magnetic as well as luminescence properties can be expected [9–13].

TPTZ is a nearly planar molecule and there are three different "coordination sites" in this molecule (Fig. 1). The major coordination site, contains three nitrogen atoms, two pyridyl and one triazin, and can form complexes with cation; the middle coordination site contains two nitrogen atoms, one pyridyl and one triazine; The minor coordination site contains only one nitrogen atom from the triazine, which makes it unlikely to form complexes with any ions. The complexation ability of TPTZ depends in part upon the size of the metal cations, which normally coordinate as a tridentate ligand to give a 1:1 metal/ligand ratio.

Complexes of the lanthanide with TPTZ were first reported by Durham et al. [14] in 1969. In this paper, our interest is studied on the synthesis, luminescent property and crystal structure of terbium and gadolinium with TPTZ complex.

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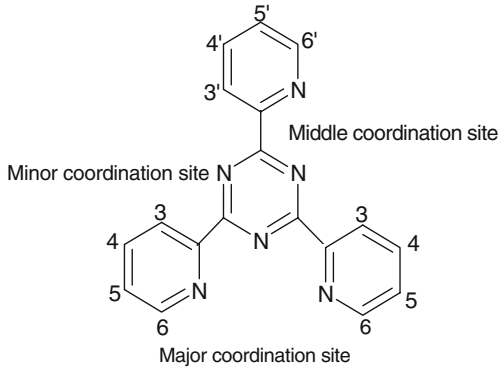

Fig. 1 The three coordination sites in TPTZ

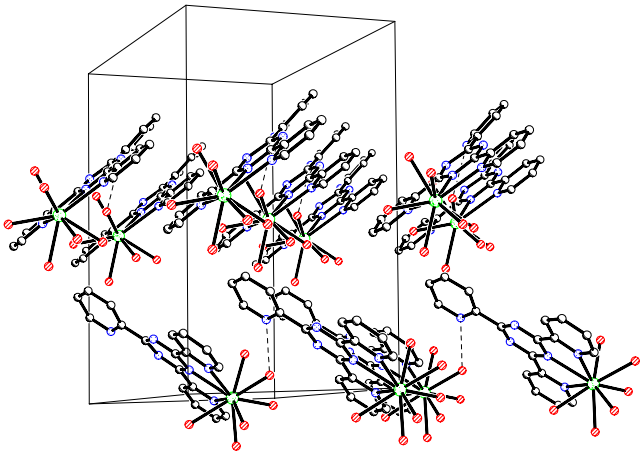

Fig. 3 Unit cell packing diagram of the complex

Experimental

Synthesis of the complex

A mixture of $TbCl_3 \cdot 6H_2O$ (0.037 g, 0.1 mmol) with $GdCl_3 \cdot 6H_2O$ (0.335 g, 0.9 mmol) in absolute ethanol (20 mL) added to a stirred ethanol solution containing TPTZ (0.312 g, 1 mmol). The resulting mixture was stirred under reflux for 3 h at 55 °C. A white precipitate deposited from the solution. After depositing for 24 h, the crude product was filtered, washed with deionized water and absolute ethanol. The filtrate was collected. Suitable crystals were obtained from the filtrate after 2 weeks at room temperature.

Apparatuses and measurements

Elemental analysis was carried out on a PE-2400 elemental analyzer. The contents of terbium and gadolinium were determined by a Varian 725–1S plasma emission spectrum. The excitation and emission spectra were measured using a Shimadzu RF-5301PC fluorescence spectrophotometer at room temperature, and the excitation and emission slit are all 3.0 nm. Luminescence lifetime measurements were carried out on an Edinburgh FLS920 phosphorimeter using a 450 W xenon lamp as excitation source. X-ray data were collected on a Bruker SMART 1000 CCD diffactometer with graphite-monochromated Mo Kα radiation (λ= 0.071073 nm) at a temperature of 294(2) K.

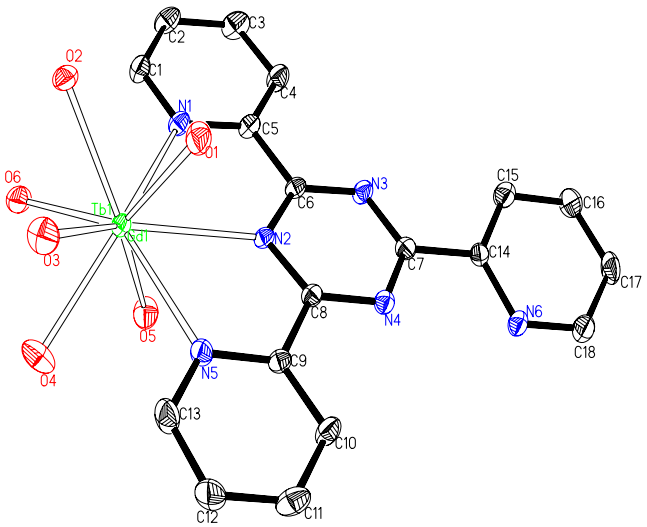

Fig. 2 The structure of $[Tb_{0.1}Gd_{0.9}(TPTZ)(H_2O)_6]^{3+}$ cation in crystal of $[Tb_{0.1}Gd_{0.9}(TPTZ)(H_2O)_6]Cl_3 \cdot 3H_2O$

Table 1 Crystallographic data of the complex

Empirical formula	$[Tb_{0.1}Gd_{0.9}(TPTZ)(H_2O)_6]Cl_3 \cdot 3H_2O$
Formula weight	738.25
Temperature	294(2) K
Wavelength	0.071073 nm
Crystal system	Monoclinic
space group	Cc
Unit cell dimensions	a=1.4874(2) nm α=90°
	b=1.06638(16) nm β=93.949 (2)°
	c=1.7496(3) nm γ=90°
Volume	2.7686(7) nm^3
Z	4
Density (calculated)	1.771 g/cm^3
Absorption coefficient	2.757 mm^{-1}
F(000)	1468
Crystal size	0.20×0.16×0.10 mm
θ range for data collection	2.33° to 26.36°
Limiting indices	$-18 \le h \le 18$, $-12 \le k \le 13$, $-9 \le l \le 21$
Reflections collected	7453
Independent reflections	3679 [R(int)=0.0176]
Max. and min. transmission	1.000000 and 0.652234
Data/restraints/parameters	3679/11/335
Goodness-of-fit on F^2	1.066
Final R indices [I>2σ(I)]	R_1=0.0200, wR_2=0.0490

Table 2 Selected bond lengths (nm) and bond angles (°) for the complex

	Bond lengths		Bond lengths		
Tb(1)-O(3)	0.2397(3)	Tb(1)-O(6)	0.2413(3)	Tb(1)-O(2)	0.2436(3)
Tb(1)-O(1)	0.2439(4)	Tb(1)-O(4)	0.2450(4)	Tb(1)-O(5)	0.2499(3)
Tb(1)-N(2)	0.2591(3)	Tb(1)-N(5)	0.2638(4)	Tb(1)-N(1)	0.2652(4)
O(3)-Tb(1)-O(6)	97.96(13)	O(3)-Tb(1)-O(2)	73.31(12)	O(6)-Tb(1)-O(2)	69.52(12)
O(3)-Tb(1)-O(1)	73.98(14)	O(6)-Tb(1)-O(1)	137.17(12)	O(2)-Tb(1)-O(1)	67.88(12)
O(3)-Tb(1)-O(4)	68.79(14)	O(6)-Tb(1)-O(4)	72.34(13)	O(2)-Tb(1)-O(4)	120.52(13)
O(1)-Tb(1)-O(4)	135.74(13)	O(3)-Tb(1)-O(5)	137.67(14)	O(6)-Tb(1)-O(5)	75.12(12)
O(2)-Tb(1)-O(5)	136.31(12)	O(1)-Tb(1)-O(5)	138.04(12)	O(4)-Tb(1)-O(5)	69.37(13)
O(3)-Tb(1)-N(2)	130.90(12)	O(6)-Tb(1)-N(2)	131.15(12)	O(2)-Tb(1)-N(2)	118.69(12)
O(1)-Tb(1)-N(2)	69.27(11)	O(4)-Tb(1)-N(2)	120.79(13)	O(5)-Tb(1)-N(2)	68.77(12)
O(3)-Tb(1)-N(5)	78.56(12)	O(6)-Tb(1)-N(5)	144.46(13)	O(2)-Tb(1)-N(5)	139.24(12)
O(1)-Tb(1)-N(5)	76.44(13)	O(4)-Tb(1)-N(5)	73.53(14)	O(5)-Tb(1)-N(5)	83.91(12)
N(2)-Tb(1)-N(5)	62.18(11)	O(3)-Tb(1)-N(1)	145.02(13)	O(6)-Tb(1)-N(1)	77.96(12)
O(2)-Tb(1)-N(1)	72.78(11)	O(1)-Tb(1)-N(1)	85.55(13)	O(4)-Tb(1)-N(1)	138.50(13)
O(5)-Tb(1)-N(1)	75.49(12)	N(2)-Tb(1)-N(1)	62.14(11)	N(5)-Tb(1)-N(1)	124.31(11)

Results and discussion

Elemental analysis

The elemental analysis data for C_{18} H_{30} Cl_3 $Gd_{0.90}$ N_6 O_9 $Tb_{0.10}$ ($[Tb_{0.1}Gd_{0.9}(TPTZ)(H_2O)_6]Cl_3{\cdot}3H_2O$) were: found (calculated)/%: C 29.01 (29.28), H 3.78 (4.10), N 11.68 (11.39), Tb 2.02 (2.15) and Gd 18.91 (19.18).

Crystal structure

The molecular formula of the complex crystal is $[Tb_{0.1}Gd_{0.9}(TPTZ)(H_2O)_6]Cl_3{\cdot}3H_2O$. Figures 2 and 3 show the molecular structure and the unit cell packing diagram of the crystal. The crystal size is 0.20×0.16×0.10 mm. The complex crystallizes in Monoclinic Cc space group. The metal atom is nine-coordinated with three nitrogen atoms from one TPTZ ligand and six oxygen atoms from six water molecules.

Main crystallographic data are shown in Table 1, and main bond lengths and bond angles of the crystal are shown in Table 2. The average bond lengths of Tb-O (0.2439 nm) are shorter than that of Tb-N (0.2627 nm).

The structure of TPTZ with nickel complex has been published previously, $[Ni(HTPTZ)(H_2O)_3]$[15], in which the metal is six-coordinated with three nitrogen atoms from one TPTZ ligand and three oxygen atoms from three water molecules. The Tb-N bond lengths [0.2591(3), 0.2638(4), 0.2652(4) nm] in the title compound structure are, as

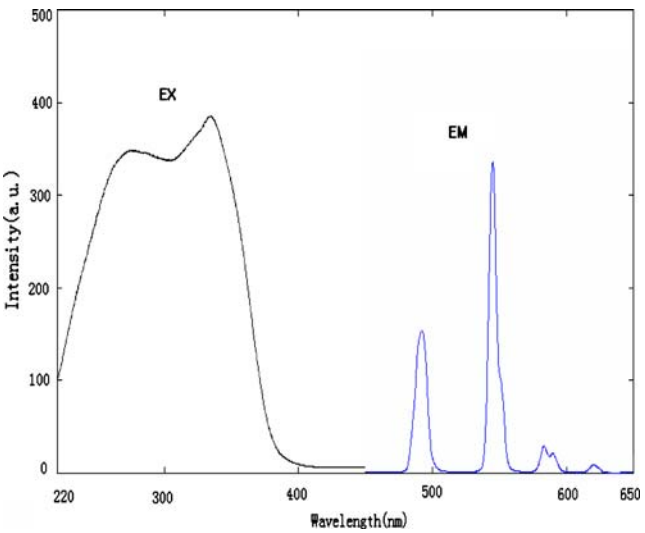

Fig. 4 Excitation and emission spectra of the complex

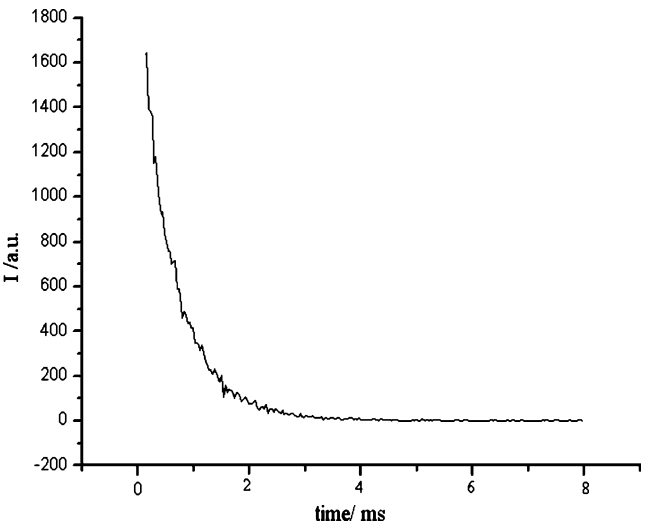

Fig. 5 Decay curve of the complex $[Tb_{0.1}Gd_{0.9}(TPTZ)(H_2O)_6]Cl_3{\cdot}3H_2O$

expected, more longer than the Ni-N distances [0.2011(6), 0.2166(6), 0.2181(6) nm].

Fluorescence spectra

The photoluminescence of the crystal was studied in the solid state at room temperature. It emits green fluorescence when exposed under ultraviolet light. Monitoring the emission wavelength at 545 nm, it shows that the excitation spectra of terbium compounds are band spectra, and terbium compounds can be excited in a wide area, whose optimal excitation wavelength is 334 nm. The excitation and emission spectrum of $[Tb_{0.1}Gd_{0.9}(TPTZ)(H_2O)_6]Cl_3{\cdot}3H_2O$ are given in Fig. 4, emission peaks at 492, 545, 583 and 619 nm contribute to the transition of $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ respectively, among which the $^5D_4 \rightarrow {}^7F_5$ transition is the strongest. It shows that the lowest excitation state energy level of Tb(III) with the triplet state energy level of TPTZ match well each other.

The luminescence decay curve of Tb^{3+} ($^5D_4 \rightarrow {}^7F_5$ at 545 nm) in complex $[Tb_{0.1}Gd_{0.9}(TPTZ)(H_2O)_6]Cl_3{\cdot}3H_2O$ was obtained at room temperature. The lifetime of the $^5D_4$ Tb^{3+} excited level in the complex was determined to be 0.91 ms, as shown in Fig. 5. It is clear that the luminescence of Tb^{3+} in the complex shows simple decay behavior.

Conclusions

A novel compound of $TbCl_3$ and $GdCl_3$ with TPTZ was synthesized and the crystal structure of $[Tb_{0.1}Gd_{0.9}(TPTZ)(H_2O)_6]Cl_3{\cdot}3H_2O$ was determined. The metal atom is nine-coordinated with three nitrogen atoms from one TPTZ ligand and six oxygen atoms from six water molecules. The complex emits intense green fluorescence under ultraviolet light.

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