Polyhedron 50 (2013) 112–120

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Lanthanide phenolates with heterocyclic substituents. Synthesis, structure and luminescent properties

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ARTICLE INFO

Article history:
Received 13 August 2012
Accepted 5 October 2012
Available online 13 October 2012

Keywords:
Lanthanide complex
OLEDs
X-ray structure
2-(2-Benzoimidazol-2-yl)phenolate
2-(2-Benzoxyazol-2-yl)phenolate
2-(2-Benzothiazol-2-yl)phenolate
Electroluminescence

ABSTRACT

The complexes of trivalent lanthanides Ce, Sm, Eu, Gd, Tb, Dy with 2-(2-benzoxyazol-2-yl)phenolate (OON), 2-(2-benzothiazol-2-yl)phenolate) (SON) and 2-(2-benzoimidazol-2-yl)phenolate (NON) ligands were synthesized by the reactions of silylamides $Ln[N(SiMe_3)_2]_3$ with respective phenol. Heteroleptic complex $Tb(NON)_2(SON)$ was obtained when $Tb[N(SiMe_3)_2]_3$ was treated simultaneously with NONH and SONH. X-ray analysis of $Ce(OON)_3$, $Eu(OON)_3$, $Sm(SON)_3$, $Gd(NON)_3$, $Dy(NON)_3$ and $Tb(NON)_2(SON)$ revealed that all the compounds are dimers with two bridging and four terminal XON ligands $(XON)_2Ln(\mu\text{-}XON)_2Ln(XON)_2$. In the heteroleptic complex the SON ligands are bridging but the NON groups are terminal. The molecules of the complexes in crystals are stacked with short intra- and intermolecular distances between planar ligands. This feature is reflected in the luminescence spectra of Gd, Tb (with SON ligands) and Dy complexes. Photo- and electroluminescence spectra of Ce, Gd and Dy derivatives showed only ligands emission in the region from 430 to 530 nm. The spectra of Sm and Tb complexes contain as well the bands of f-f transitions typical for corresponding metal ion. The complexes of Eu revealed no luminescence.

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1. Introduction

Despite the attractiveness of organic lanthanide complexes as emissive materials for various optoelectronic devices (due to the specifics of the luminescence of Ln^{3+} ions [1]) so far they are not widely used. The main reason for it is low efficiency of devices based on lanthanide complexes, which, in turn, is due to difficulty of excitation of f electrons in Ln^{3+} ions because f–f transitions are parity forbidden and 4f orbitals are well shielded by the $5s^2$ and $5p^6$ electrons. In general this leads to a low absorption coefficient of lanthanide ions ($\varepsilon \leqslant 10\ M^{-1}\ cm^{-1}$), which makes them impossible to effectively populate the emitting levels under direct excitation [2]. Well-known and virtually the only way to increase the luminescence efficiency of lanthanide ions is the selection of suitable ligands, which provide an additional influx of excitation energy due to the antenna effect. For this purpose most often used are β-diketonate [1f,3], carboxylate [3c,4] and 8-quinolinolate [3c,5] ligands. Recently we have found that 2-(2-benzoxyazol-2-yl) phenolate, 2-(2-benzothiazol-2-yl)phenolate) and 2-(2-benzoimidazol-2-yl)phenolate also are suitable ligands for preparation of luminescent complexes of rare earth metals. In particular, emissive complexes of Sc [6] and NIR luminescent compounds of Pr^{3+}, Nd^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} were synthesized [7]. Note that the (benzoxyazol)phenolates of Nd, Sm, Eu and Dy have been synthesized previously [8], but their luminescent properties were not studied. In this paper we report on the synthesis, structure and luminescent properties of the complexes of these O,N-chelate ligands with Ce^{3+}, Eu^{3+}, Sm^{3+}, Tb^{3+} and Dy^{3+} which can to emit in visible region. Complexes of Gd^{3+} were prepared as well to record the spectra of pure ligand-centered emission because high resonant level of this metal excludes the metal-centered luminescence.

2. Results and discussion

2.1. Synthesis

The homoleptic compounds **1–18** were obtained by the reactions of silylamides $Ln[N(SiMe_3)_2]_3$ with appropriate phenol which smoothly proceed in DME at room temperature to give the products in 81–95% yield.

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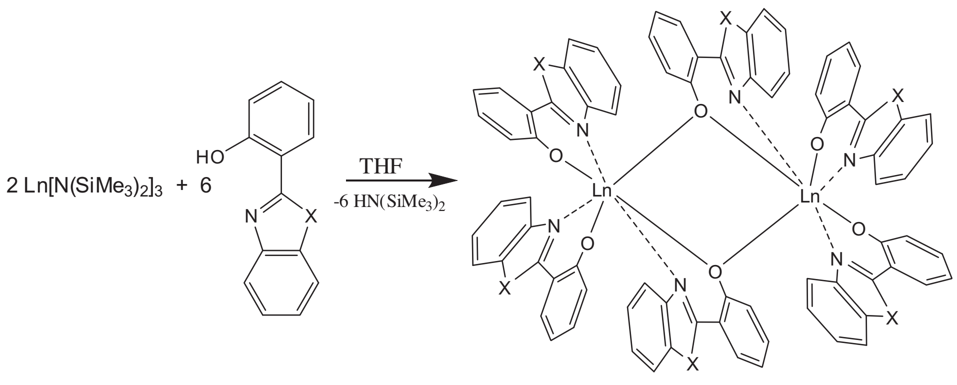
http://dx.doi.org/10.1016/j.poly.2012.10.007



1-18

Ln = Ce, x = O (**1**); S (**2**); NH (**3**); Ln = Sm, x = O (**4**); S (**5**); NH (**6**); Ln = Eu, x = O (**7**); S (**8**); NH (**9**); Ln = Gd, x = O (**10**); S (**11**); NH (**12**); Ln = Tb, x = O (**13**); S (**14**); NH (**15**); Ln = Dy, x = O (**16**); S (**17**); NH (**18**).

Simultaneous treatment of $Tb[N(SiMe_3)_2]_3$ with 2-(2-hydroxyphenyl)benzothiazole (SONH) and 2-(2-hydroxyphenyl)-1H-benzimidazole (NONH) in a ratio 1:2 resulted in formation of the heteroleptic complex $(NON)_2Tb(\mu\text{-}SON)_2Tb(NON)_2$ (**19**).

The compounds **1**–**19** precipitate from the reaction solutions as white or pale yellow crystalline solids stable in air and sublimable in vacuum without decomposition, except Ce complexes **1**–**3** and (benzoimidasolyl)phenolates **6**, **9**, **12**, **15** and **18** sublimation of which is accompanied by partial destruction. The DSC and TGA study of **7**–**9** and **13**–**15** showed that decomposition of the compounds in air begins at temperatures above 362 °C [9]. IR spectra of the complexes in the region of 400–3500 cm^{-1} are identical for each group of ligands (OON, SON, NON) independently on the metal, which indicates the similarity of the structure of the compounds.

2.2. Structure

X-ray analysis of **1**, **5**, **7**, **12**, **18** and **19** revealed that all the compounds are binuclear complexes with two bridging and four terminal ligands (Fig. 1). The coordination number of Ln cations is 7. In the crystal complexes **1**, **5**, **7**, **12** and **19** are centrosymmetrical dimers. In contrast to complexes **1**, **5**, **7**, **12** and **19** which lie on the inversion center, the dimeric complex **18** is disposed in common position. In all these dimers the XON ligands are chelately bonded to the metal atoms via O atom of phenoxy group and N atom of heterocycle. It should be noted that the complex $[Tb(SON)(NON)_2]_2$ (**19**) is a single, which contains two different type of ligands: (benzothiazolyl)phenolate (SON) and (benzoimidazolyl)phenolate (NON). Two SON ligands are bridging while four NON groups occupy the terminal positions (Fig. 1c). Two Ln atoms are linked to each other via oxygen atoms of phenoxy groups of two bridging ligands.

The Ln(1)–O(1) and Ln(1)–O(1A) distances of bridging O atoms in **1**, **5**, **7**, **12**, and **19** are close to each other ($Ln–O^{brd}$ in Table 1, Table S1), while in **18** the same distances are noticeably different: Ln(1)–O(3) = 2.301(4) Å, Ln(2)–O(3) = 2.375(4) Å; Ln(1)–O(6) = 2.371(4) and Ln(2)–O(6) = 2.299(4) Å. Just as in the complexes of $Pr_2(OON)_6$ and $Nd_2(NON)_6$ studied previously [7], the terminal Ln–O distances in **1**, **5**, **7**, **12**, **18** and **19** are shorter than the bridging. Terminal Ln–O distances in these complexes, except **19**, are close to each other. In **19** the terminal distances are significantly different (Ln(1)–O(2) = 2.254(3) and Ln(1)–O(3) = 2.176(3) Å). The study of the coordination environment of metal atoms in the complexes showed that the arrangement of terminal and bridging ligands in **19** differs from that in **1**, **5**, **7**, **12** and **18** (Fig. 2). Two terminal ligands in **19** coordinate the Tb(1) cation by the O(2), N(2) and the O(3), N(4) atoms (Fig. 3(b)) whole the appropriate ligands in **1**, **5**, **7**, **12** coordinate the Ln(1) cation by O(3), N(2) and O(5), N(3) atoms but not O(5), N(2) and O(3), N(3) like in **19**. Note that the molecular structures of dimers **1**, **5**, **7**, **12** are more similar to each other than to structure of **18**. The O(1A)–Ln(1)–O(3) and O(1A)–Ln(1)–O(5) angles in **1**, **5**, **7**, **12** vary in the ranges of 120.21(6)–129.41(14)° and 88.83(6)–92.26(6)°, respectively while the analogous angles in dysprosium complex **18** are 105.05(15)° (O(6)–Dy(2)–O(4)), 106.63(15)° (O(3)–Dy(1)–O(1)), and 103.91(16)° (O(6)-Dy(2)–O(5)), 103.29(16)° (O(3)–Dy(1)–O(2)). Different disposition of terminal ligands of **18** as compared to that in **1**, **5**, **7** and **12** are probably caused by the presence in **18** of crystallized DME molecules.

The Ln…Ln distances decrease on going from **1**(Ce^{3+}) to **5**(Sm^{3+}), **7**(Eu^{3+}), **19**(Tb^{3+}), **12**(Gd^{3+}) and **18**(Dy^{3+}). It is consistent with the trend in ionic radii reduction in this row: Ce^{3+} – 1.07 Å, Sm^{3+} – 1.02 Å, Eu^{3+} – 1.01 Å, Gd^{3+} – 1.00 Å, Tb^{3+} – 0.98 Å and Dy^{3+} – 0.97 Å [10]). Only the Ln…Ln distances in **19** falls outside of this trend possibly due to the presence of two different types of ligands (SON and NON) in the letter.

The terminal Ln–O distances in complex **5** (Ln(1)–O(3) = 2.225(4) and Ln(1)–O(5) = 2.190(4) Å) are shorter than those in **7** (2.253(3), 2.242(3) Å) and are close to the analogous distances in complex **12** (2.221(2), 2.216(2) Å). The similar tendency is observed for bridging Ln(1)–O(1) and Ln(1)–O(1A) bonds in **5**, **7** and **12**. This observation is not consistent with a decrease in the radii of lanthanide ions in the series Ce^{3+}(**1**), Sm^{3+}(**5**), Eu^{3+}(**7**) and Gd^{3+}(**12**) and has no reasonable explanation other than crystal packing effects.

It should be noted, that Ln–O and Ln–N distances in all complexes **1**, **5**, **7**, **12**, **18** and **19** are comparable with those in the similar Ln complexes, containing chelate salicylaldiminate fragments –OPh-*ortho*-CH=N(R)–(Ce [11–13], Sm [14], Eu [15], Gd [16], Dy [17], Tb [14,16]). The crystal packing analysis showed that the crystals of **1**, **7** and **12** have crystallographic motif similar to that in the crystals of $Pr_2(OON)_6$ and $Nd_2(NON)_6$. Intermolecular $\pi\cdots\pi$ stacking interactions are observed along the crystallographic axis *a* (Fig 4). The distances between the planes of the $\pi\cdots\pi$ interacting OON ligands of adjacent molecules are 3.388 (**1**), 3.368 (**7**), 3.371 Å (**12**) which is close to those in $Pr_2(OON)_6$ and $Nd_2(NON)_6$ (3.425 and 3.362 Å). The angles between the mean planes of terminal and bridging ligands in the molecules of **7** and **12** are 28.9° and

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