

Preparation, spectroscopic properties of 1,4-di (*N,N*-diisopropylacetamido)-2,3(1*H*,4*H*)-quinoxalinedione (L) lanthanide complexes and the supramolecular structure of $[\text{Nd}_2\text{L}_2(\text{NO}_3)_6(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$

Xue-Qin Song^{a,b}, Yang Yu^a, Wei-Sheng Liu^{a,*}, Wei Dou^a, Jiang-Rong Zheng^a, Jun-Na Yao^a

^aCollege of Chemistry and Chemical Engineering, State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

^bSchool of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

Received 11 April 2007; received in revised form 15 June 2007; accepted 20 June 2007

Available online 20 July 2007

Abstract

The reaction of lanthanide nitrate with 1,4-di (*N,N*-diisopropylacetamido)-2,3(1*H*,4*H*)-quinoxalinedione (L) yields six novel Ln(III) complexes $[\text{Ln}_2\text{L}_2(\text{NO}_3)_6(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ which are characterized by elemental analysis, thermogravimetric analysis (TGA), conductivity measurements, IR, electronic and ¹H NMR spectroscopies. A new quinoxalinedione-based ligand is used as antenna ligand to sensitize the emission of lanthanide cations. The lowest triplet state energy level of the ligand in the nitrate complex matches better to the resonance level of Eu(III) and Sm(III) than Tb(III) and Dy(III) ion. The *f*–*f* fluorescence is induced in the Eu³⁺ and Sm³⁺ complexes by exciting into the π – π^* absorptions of the ligand in the UV. Furthermore, the crystal structures of a novel binuclear complex $[\text{Nd}_2\text{L}_2(\text{NO}_3)_6(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ has been determined by single-crystal X-ray diffraction. The binuclear $[\text{Nd}_2\text{L}_2(\text{NO}_3)_6(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ complex units are linked by the intermolecular hydrogen bonds and π – π interactions to form a two-dimensional (2-D) layer supramolecule.

© 2007 Elsevier Inc. All rights reserved.

Keywords: 2,3(1*H*,4*H*)-quinoxalinedione; Lanthanide complex; Crystal structure; Hydrogen bond; π – π interaction; Luminescence properties

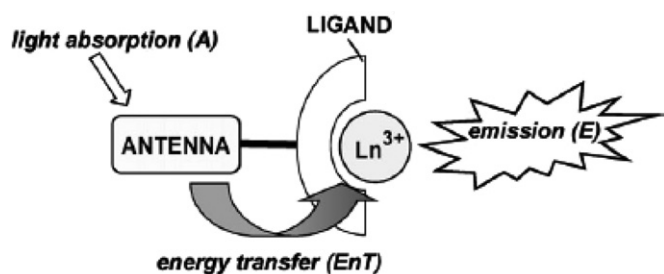
1. Introduction

Although the 4*f* block ions display mainly the same formal charge (3+) and similar chemical properties, their coordination chemistry has become of increasing significance in the last few years. This is due to their electronic, magnetic and spectroscopic properties, which are different along the complete series and may be widely applied in various fields [1]. The favorable luminescence properties of lanthanides have fostered their application in the development of chemosensors [2–5], supramolecular devices such as logic gates [6,7], bioassays (e.g., for enzyme activity or DNA hybridization) [8], electroluminescent devices [9] or in optical telecommunication [10]. However, the application of lanthanide-based luminescence suffers from two serious

drawbacks: (1) the poor light absorption properties and (2) the efficient non-radiative deactivation of their excited states by OH oscillators such as water [11]. In order to avoid these obvious disadvantages for the application of lanthanides, a strategy has been developed that involves the so-called antenna effect (Scheme 1). In this approach, the lanthanide ion is linked via complexation with a ligand, which includes an organic chromophore capable of absorbing light energy with a higher efficiency than the metal itself. In a subsequent energy transfer process, this chromophore acts as a sensitizer of the lanthanide-excited state, which can subsequently deactivate through luminescence. Owing to the large spectral gap between antenna excitation (often UV light) and emitted photons (visible to near IR), lanthanide-antenna conjugates have been often referred to as “molecular devices for wavelength conversion” [12]. Furthermore, complexation with a ligand provides lanthanides with a certain degree of protection

*Corresponding author. Fax: +86 931 8912582.

E-mail address: liuws@lzu.edu.cn (W.-S. Liu).



Scheme 1. Sensitization of lanthanide excited states by energy transfer from an antenna.

from surrounding water, hence, increasing their luminescence quantum yields.

Our group has been concentrating on the investigation of the supramolecular coordination chemistry and the luminescent properties of lanthanide (III) ions with the amide-type ligands which possess spheroidal cavities and hard binding sites. 2,3(1*H*,4*H*)-quinoxalinedione derivatives have been reported as excitatory amino acid antagonist with combined glycine/NMDA and AMPA receptor affinity [13–15]. However, their related coordination complexes as well as fluorescence properties have rarely been studied due to their low solubility [16]. In order to enhance the solubility as well as coordination ability of 2,3(1*H*,4*H*)-quinoxalinedione, we introduced a long amide chain to it and as continuation of our work on lanthanide coordination, we report here the synthesis, crystal structure and spectroscopic properties of the 1,4-di(*N,N*-diisopropylacetamido)-2,3(1*H*,4*H*)-quinoxalinedione (**L**) lanthanide complexes. To our best knowledge, they are the first examples of coordination structure of lanthanide complexes with 2,3(1*H*,4*H*)-quinoxalinedione ligand. Under excitation, Eu and Sm complex exhibited characteristic emissions. The lowest triplet state energy level of the ligand which was calculated from the phosphorescence spectrum of the Gd complex at 77 K indicates that the triplet state energy level of the ligand matches better to the resonance level of Eu(III) and Sm(III) than Tb(III) and Dy(III) ion.

2. Experimental

2.1. Materials

2,3-Dihydroxyquinoxaline was obtained from Aldrich Chemical Co. DMF was dried using 4 Å molecule sieves. The other commercially available chemicals were of A.R. grade and were used without further purification.

2.2. Methods

The metal ions were determined by EDTA titration using xylenol orange as an indicator. Combustion analyses were determined using a Vario EL elemental analyzer. The IR spectra were recorded on a Nicolet FT-170SX instrument using KBr disks in the 400–4000 cm^{−1}. Conductivity measurements were carried out with a DDS-307-type

conductivity bridge using 1.0 × 10^{−3} mol dm^{−3} solutions in acetone at 25 °C. ¹H NMR spectra were measured on a Varian Mercury plus 400 spectrometer in CDCl₃ solution with TMS as internal standard. Thermogravimetric analyses (TGA) were performed with a WCT-2A thermogravimetric analyzer under air atmosphere (30–700 °C) at a heating rate of 10 °C min^{−1}. Electronic spectra from 200 to 450 nm were recorded at room temperature using a Varian Cary 100 spectrophotometer. Fluorescence measurements were made on a Hitachi F-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length. The samples of the solid-state fluorescence measurements are prepared as a powder film and the excitation and emission slit widths were 2.5 nm (in solid) and 5 nm (in solution), respectively.

2.3. Crystal structure determination

Suitable single crystal of the neodymium nitrate complex was carefully selected under an optical microscope and mounted in a fine-focus sealed tube. Crystallographic data for the compound was collected with graphite-monochromatic MoK α radiation on a Bruker APEX area-detector diffractometer by the phi and omega scans technique. Primary non-hydrogen atoms were solved by direct method and refined anisotropically by full-matrix least-squares methods on *F*². The hydrogen atoms except for those of water molecules were generated geometrically. All calculations were performed using the programs SHELXS-97 and SHELXL-97. The [Nd₂L₂(NO₃)₆(H₂O)₂] · H₂O complex with chemical formula of C₄₈H₇₈N₁₄Nd₂O₂₉ crystallizes in the triclinic space group *P*−1, with lattice parameters *a* = 10.452(6) Å, *b* = 13.129(8) Å, *c* = 13.474(8) Å, α = 93.603(7)°, β = 97.059(7)°, γ = 91.238(7)°, GOF = 1.066, *R*1 = 0.0461, *wR*2 = 0.1115, *Z* = 1.

2.4. Synthesis of the ligand

α -Chloride-*N,N*-diisopropylacetamide was prepared according to the literature [17]. The ligand **L** (Scheme 2) was prepared according to the literature [18]. This ligand bears an amide chain to provide a diffuent ligand to complex lanthanide ions. ¹H NMR (CDCl₃, ppm): δ 7.19–7.16 (dd, 2H; quinoxaline: 5H and 8H); 6.99–6.96 (dd, 2H; quinoxaline: 6H and 7H); 5.00 (s, 4H, N–CH₂–C(O)); 4.09–4.05 (m, 2H; N–CH–(CH₃)₂); 3.55–3.50 (t, 2H; N–CH–(CH₃)₂); 1.37–1.13 (t, 24H; –CH₃). Analytical data, Calc. for **L** (%): C, 64.84; H, 8.16; N, 12.60; Found (%): C, 64.97, H, 8.44, N, 12.23.

2.5. Syntheses of the complexes

To a stirred acetonitrile solution (5.0 mL) containing 0.1 mmol **L** was added 0.1 mmol Ln(NO₃)₃ · 6H₂O. The mixture was stirred for 8 h at room temperature. After removing solvents in vacuum, 10 mL ethyl acetate was added, the pale white precipitate was obtained and dried in vacuum over P₂O₅ for 48 h. All the complexes were

Download English Version:

<https://daneshyari.com/en/article/1333796>

Download Persian Version:

<https://daneshyari.com/article/1333796>

[Daneshyari.com](https://daneshyari.com)