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SHORT COMMUNICATION

SYNTHESIS, CRYSTAL STRUCTURE AND LUMINESCENT PROPERTY OF A DINUCLEAR Tb(II) COMPLEX WITH HOMOPHTHALIC ACID AND 2,2'-BIPYRIDYL

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Abstract: A novel dinuclear Tb(III) complex, $[Tb(bpy)_2L_2]$ (bpy = 2,2'-bipyridine, H_2L = homophthalic acid), has been synthesized and characterized by elemental analysis and single-crystal X-ray diffraction. The Tb(III) complex is monoclinic, space group P_{21}/c with a = 9.368(2) Å, b = 15.948(4) Å, c = 12.216(3) Å, β = 103.023(4)º, V= 1778.2(7) Å^3, Z = 2, Dc = 1.910 mg·m^{-3}, μ = 4.011 mm^{-1}, F(000) = 996, and final R_1 = 0.0602, ωR_2 = 0.2192. The result shows that the Tb(III) center is seven-coordination with a N_2O_5 distorted pengonal bipyramidal geometry. The luminescent property of Tb(III) complex was investigated.

Keywords: d*inuclear Tb(III) complex, luminescence property, synthesis, structural characterization*

INTRODUCTION

The design and synthesis of rare earth complexes with multi-carboxylate ligands have received many attentions, because they have novel structural architectures and topologies and potential applications in luminescence probe, biological medicine, magnetism, catalysis and so on [1 - 5]. Bipyridines have been used as secondary ligands to enhance the luminescence intensity of rare earth complex [6 - 8]. In this paper, we synthesized a novel dinuclear Tb(III) complex, $[Tb(bpy)_2L_2]$ (bpy = 2,2'-bipyridine, H_2L = homophthalic acid), and studied its crystal structure and luminescence property.

EXPERIMENTAL

Materials and methods

$Tb(NO_3)_3 \cdot 6H_2O$ was prepared according to ref. [9]. Homophthalic acid, 2,2'-bipyridine, NaOH and solvents were commercially available and used without further purification. Elemental analysis (C, H, N) was carried out on a Elementar Vario III EL elemental analyzer. The crystal data was collected on a Bruker smart-100 CCD Area Detector. The luminescence emission was recorded on a LS-55 spectroflurimeter (PE).

Synthesis of dinuclear Tb(III) complex

The mixture of homophthalic acid (0.5 mmol, 0.090 g), 2,2'-bipyridine (0.5 mmol, 0.078 g), NaOH (1.0 mmol, 0.040 g), and $Tb(NO_3)_3 \cdot 6H_2O$ (0.5 mmol, 0.227 g) were dissolved in 10 mL CH_3CH_2OH/H_2O (v:v = 2:1). Then the solution was stirred at 70 °C for 6 h. After cooling to room temperature, the colourless block crystals were obtained by evaporating slowly the filtrate for two weeks. Elementary analysis: calcd for $C_{38}H_{32}N_4O_{10}Tb_2$: C, 44.60; H, 3.13; N, 5.48 %. Found: C, 44.28; H, 3.52; N, 5.19 %.

Crystal data and structure refinement

A crystal with dimensions of 0.26 × 0.24 × 0.22 mm was selected for measurement. Diffraction data of the single crystal were collected by φ~ω scan mode using a graphite-monochromatic Mo $K\alpha$ radiation (λ = 0.71073 Å) at 293 (2) K on a Bruker Smart Apex CCD diffractometer. Empirical formula: $C_{38}H_{32}N_4O_{10}Tb_2$; Formula weight: 1022.52; Crystal system: monoclinic; Space group: P_{21}/c; a: 9.368(2) Å; b: 15.948(4) Å; c: 12.216(3) Å; β: 103.023(4)°; V: 1778.2(7) Å^3; Z; 2; Dc: 1.910 mg·m^{-3}; μ: 4.011 mm^{-1}; F(000): 996; Refl'ns collected: 11232; Independent refl'ns [R(int)]: 4275 [0.0581]; Refl'ns observed (>2δ): 3716; Goodness-of-fit: 1.095; Final R indices [I > 2δ(I)]: 0.0602, 0.2192; R indices (all data): 0.0655, 0.2257; Limiting indices: -12 ≤ h ≤ 11, -21 ≤ k ≤ 15, -16 ≤ l ≤ 15; Min. and max. resd. dens. (e/Å^3): 1.710, -1.215; The structure of Tb(III) complex was refined with program packages of SHELXL-97 and SHELXTL-97 [10, 11].

RESULTS AND DISCUSSION

Crystal structure

The crystal structure of dinuclear Tb(III) complex is shown in Figure 1. The result of structural analysis shows that each Tb(III) atom is seven-coordinated with four oxygen atoms of homophthalic acid [(O1, O2, O3A, O4A) and (O1A, O2A, O3, O4)], two nitrogen atoms of the 2,2'-bipyridine ligand [(N1, N2) and (N1A, N2A)] and one oxygen atom (O5 and O5A) of coordinated water molecule, respectively. The carboxylate groups of homophthalic acid both adopt bidentate coordination mode. Each Tb(III) ion adopts a distorted pengonal bipyramidal coordination environment. The complex molecules form 2D layered structure by the π-π stacking interaction of 2,2'-bipyridine (Figure 2).

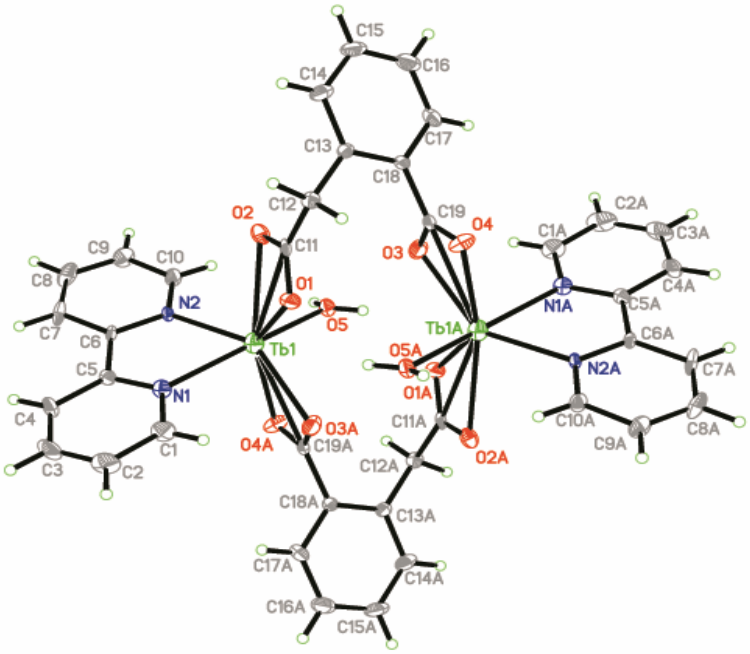

Figure 1. *Molecular structure of the Tb(II) complex*

Selected bonds: Tb1-O1 2.292(5) Å; Tb1-N2 2.318(4) Å; Tb1-N1 2.353(6) Å; Tb1-O5 2.362(4) Å; Tb1A-O3 2.395(6) Å; Tb1A-O4 2.433(5) Å; Tb1-O2 2.610(5) Å; C11-O1 1.271(8) Å; C11-O2 1.236(8) Å; C19-O3 1.265(8) Å; Tb1-O3A 2.395(6) Å; Tb1-O4A 2.433(5) Å; C19-O4 1.216(9) Å; C5-N1 1.336(8) Å; C1-N1 1.350(8) Å; C10-N2 1.331(8) Å; C6-N2 1.347(7) Å;

Selected angles: O1-Tb1-N2 124.12(17)°; O1-Tb1-N1 98.35(17)°; N2-Tb1-N1 70.17(18)°; O1-Tb1-O5 99.74(17)°; N2-Tb1-O5 96.82(16)°; O5-Tb1-N1 161.64(16)°; O3A-Tb1-O1 85.34(16)°; N2-Tb1-O3A 143.68(17)°; N1-Tb1-O3A 86.2(2)°; O5-Tb1-O3A 98.4(2)°; O1-Tb1-O4A 137.90(18)°; N2-Tb1-O4A 97.46(18)°; O4A-Tb1-N1 89.16(19)°; O4A-Tb1-O5 79.51(18)°; O3A-Tb1-O4A 53.73(18)°; O1-Tb1-O2 52.94(16)°; N2-Tb1-O2 81.40(15)°; O2-Tb1-N1 114.20(17)°; O5-Tb1-O2 75.03(15)°; O3A-Tb1-O2 134.47(15)°; O2-Tb1-O4A 154.16(17)°.

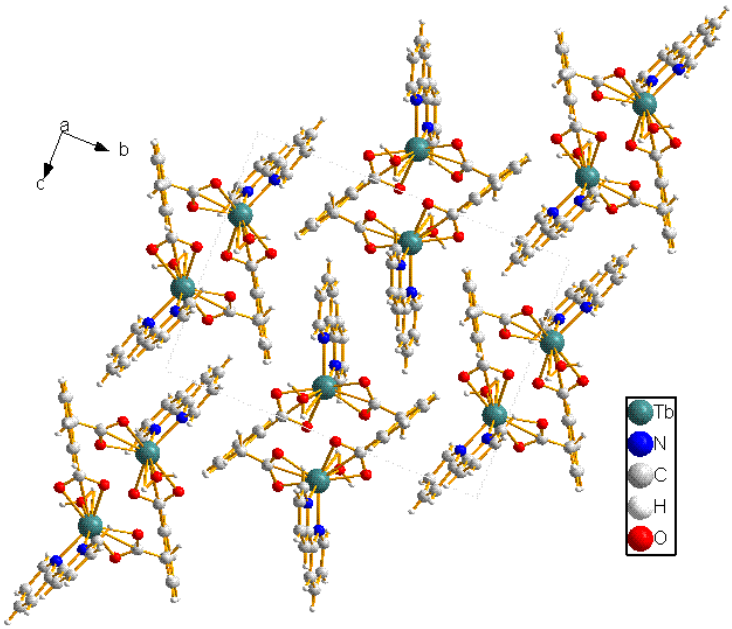

Figure 2. *π-π Stacking interaction of Tb(II) complex molecules*

Luminescence property

The luminescence property of Tb(III) complex has been investigated in solid state. The luminescence emission spectrum of Tb(III) complex is given in Figure 3. The Tb(III) complex exhibits two luminescence emission peaks at 549 nm and 491 nm when exicted at 379 nm.

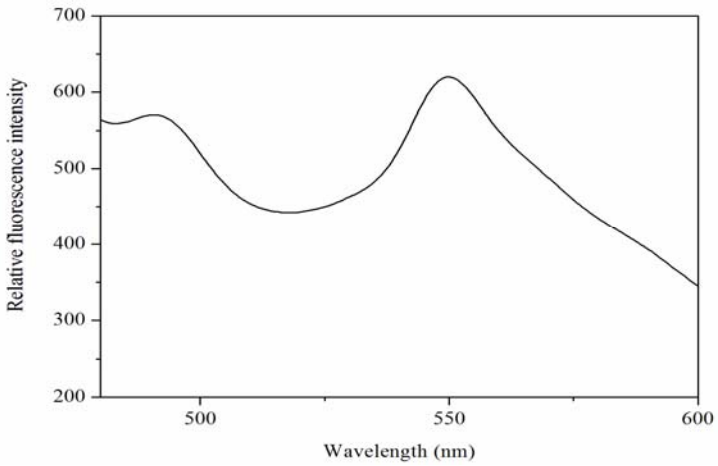

Figure 3. *The emission spectrum of Tb(II) complex. The excitation and emission slit widths were 5 nm*

CONCLUSIONS

A novel dinuclear Tb(III) complex has been synthesized and characterized by elemental analysis and single-crystal X-ray diffraction. The result shows that the Tb(III) center is seven-coordination with a N_2O_5 distorted pengonal bipyramidal geometry. The luminescent property of Tb(III) complex has also been investigated.

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