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Journal of Luminescence 93 (2001) 115–118

JOURNAL OF
LUMINESCENCE

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Mono-thio- β -diketones – a new type of ligands suitable for sensitization of lanthanide luminescence. Infrared luminescence of an intensely colored neodymium and ytterbium mono-thio- β -diketonate chelates

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Received 8 September 2000; received in revised form 18 December 2000; accepted 18 December 2000

Abstract

Intensely colored and air/moisture stable mono-thio- β -diketonates of trivalent neodymium and ytterbium show sensitized infrared emission of lanthanide ion when excited with UV and visible light. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanide ions; Neodymium; Ytterbium; β -Diketonate complexes; Mono-thio- β -diketonate complexes

1. Introduction

Lanthanide ions tend to coordinate with O and N donor atoms while ligands having S-donor atoms are not considered to be suitable for obtaining air/moisture-stable Ln^{3+} complexes. Luminescent Ln^{3+} complexes with O, N coordinating ligands are used as light-converting materials since upon UV excitation of ligand moiety they emit ff-luminescence characteristic of the metal ion [1–13]. Special interest has been given recently to

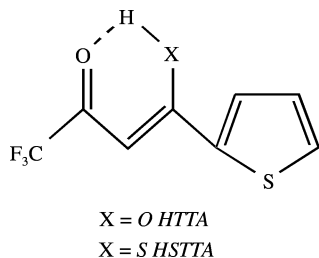
the Nd^{3+} and Yb^{3+} chelates emitting in infrared region [7–11].

Herein attention is drawn to the ligands that were overlooked in lanthanide chemistry, probably since they contain sulphur as a donor atom – the mono-thio- β -diketones, taking mono-thio-thenoyltrifluoroacetone (HSTTA) as an example [14,15] and showing it to be suitable to prepare new luminescent chelates of Nd^{3+} and Yb^{3+} . Contrary to the β -diketones [2–7], the mono-thio- β -diketones were rarely used to prepare Ln^{3+} chelates and never used to sensitize Ln^{3+} emission. The formation constants of Ln^{3+} ions with mono-thio-benzoylacetone [16], solvent extraction of Nd^{3+} with HSTTA [17], synthesis and

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characterization of Ln^{3+} mono-thio-dibenzoyl-methanates [18] were studied before.



2. Experimental

HSTTA: a modification of the known procedure [14] was applied. A solution of 2.5 g of HTTA in 100 ml of dry CH_3OH was saturated at -70°C first with dry H_2S and then with dry HCl . The solution was allowed to warm up slowly to the r.t. and left overnight. The resulting dark red solution was diluted with equal volume of water and extracted with pentane. The pentane extract was rotor-evaporated to give HSTTA as a dark-red solid with 50% yield.

$\text{Ln}(\text{L})_3(\text{TPPO})_2$ ($\text{L} = \text{TTA}$ or STTA): 1 mmol of LnCl_3 in 2 ml of water was added to 10 ml of ethanol containing 3.05 mmol of ligand + 3 mmol of NaOH + 2 mmol of triphenylphosphineoxide (TPPO) at 50°C . The chelate precipitate formed immediately or at dilution with water was filtered, washed with water, pentane and dried in a desiccator. $\text{Nd}(\text{STTA})_3(\text{TPPO})_2$ (red): observed (calculated) C = 52.0% (51.0%), H = 3.7% (3.0%).

3. Results

The ligand HSTTA was synthesized by the general method for preparation of fluorinated mono-thio- β -diketones [14]. It is completely enolized in solutions with a hydrogen atom situated at the sulphur atom [14,15] and gives complexes with transition metal [14,15] and lanthanide ions [16–18].

We have obtained the adduct of mono-thio-thenoyltrifluoroacetate of Nd^{3+} (Yb^{3+}) with TPPO of the composition $\text{Ln}(\text{STTA})_3(\text{TPPO})_2$ in a

quantitative yield by a simple method using aqueous ethanol as solvent. The STTA chelates obtained are air-stable, non-hygroscopic solids soluble in polar/non-polar organic solvents as are the respective TTA chelates. Such unusual stability of S-coordinated lanthanide compounds can be ascribed to the formation of chelate ring in which the Ln^{3+} ion is coordinated both by S and O atoms. However, thio-substitution results in the lower thermal stability of the chelate, thus $\text{Nd}(\text{STTA})_3(\text{TPPO})_2$ melts with decomposition at $140\text{--}150^\circ\text{C}$, while $\text{Nd}(\text{TTA})_3(\text{TPPO})_2$ stays intact and does not melt even at 250°C in open capillary.

Thio-substitution results in the drastic change of the absorption spectrum of the Ln^{3+} chelate (Fig. 1). TTA chelates are faintly colored in the color of Ln^{3+} ion, since the ligand moiety absorbs only in the UV region with the main peak at $\lambda_{\text{max}} = 340\text{ nm}$, $\varepsilon_{\text{max}} = 60\,200\text{ M}^{-1}\text{ cm}^{-1}$. For STTA chelate the ligand absorption is shifted to the visible region of the spectrum giving the ligand/chelate a red or brownish-red color. Absorption spectrum of $\text{Nd}(\text{STTA})_3(\text{TPPO})_2$ at $\lambda > 300\text{ nm}$ consists of at least two overlapping bands the first situated at $\lambda_{\text{max}} = 367\text{ nm}$ with $\varepsilon_{\text{max}} = 49\,800\text{ M}^{-1}\text{ cm}^{-1}$, while the other is observed as a long wavelength shoulder determining visible absorption of chelate.

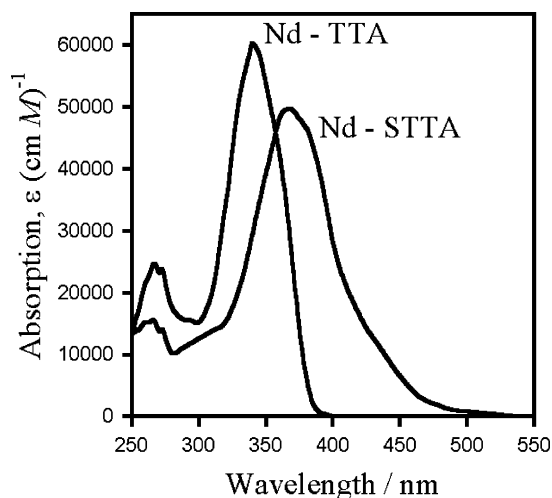


Fig. 1. Absorption spectra of $\text{Nd}(\text{STTA})_3(\text{TPPO})_2$ and $\text{Nd}(\text{TTA})_3(\text{TPPO})_2$ in MeCN at 25°C . Similar spectra were observed for corresponding Yb^{3+} chelates.

Excitation of chelates with UV light, 365 nm in the ligand absorption band, results in the appearance of the sensitized infrared f-f-luminescence of both TTA and STTA chelates of Yb^{3+} and Nd^{3+} (Fig. 2). Their emission is caused by radiative f-f-transitions of Nd^{3+} from $^4\text{F}_{3/2}$ emitting level and of Yb^{3+} from $^2\text{F}_{5/2}$ one. For STTA chelate the luminescence efficiency is lower than for TTA chelates 5-fold for Yb^{3+} , and 2.6-fold for Nd^{3+} , as measured for 10^{-3} M chelate solutions in DMSO at 25°C . Probably energy losses in the ligand determine lower emission efficiency of mono-thio-chelate.

In organic chelates of Ln^{3+} (e.g. β -diketonates) population of excited f-f-levels of Ln^{3+} at excitation of the ligand moiety occurs by energy transfer from the ligand's triplet state [1–13]. The triplet state of STTA should be situated lower than that of TTA ($\approx 20\,000\text{ cm}^{-1}$) and higher than $12\,000\text{ cm}^{-1}$,

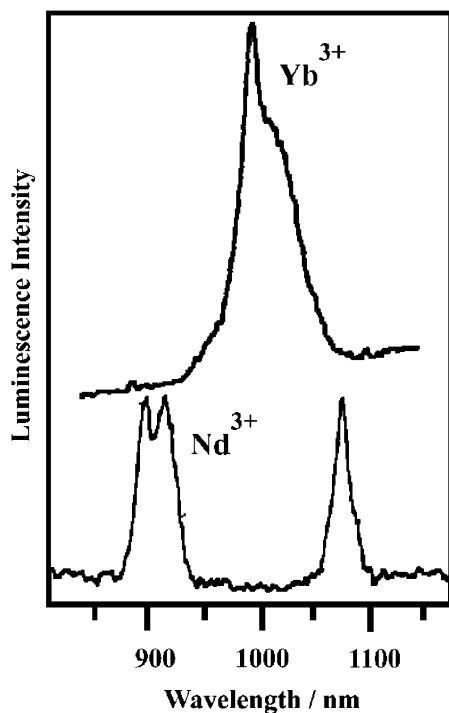


Fig. 2. Luminescence spectra of 10^{-3} M solutions of $\text{Nd}(\text{STTA})_3(\text{TPPO})_2$ and $\text{Yb}(\text{STTA})_3(\text{TPPO})_2$ in dry DMSO at 25°C (emission slit 7 nm). Excitation was performed into ligand at 365 nm. Similar spectra were observed for TTA chelates of these ions.

since sensitized luminescence of $\text{Nd}(\text{STTA})_3(\text{TPPO})_2$ could be observed from the emitting $^4\text{F}_{3/2}$ state of Nd^{3+} situated at $\approx 12\,000\text{ cm}^{-1}$.

It should be noted that excitation of Yb^{3+} luminescence in its organic chelates may occur both by energy transfer and by reversible electron transfer from ligand (e.g. in complexes with porphyrins [19] or proteins [20]), since Yb^{3+} is relatively easily reduced to Yb^{2+} (-1.05 V versus NHE) [20]. However, in order to estimate the relative contribution of both channels to the excitation of observed emission of Yb^{3+} in mono-thio- β -diketonates, one should perform the electrochemical/photophysical experiments, that are beyond the scope of this communication.

Commonly used β -diketonates, e.g. HTTA, do not have absorption in the visible region and thus their Ln^{3+} chelates could be excited with UV light only. However, mono-thio- β -diketonates and their chelates are intensely colored, thus allowing excitation of Ln^{3+} emission with visible light. In fact, the luminescence of STTA chelates of $\text{Nd}^{3+}/\text{Yb}^{3+}$ could be excited with 465 nm blue light (unfortunately excitation spectrum could not be recorded with the available equipment).

4. Conclusions

Luminescent lanthanide mono-thio- β -diketonates can be used as new light-converting molecular devices since they (a) are air/moisture stable, (b) show luminescence efficiency comparable to that of the parent β -diketonates, (c) the ligand moiety possesses intense UV and VIS absorption bands suitable for pumping Ln^{3+} luminescence, and at the same time (d) the ligand can be easily prepared from widely used β -diketonates.

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