

Synthesis, structural, photophysical and thermal studies of benzoate bridged Sm(III) complexes

Udai P. Singh ^{a,*}, Rajeev Kumar ^a, Shailesh Upreti ^b

^a Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India

^b Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110 016, India

Received 25 May 2006; received in revised form 19 July 2006; accepted 22 July 2006

Available online 1 September 2006

Abstract

One samarium coordination polymer (chain like) **1** with composition $[\{\text{Sm}(\text{OBz})_3(\text{MeO})_2\}_2]_n$ has been prepared from the reaction of SmCl_3 and sodium benzoate in 1:3 ratio whereas four binuclear samarium complexes with chemical composition $[\{(\text{tp})\text{Sm}(\mu\text{-}p\text{-}\text{X}\text{-}\text{OBz})_2\}_2]$ have been prepared by the reaction of SmCl_3 , potassium hydrotris(pyrazol-1-yl)borate $[\text{K}(\text{tp})]$ and sodium *p*-X-benzoate (where X = H, Cl, F, NO_2) in 1:1:2 ratio. These complexes have been characterized by elemental analysis, IR spectroscopy, thermogravimetry, optical properties, X-ray and magnetic measurement studies. The X-ray structure shows that the complexes **2–5** are isostructural whereas the structure of **1** is different. The coordination number around metal center in **1** is eight whereas in complexes **2–5**, each samarium is seven coordinate. The X-ray studies indicate that the complex **1** crystallizes in monoclinic space group $P2(1)/c$ with the cell dimensions $a = 9.75(7)$, $b = 21.83(15)$, $c = 22.28(15)$ Å, whereas the complexes **2** and **3** crystallizes isostructurally in the triclinic space group $P\bar{1}$ with the cell dimension $a = 11.77(10)$, $b = 12.60(10)$, $c = 17.57(13)$ Å and $a = 9.55(3)$, $b = 12.80(4)$, $c = 14.47(5)$ Å, respectively. The samarium ions in **2** and **3** are coordinated by three N atoms of pyrazolylborate ligand and four O atoms from benzoate groups. The photophysical properties of above complexes have been studied with ultraviolet absorption, excitation and emission spectral studies. The complexes **1–5** excited at 240 nm wavelength produced characteristic luminescence features, arising mostly due to the f–f transitions. © 2006 Elsevier B.V. All rights reserved.

Keywords: Samarium(III); Carboxylate ligands; Photophysical properties; X-ray studies

1. Introduction

Over the past decades, many attempts have been made for the design and synthesis of luminescent lanthanide complexes due to their excellent photophysical properties and potential applications in different interesting area [1–5]. Different type of ligands have been used for the preparation of such complexes, some are listed below – cryptands, [6,7] calixarenes, [8–10] macrocyclic ligands, [11–13] carboxylic acid derivatives, [14–17]. Benzoic acid and its derivatives have also been widely used in the coordination complexes of rare-earth because of their versatile coordination modes. The donor ability of oxygen atoms toward

different lanthanides (especially Eu^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+}) in benzoic acid changes by using different substituent at benzene ring which in turn causes for the increased fluorescence intensity in lanthanides. The intensity of fluorescence depends upon the quantity of energy available in the triplet state, the efficiency of the transfer of energy to the metal ion, and probability that ionic emission, rather than non-radiative deactivation, occurs. The efficiency of transfer is related to the energy difference between the triplet state and the resonance level of the cation as well as to the nature of the bond between cation and ligand.

Among lanthanide ions, samarium has recently received a closer attention because of the additional use of this metal (as ^{153}Sm) in radiotherapy. Lanthanide carboxylate complexes show interesting crystal structures due to the variable coordination number of metal centers as well as

* Corresponding author. Tel.: +91 1332 285329; fax: +91 1332 273560.
E-mail address: udaipfcy@iitr.ernet.in (U.P. Singh).

coordination versatility of carboxylate ligands. Large number of lanthanide carboxylate complexes having polymeric/dimeric structure with good luminescent, thermal as well as good ultraviolet absorption properties are available in literature [18–23]. The objective of present work is to see whether the inductive effect of the different halogen on benzene rings would affect the structure and photophysical properties of the Sm(III) complexes compared to its parent benzoate complex as it has been reported that the appropriate organic ligands can act as light collectors (antenna) and transfer absorbed energy to the coordinated lanthanide ion (emitter). In view of the potential applications of lanthanide carboxylate complexes and the fascinating properties of carboxylate ligands, the present paper reports the synthesis, structural, photophysical and thermal properties of some samarium(III) complexes with benzoate and its derivatives.

2. Experimental

All solvents were purified with suitable drying agents using literature methods [24]. The benzoic acid and its derivatives were commercially available and their sodium salts were prepared by reacting with the appropriate amount of sodium hydroxide in water. Samarium chloride of the highest grade was purchased from Indian Rare Earths Ltd., India. The potassium salt of the ligand hydrotris(pyrazol-1-yl)borate [K(tp)] was prepared as described previously [25].

2.1

2.1.1. Synthesis of $[(tp)Sm(OBz)_3(MeO)_2]_n$ (**1**)

The methanolic solution (25.0 ml) of $SmCl_3 \cdot 6H_2O$ (0.191 g, 0.5 mmol) and sodium benzoate (0.216 g, 1.5 mmol) was stirred for 3 h. and the resultant complex was filtered through celite. The filtrate was dried under vacuum and the colorless powder in 74.9% (0.215 g) yield was recrystallized from the mixture of acetonitrile–methanol at 4 °C. The elemental analysis was performed on a carefully dried sample under vacuum for several hours. Anal. Calcd. (%) for $C_{46}H_{42}O_{16}Sm_2$: C, 47.95; H, 3.64. Found C, 48.51; H, 3.13; IR (KBr, cm^{-1}): 1599 (ν_{as} COO), 1409 (ν_s COO). Magnetic moment μ_{eff} (290 K): 1.75 μ_B .

2.1.2. Synthesis of $[(tp)Sm(\mu-OBz)_4Sm(tp)]$ (**2**)

A mixture of sodium benzoate (0.1441 g, 1.0 mmol) and [K(tp)] (0.151 g, 0.5 mmol) in 15.0 ml methanol was added to the methanolic solution of $SmCl_3 \cdot 6H_2O$ (0.191 g, 0.5 mmol) and the solution was stirred at room temperature for 4 h. After removal of the solvent under vacuum, the desired compound was extracted with dichloromethane (three times) and the combined solution was filtered on celite. The filtrate was dried under vacuum to afford colorless powder in 80.0% (0.241 g) yield. Recrystallization of the compound from dichloromethane at 4 °C gave crystals suitable for X-ray measurements. The elemental analysis was performed on a completely dried sample for several hours. Anal.

Calcd. (%) for $C_{46}H_{40}N_{12}O_8B_2Sm_2$: C, 45.61; H, 3.32; N, 13.87. Found C, 45.33; H, 3.45; N, 13.81. IR (KBr, cm^{-1}): 2457 (ν_B-H), 1608 (ν_{as} COO), 1508 (ν_s COO). MS (ESI +, CH_3CN): m/z 1091 (30.0%) $[(tp)_2Sm_2(O_2CPh)_3]^+$; 695 (5.0%) $[(tp)_2Sm(O_2CPh)]^+$; 574 (100.0%) $[(tp)_2Sm]^+$. Magnetic moment μ_{eff} (290 K): 1.85 μ_B .

2.1.3. Synthesis of $[(tp)Sm(\mu-p-Cl-OBz)_4Sm(tp)] \cdot 2(CH_2Cl_2) \cdot 2(CCl_2)$ (**3**)

This complex was prepared in 78.0% (0.262 g) yield by the method as outlined above for **2**. Anal. Calcd. (%) for $C_{46}H_{36}N_{12}O_8B_2Cl_4Sm_2$: C, 40.95; H, 2.68; N, 12.45. Found C, 41.08; H, 2.77; N, 12.62. IR (KBr, cm^{-1}): 2457 (ν_B-H), 1607 (ν_{as} COO), 1506 (ν_s COO). MS (ESI +, CH_3CN): m/z 1189 (25.0%) $[(tp)_2Sm_2(p-Cl-O_2CPh)_3]^+$; 729 (8.0%) $[(tp)_2Sm(p-Cl-O_2CPh)]^+$; 574 (100.0%) $[(tp)_2Sm]^+$. Magnetic moment μ_{eff} (290 K): 1.52 μ_B .

2.1.4. Synthesis of $[(tp)Sm(\mu-p-F-OBz)_4Sm(tp)]$ (**4**)

This complex was prepared in 81.0% (0.259 g) yield by the method as outlined above for **2**. Anal. Calcd. (%) for $C_{46}H_{36}N_{12}O_8B_2F_4Sm_2$: C, 43.05; H, 2.82; N, 13.09. Found C, 43.22; H, 2.88; N, 13.17. IR (KBr, cm^{-1}): 2457 (ν_B-H), 1607 (ν_{as} COO), 1506 (ν_s COO). MS (ESI +, CH_3CN): m/z 1146 (5.0%) $[(tp)_2Sm_2(p-F-O_2CPh)_3]^+$; 737 (30.0%) $[(tp)_2Sm(p-F-O_2CPh)+Na]^+$; 574 (100.0%) $[(tp)_2Sm]^+$. Magnetic moment μ_{eff} (290 K): 1.41 μ_B .

2.1.5. Synthesis of $[(tp)Sm(\mu-p-NO_2-OBz)_4Sm(tp)]$ (**5**)

This complex was prepared in 75.0 % (0.260 g) yield by the method as outlined above for **2**. Anal. Calcd. (%) for $C_{46}H_{36}N_{16}O_{16}B_2Sm_2$: C, 39.71; H, 2.60; N, 16.10. Found C, 39.79; H, 2.51; N, 16.18. IR (KBr, cm^{-1}): 2457 (ν_B-H), 1605 (ν_{as} COO), 1505 (ν_s COO). MS (ESI +, CH_3CN): m/z 1226 (19.0%) $[(tp)_2Sm_2(p-NO_2-O_2CPh)_3]^+$; 740 (10.0%) $[(tp)_2Sm(p-NO_2-O_2CPh)]^+$; 574 (100.0%) $[(tp)_2Sm]^+$. Magnetic moment μ_{eff} (290 K): 1.65 μ_B .

2.2. X-ray crystallographic studies

Colorless single crystals of **1**, **2** and **3** suitable for X-ray crystallographic analyses were mounted on sealed glass capillaries. Diffraction data were collected with Bruker AXS SMART-CCD diffractometer by use of graphite monochromated Mo-K α radiation ($\lambda = 0.71073$) at 100 K. The structures were solved by direct methods and in anisotropic approximation refinement using the SHELX TL package [26,27]. Hydrogen atoms were constrained by rigid model. A summary of crystallographic data and refined parameters for complexes **1**, **2** and **3** are given in Table 1.

2.3. Physical measurements

Elemental analysis (C, H, N) were determined on vario EL elemental analyser. Infrared spectra were obtained on a Thermo Nicolet Nexus spectrometer in KBr. Electro Spray

Download English Version:

<https://daneshyari.com/en/article/1410979>

Download Persian Version:

<https://daneshyari.com/article/1410979>

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