

Available online at www.sciencedirect.com



INORGANIC CHEMISTRY COMMUNICATIONS

Inorganic Chemistry Communications 10 (2007) 393-396

www.elsevier.com/locate/inoche

3-Phenyl-4-aroyl-5-isoxazolonate complexes of Tb³⁺ as promising light-conversion molecular devices

S. Biju^a, M.L.P. Reddy^{a,*}, Ricardo O. Freire^b

^a Chemical Sciences and Technology Division, Regional Research Laboratory (CSIR), Thiruvananthapuram 695 019, India ^b Departmento de Quimica Fundamental – UFPE, 50 670-901, Recife, PE, Brazil

> Received 6 November 2006; accepted 12 December 2006 Available online 21 December 2006

Abstract

New tris(3-phenyl-4-aroyl-5-isoxazolonate)terbium(III) complexes have been synthesized and characterized by various spectroscopic techniques. Due to an efficient energy transfer from the heterocyclic β -diketonate ligand to the central Tb³⁺, these complexes show a strong emission corresponding to Tb³⁺ ${}^{5}D_{4}{}^{-7}F_{J}$ (J = 6, 5, 4, 3) transitions, with ${}^{5}D_{4}{}^{-7}F_{5}$ (545 nm) green emission as the most prominent one. The overall quantum yields and luminescent lifetimes of these complexes were found to be promising as compared to previously reported terbium-1-phenyl-3-methyl-4-acyl-5-pyrazolonate complexes. © 2006 Elsevier B.V. All rights reserved.

Keywords: Tb³⁺; 3-Phenyl-4-aroyl-5-isoxazolonate complexes; Crystal structure; Luminescence

Recently, luminescent lanthanide complexes have attracted much attention because of their academic interest and potential application in a wide variety of photonic applications, such as planar waveguide amplifiers, plastic lasers, light emitting diodes and luminescent probes [1,2]. The two most useful lanthanides, Eu³⁺ and Tb³⁺, have unusual spectroscopic characteristics, including millisecond lifetime, very sharp emission bands, and large Stokes shifts [2]. Generally, the Eu^{3+} and Tb^{3+} ions show very weak absorption in the visible region of the spectrum and often require the application of strongly absorbing "antennae" for light harvesting to obtain efficient photoluminescence. Among them, β -diketone ligand is one kind of important antennae for the Eu^{3+} and Tb^{3+} ions [3]. Although the use of tris(8-hydroxyquinoline) aluminum (ALQ) as a green-emitting material has been investigated extensively. terbium complexes are still of great interest in electroluminescent devices because they offer several distinct advantages such as 100% quantum efficiency theoretically, extremely sharp emission bands and the ability to modify the ligand without affecting the emission characteristics of the central metal ion. Previous reports showed efficient green electroluminescence from terbium complexes containing 1-phenyl-3-methyl-4-isobutyl-5-pyrazolone or 1-phenyl-3-methyl-4-(2-ethylbutyryl)-5-pyrazolone and triphenylphosphine oxide [4,5]. However, another novel class of heterocyclic β-diketones such as 3-phenyl-4-aroyl-5-isoxazolones has not been utilized for the preparation of terbium luminescent materials even though they are well known as complexing agents for lanthanides [6,7]. In this paper, new tris(heterocyclic β -diketonato)terbium(III) complexes, $Tb(PBI)_3(H_2O)_2$ (1) and $Tb(TPI)_3(H_2O)_2$ (2) (where HPBI = 3-phenyl-4-benzoyl-5-isoxazolone and HTPI = 3-phenyl-4-(4-toluoyl)-5-isoxazolone) have been synthesized and characterized by elemental analyses, Fourier transform infrared, high resolution mass spectrometry, thermogravimetric analysis and photoluminescence spectroscopy.

The synthesis procedures of terbium complexes are shown in Scheme 1 (Supplementary data). The elemental and HRMS analyses of the complexes 1 and 2 show that Tb^{3+} ion has reacted with HPBI and HTPI in a metal-toligand mole ratio of 1:3. The IR spectrum of the complexes

^{*} Corresponding author. Tel.: +91 471 2515360; fax: +91 471 249712. *E-mail address:* mlpreddy@yahoo.co.uk (M.L.P. Reddy).

^{1387-7003/\$ -} see front matter @ 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2006.12.008



R = H(1) and $R = CH_2(2)$; Ln = Tb(1,2) or Gd

Scheme 1. Synthesis route of the complexes: $Tb(PBI)_3(H_2O)_2$, $Tb(TPI)_3-(H_2O)_2$, $Gd(PBI)_3(H_2O)_2$ and $Gd(TPI)_3$ $(H_2O)_2$. R = H (1) and $R = CH_3$ (2); Ln = Tb (1,2) or Gd.

1 and 2 shows a broad absorption in the region 3000- 3500 cm^{-1} , indicating the presence of solvent molecules in the complex. The existence of solvent molecules in lanthanide complexes with heterocyclic β -diketones such as 1-phenyl-3-methyl-4-acylpyrazolones and 3-phenyl-4arovl-5-isoxazolones is well documented [8,9]. The carbonyl stretching frequency of HPBI (1699 cm⁻¹) and HTPI (1705 cm^{-1}) has been shifted to lower wave numbers in complexes 1 and 2 (1641 cm^{-1} in 1 and 1639 cm^{-1} in 2), indicating the involvement of carbonyl oxygen in the complex formation with Tb³⁺ ion. It is clear from the thermogravimetric analysis data that the complexes 1 and 2 undergo a mass loss of 4% (calcd.: 3.6% for 1 and 3.5% for 2) up to 200 °C, which corresponds to the removal of coordinated water molecules. Further, decomposition takes place in the region 200-800 °C for both the complexes.

The structure of the complex $Tb(PBI)_3(EtOH)$ (H₂O) \cdot 0.25(H₂O) was characterized by single crystal Xray crystallography and it is interesting to note that one of the water molecules in complex 1 is replaced by an ethanol molecule from the medium (ethanol/CH₂Cl₂) during crystallization process. One water molecule is present in the lattice with 0.25 occupancy, i.e., one full water molecule in the unit cell. Details of crystal data and data collection parameters are given in Table 1 in Supplementary Material. The asymmetric unit of Tb(PBI)₃(EtOH)(H₂O) $\cdot 0.25(H_2O)$ is shown in Fig. 1. The central Tb³⁺ ion is coordinated with eight oxygen atoms, six of which from the three bidentate HPBI ligands, one is from water molecule and another from an ethanol molecule. The coordination geometry of the metal centre is best described as a bicapped triagonal prism. The average bond length between the terbium ion and the isoxazolone oxygen atoms is 2.36 Å, which is slightly shorter than that of terbium and water oxygen atom (2.38 Å) and also than that of terbium and ethanol oxygen atom (2.44 Å). This may be due to the result of the negative charge of the isoxazolone oxygen, which could be more strongly coordinated to the terbium ion due to electrostatic effects. Similar behaviour has been reported elsewhere in the X-ray single-crystal structure of $Tb(PMPP)_3 \cdot 2H_2O$ (where PMPP = 1-phenyl-3-methyl-4-propionyl-5-pyrazolone) [12], here the average bond length between the terbium ion and the PMPP oxygen atoms is 2.34 Å and that of terbium and water oxygen atom is 2.45 Å. The coordination geometries of the complexes Tb(PBI)₃(EtOH)(H₂O) and Tb(TPI)₃(EtOH)(H₂O) were calculated using Sparkle/AM1 model [10,11]. The optimized structures, selected bond lengths and bond angles for complexes are given in Supplementary data. The average bond length between the terbium ion and the isoxazolone oxygen atoms (2.39 Å) obtained from sparkle model is also in good agreement with the crystal data.



Fig. 1. The asymmetric unit of compound $\text{Tb}(\text{PBI})_3(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O}) \cdot 0.25(\text{H}_2\text{O})$.

The excitation spectra of the complexes 1 and 2 monitored around the peak of the intense ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition of the Tb³⁺ ion, exhibits a broad band between 250 and 450 nm ($\lambda_{max} = 370$ nm) which can be assigned to $\pi - \pi^*$ electron transition of the ligands [8]. A small peak at 490 nm observed as a result of f-f absorption transition $({}^{7}F_{6} \rightarrow {}^{5}D_{4})$ of Tb³⁺ ion. This transition is much weaker than the absorption of organic ligands, which proves that luminescence sensitization via excitation of the ligand, is more effective than direct excitation of the Tb^{3+} ion. The room-temperature normalized emission spectra of Tb³⁺ complexes 1 and 2 (Fig. 2) shows characteristic emission bands of Tb³⁺ ($\lambda_{ex} = 370$ nm) centered at 490, 545, 585 and 620 nm, resulting from the deactivation of the ${}^{5}D_{4}$ excited state to the corresponding ground state ${}^{7}F_{I}$ (J = 6, 5, 4, 3) of the Tb³⁺ ion. The strongest emission is centered on 545 nm, which corresponds to the hypersensitive transition of ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ [13,14]. The broad emission peaks obtained may be due to the greater non-homogeneity for Tb^{3+} local coordination site due to the presence of water molecules.

The overall quantum yields ($\Phi_{overall}$) of terbium complexes (1 and 2) were measured at room-temperature using the technique for powdered samples described by Bril and De Jager-Veenis [15]. The overall quantum yields of complexes 1 and 2 were calculated as 11% and 22%, respectively, and were found to be promising as compared to the recently reported Tb(PMIP)₃(H₂O)₂ (where PMIP = 1-phenyl-3-methyl-4-isobutaryl-5-pyrazolone; $\Phi_{overall} =$ 29.7 × 10⁻³%) [16] and terbium-1-phenyl-3-[G-3]-4-phenylacetyl-5-pyrazolonates (G stands for poly aryl ether; $\Phi_{overall} =$ 2.26%) [17]. Among complexes 1 and 2, the later shows better quantum yields due to the presence of electronreleasing group (-CH₃) on the benzoyl moiety.

The luminescence lifetimes (τ) were also investigated for terbium complexes and found to be 400 and 472 µs, respectively for **1** and **2** (Fig. 3). The measured luminescent



Fig. 2. Room-temperature emission spectra of the complexes 1 and 2 excited at 370 nm.



Fig. 3. Decay profile of the complexes **1** and **2** monitored at 545 nm and excited at 370 nm.

decays of complexes could be described by mono-exponential kinetics, which suggests that only one species exists in the excited state of these complexes. In combination with the data for the overall quantum yields, the data for the luminescence lifetimes show that longer the luminescent lifetimes, higher the quantum yields of the complexes.

The singlet and triplet energy levels of HPBI and HTPI were estimated by referring to the wavelengths of UV-Vis absorbance edges (HPBI and HTPI are 365 and 360 nm) and the lower wavelength emission edges (HPBI and HTPI are 450 and 442 nm) of the corresponding phosphorescence spectra of the complexes Gd(PBI)₃(H₂O)₂ and Gd(TPI)₃- $(H_2O)_2$ (Supplementary data). The triplet energy level of HTPI (22620 cm^{-1}) was found to be moderately higher than HPBI (22220 cm^{-1}), may be due to the presence of electron-donating group (-CH₃) on the benzoyl moiety of the HPBI system. Generally, the sensitization pathway in luminescent terbium complexes consists of the excitation of the ligands from the ground state to their excited singlet states, and subsequently through the intersystem crossing of the ligands to their triplet states, following the energy transfer from the triplet state of the ligand to the central ion. In this process, the 4f electrons of the Tb^{3+} ion are excited to the ${}^{5}D_{I}$ manifold from the ground state, finally the Tb³⁺ion emits when the 4f electrons undergo a transition from the excited state of ${}^{5}D_{4}$ to the ground state. It has been noticed that the energy gaps $\Delta E({}^{1}\pi\pi^{*}-{}^{3}\pi\pi^{*})$ between the ${}^{1}\pi\pi^{*}$ and ${}^{3}\pi\pi^{*}$ levels are 5180 and 5160 cm⁻¹ for HPBI and HTPI, respectively. According to Reinhoudt's empirical rule [18] that the intersystem crossing process will be effective when $\Delta E(\pi\pi^*-\pi^*\pi\pi^*)$ is at least 5000 cm^{-1} , thus the intersystem crossing processes are effective for all the ligands. According to Latva's empirical rule [19], an optimal ligand-to-metal energy transfer process for Tb³⁺ is when $\Delta E({}^{3}\pi\pi^{*}-{}^{5}D_{4}) > 2000 \text{ cm}^{-1}$. It can be concluded that the transfer process is effective from HTPI to Tb³⁺ and that HTPI is a suitable as a sensitizer for Tb³⁺ ($\Delta E({}^{3}\pi\pi^{*}-{}^{5}D_{4}) > 2220 \text{ cm}^{-1}$). On the other hand,

the ${}^{3}\pi\pi^{*}$ state (22220 cm⁻¹) of HPBI is so close to ${}^{5}D_{4}(20400 \text{ cm}^{-1})$ of Tb³⁺, giving $\Delta E({}^{3}\pi\pi^{*}-{}^{5}D_{4}) = 1820 \text{ cm}^{-1}$, which is too low to prevent the back-energy transfer from the Tb³⁺ excited state to the triplet state of HPBI.

Acknowledgements

The authors acknowledge the financial support from Defence Research and Development Organization and University Grants commission, New Delhi, India. The Brazilian author acknowledges CNPq and Instituto do Milenio de Materiais Complexos, for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche. 2006.12.008.

References

- [1] J. Kido, Y. Okamoto, Chem. Rev. 102 (2002) 2357.
- [2] J.C.G. Bunzli, C. Piguet, Chem. Soc. Rev. 34 (2005) 1048.
- [3] G.F. de Sa, O.L. Malta, C. de Mello Donega, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. da Silva Jr., Coord. Chem. Rev. 196 (2000) 165.

- [4] H. Xin, M. Shi, X.C. Gao, Y.Y. Huang, Z.L. Gong, D.B. Nie, H. Cao, Z.Q. Bian, F.Y. Li, C.H. Huang, J. Phys. Chem. B 108 (2004) 10796.
- [5] H. Xin, F.Y. Li, M. shi, Z.Q. Bian, C.H. Huang, J. Am. Chem. Soc. 125 (2003) 7166.
- [6] L. Gan, L. Xu, C. Luo, C. Huang, S. Umetani, M. Matsui, Polyhedron 13 (1994) 3167.
- [7] R. Pavithran, M.L.P. Reddy, Radiochim. Acta 92 (2004) 31.
- [8] R. Pavithran, N.S. Saleesh Kumar, S. Biju, M.L.P. Reddy, S. Alves Jr., R.O. Freire, Inorg. Chem. 45 (2006) 2184.
- [9] C. Pettinari, F. Marchetti, A. Cingolann, A. Drozdov, I. Timokhin, S.I. Troyanov, V. Tsaryuk, V. Zolin, Inorg. Chim. Acta 357 (2004) 4181.
- [10] R.O. Freire, G.B. Rocha, A.M. Simas, Inorg. Chem. 44 (2005) 3299.
- [11] G.B. Rocha, R.O. Freire, N.B. da Costa Jr., G.F. de Sa, A.M. Simas, Inorg. Chem. 4 (2004) 2346.
- [12] D. Zhou, Q. Li, C.H. Huang, G. Yao, S. Umetani, M. Matsui, L. Ying, A. Yu, X. Zhao, Polyhedron 16 (1997) 381.
- [13] A. Dias, S. Viswanathan, Dalton Trans. 34 (2006) 4093.
- [14] Z-Q. Zhang, Q. Shen, Y. Zhang, Y-M. Yao, J. Lin, Inorg. Chem. Commun. 7 (2004) 305.
- [15] A. Bril, A.W. De Jager-Veenis, J. Electrochem. Soc. 123 (1976) 396.
- [16] D. Zhang, M. Shi, Z. Liu, F. Li, T. Yi, C. Huang, Eur. J. Inorg. Chem. 11 (2006) 2277.
- [17] L. Shen, M. Shi, F. Li, D. Zhang, X. Li, E. Shi, T. Yi, Inorg. Chem. 45 (2006) 6188.
- [18] F.J. Steemers, W. Verboom, D.N. Reinhoudt, E.B. Vander Tol, J.W. Verhoeven, J. Am. Chem. Soc. 117 (1995) 9408.
- [19] M. Latva, H. Takalo, V.M. Mukkala, C. Matachescu, J.C. Rodriguez-Ubis, J. Kanakare, J. Lumin. 75 (1997) 149.