



Synthesis and luminescence properties of terbium complexes based on 4-acyl pyrazolone derivatives



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ABSTRACT

Six new 4-acyl pyrazolone derivatives and their complexes with the terbium nitrates were synthesized and characterized by mass spectra, elemental analysis, EDTA titrimetric analysis, UV spectra, infrared spectra, molar conductivity and thermal analysis. The results showed that pyrazolone derivatives formed good coordination with the terbium ions. The introduction of electron-donating group in the ligands not only increased the luminescence intensity and fluorescence quantum yield, but also enlarged the HOMO and LUMO energy levels of corresponding terbium complexes. All the complexes possessed high luminescence intensity and showed relatively high fluorescence quantum yields. These target complexes may have vast potential to be developed as luminescence materials in the future.

1. Introduction

Rare earth complexes have a very broad application prospects in the life, scientific research, industry and other fields due to their excellent optical, electrical and magnetic properties [1–6]. Especially, good luminescence properties of rare earth complexes make it used widely for fluorescent anti-counterfeiting materials [7,8], light conversion film and fluorescent tags. Therefore, it has been a diligent direction for the scientific research workers to design and synthesize the new rare earth complexes with excellent luminescent properties [9].

4-acyl pyrazolone contain aromatic and heterocyclic ring, and possess multiple ligand activity centers that enables it form a single core, dual core and dual different core of complexes with rare earth ions [10]. In order to develop good luminescence complexes, we have designed a series of pyrazolone compounds with β -diketone structure, which can be combined with rare earth ions to form a relatively stable structure, so that the complexes have a variety of properties in optical, electrical, magnetic and biological fields, etc. [11–14]. In this paper, six new 4-acyl pyrazolone derivatives and their complexes with the terbium ions were synthesized and characterized. Meanwhile, the synthetic methods, luminescence properties, fluorescence quantum yields and electrochemical properties of the title ligands and complexes are reported in detail. The synthesis route is shown in Scheme 1.

2. Experimental

2.1. Materials and methods

All the starting materials and reagents were purchased from commercial suppliers. Terbium nitrate was prepared according to the literature [15]. ¹H NMR and ¹³C NMR spectra were acquired on a Bruker-400 NMR instrument using CDCl₃ or DMSO-d₆ as solution and TMS as internal standard. Mass spectra were recorded on MAT 95 XP mass spectrometers. Melting points were determined with a TECH XT-4 melting point apparatus. Ultraviolet (UV) spectra were acquired on a LabTech UV-2100 spectrophotometer. IR spectra in the 4000–400 cm⁻¹ region were acquired with KBr disks on a IRAffinity-1 spectrometer. The thermal analysis was performed on a DTG-60 thermal analyzer operating at a heating rate of 20 °C/min. Fluorescence spectra were got on a HIACHI F-2700 spectrophotometer at a scanning rate of 1200 nm/min. The luminescence spectra of the title complexes were measured with 2.5 nm slit widths for excitation and 5.0 nm slit widths for emission in the solid state at room temperature under a drive voltage of 400 V, and an appropriated filter was placed to remove light scattering for non-absorbed wavelength. Fluorescence quantum yield of the title complexes(Φ_{fx}) can be calculated by the formula as follows [16,17].

Abbreviations: UV, Ultraviolet; NMR, nuclear magnetic resonance; EDTA, ethylenediaminetetraacetic acid; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital

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Table 1
Elementary analysis and molar conductivity data of the title complexes.

Complex	Measured value (theoretical value) (%)				Λ_m ($S\text{ cm}^2\text{ mol}^{-1}$)
	C	H	N	Tb	
TbY ¹ (NO ₃) ₃ :EtAc	35.64 (35.90)	3.57 (3.14)	9.01 (9.10)	20.32 (20.66)	24
TbY ² (NO ₃) ₃ :EtAc	36.51 (36.79)	3.82 (3.35)	8.75 (8.94)	19.97 (20.29)	31
TbY ³ (NO ₃) ₃ :EtAc	35.84 (36.06)	3.66 (3.28)	8.55 (8.76)	19.56 (19.88)	35
TbY ⁴ (NO ₃) ₃ :EtAc	34.16 (34.37)	3.31 (2.88)	8.56 (8.71)	19.53 (19.77)	39
TbY ⁵ (NO ₃) ₃ :EtAc	35.02 (35.22)	3.67 (3.21)	10.46 (10.71)	19.94 (20.26)	35
TbY ⁶ (NO ₃) ₃ :EtAc	33.75 (33.92)	3.23 (2.85)	10.14 (10.32)	19.25 (19.51)	27

Table 2
UV data of the title ligands and complexes.

compounds	λ_1 (nm)	ϵ_1 ($1.0 \times 10^4\text{ L mol}^{-1}\text{ cm}^{-1}$)	λ_2 (nm)	ϵ_2 ($1.0 \times 10^4\text{ L mol}^{-1}\text{ cm}^{-1}$)
Y ¹	273	0.84	298	0.61
TbY ¹ (NO ₃) ₃ :EtAc	280	0.93	–	–
Y ²	275	0.95	299	0.68
TbY ² (NO ₃) ₃ :EtAc	277	1.07	–	–
Y ³	276	0.98	301	0.71
TbY ³ (NO ₃) ₃ :EtAc	278	1.24	–	–
Y ⁴	275	0.96	300	0.64
TbY ⁴ (NO ₃) ₃ :EtAc	278	1.13	–	–
Y ⁵	275	0.95	295	0.85
TbY ⁵ (NO ₃) ₃ :EtAc	276	0.97	299	1.09
Y ⁶	–	–	294	1.08
TbY ⁶ (NO ₃) ₃ :EtAc	–	–	299	1.19

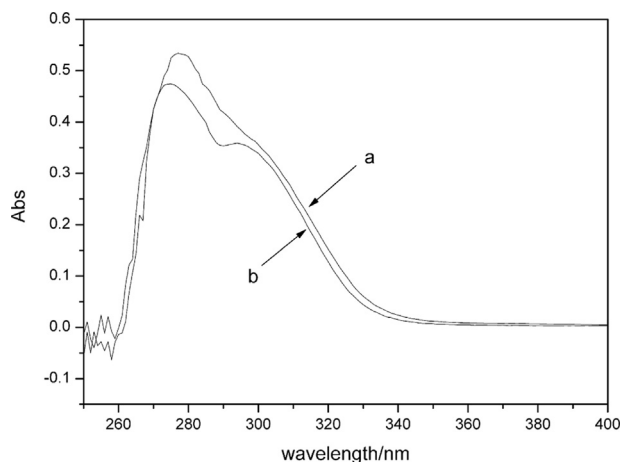


Fig. 1. UV spectra of TbY²(NO₃)₃:EtAc(a) and Y²(b).

$$\Phi_{fx} = \frac{n_x^2}{n_{std}^2} \cdot \frac{F_x}{F_{std}} \cdot \frac{A_{std}}{A_x} \cdot \Phi_{std}$$

The quinine sulfate ($1.0\ \mu\text{g mL}^{-1}$) of sulfuric acid solution ($0.1\ \text{mol L}^{-1}$) was used as a standard reference in this experiment, and the Φ_{std} was 0.55. The n_x (approximately equal to the refractive index of the solvent (DMSO)) was 1.480, and the n_{std} (the refractive index of water) was 1.337. A was the absorbance, as the point of intersection of the ultraviolet absorption curves of the standard and the sample was treated as excitation wavelength, A_{std} was equal to A_x . The luminescence spectra data were measured in DMSO solution ($1.0 \times 10^{-6}\ \text{mol L}^{-1}$) at room temperature to get the value of the

fluorescence integrated area F_x and F_{std} . The excitation wavelength was range 300–400 nm and the corresponding absorbance value A was less than 0.05, which was to reduce error in estimation of the emission quantum yield. The electrochemical properties of the complexes were got by the cyclic voltammetry data on a CHI 660d electrochemical workstation at a sweep rate of 50 mV/s (external reference: ferrocene, supporting electrolyte: 0.1 mol/L sodium nitrate solution, solvent: DMSO, the sensitivity: $1 \times 10^{-3}\ \text{A/V}$).

2.2. Synthesis

2.2.1. Synthesis of 1-phenyl-3-methyl-5-pyrazolone(A)

Phenylhydrazine(2.16 g, 20 mmol) and ethyl acetoacetate(2.60 g, 20 mmol) were dissolved in absolute alcohol (30 mL) in a 100-mL three-neck flask. The reaction solution was heated and refluxed at 80 °C for 6 h, and then the excess solvent was distilled after completion of the reaction. The distillation residue was poured into ice water, a lot of

yellow needle-shaped crystals appeared immediately. The crystals were filtered, washed with cool water, dried, and then recrystallized from absolute ethanol to get target compound A [18]. Yield 76%. ¹H NMR (CDCl₃) δ /ppm: 7.86 (d, $J = 7.8\ \text{Hz}$, 2H, ArH), 7.39 (t, $J = 8.0\ \text{Hz}$, 2H, ArH), 7.18 (t, $J = 7.4\ \text{Hz}$, 1H, ArH), 3.43 (s, 2H, CH₂), 2.20 (s, 3H, CH₃).

2.2.2. Synthesis of 1-phenyl-3-methyl-4-chloroacetyl-5-pyrazolone(B)

Compound A(3.48 g, 20 mmol) was dissolved in dioxane(30 mL) in a 100-mL three-neck flask, and then calcium hydroxide(3.0 g, 60 mmol) was added with stirring. The mixture was heated to reflux for 1 h at 90 °C after the reaction was tempered about 5 min, and then left to cool down to room temperature. Dilute hydrochloric acid(60 mL, 2 mol L⁻¹) was poured into the resulting mixture to obtain white solid. The white solid was filtered, washed with dilute hydrochloric acid, recrystallized twice from absolute ethanol, and dried in vacuum to get white needle-shaped crystals [19]. Yield 53%. ¹H NMR (CDCl₃) δ /ppm: 7.79 (d, $J = 7.8\ \text{Hz}$, 2H, ArH), 7.46 (t, $J = 8.0\ \text{Hz}$, 2H, ArH), 7.32 (t, $J = 7.4\ \text{Hz}$, 1H, ArH), 4.44 (s, 2H, CH₂), 2.51 (s, 3H, CH₃); MS (EI) m/z (%): 252 (M + 2, 7), 250 (M, 22), 223 (2), 217 (4), 216 (25), 201 (100), 173 (5), 149 (17), 130 (5), 104 (8), 92 (12), 91 (22), 77 (41), 67 (35).

2.2.3. Synthesis of the pyrazolone derivatives(Y¹⁻⁶)

As the synthesis procedures for pyrazolone derivatives Y¹⁻⁶ are similar, only the synthesis procedure of the compound Y¹ is shown for illustration. Benzoic acid(0.61 g, 5 mmol) and anhydrous potassium carbonate(1.104 g, 8 mmol) were dissolved in DMF in a 100-mL three-neck flask, and the mixture was heated to reflux for 1 h at 90 °C. Afterwards, compound B (1.25 g, 5 mmol) and a little potassium iodide were added into the mixture, and the reaction mixture was refluxed for 8 h. The resultant residue was poured into water(500 mL), and moderate dilute hydrochloric acid was poured to obtain white precipitate. The

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