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Synthesis, luminescent and magnetic properties of new tetranuclear lanthanide complexes with 4-hydroxy-2,1,3-benzothiadiazolate and dibenzoylmethanide ligands

T.S. Sukhikh [a,b], D.A. Bashirov [a,b], D.S. Kolybalov [b], A.Y. Andreeva [a], A.I. Smolentsev [a], N.V. Kuratieva [a,b], V.A. Burilov [c], A.R. Mustafina [d], S.G. Kozlova [a,b], S.N. Konchenko [a,b,*]

[a] Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, 630090 Novosibirsk, Russia
[b] Department of Natural Sciences, National Research University – Novosibirsk State University, 630090 Novosibirsk, Russia
[c] Butlerov Institute of Chemistry, Kazan Federal University, 420008 Kazan, Russia
[d] Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, 420088 Kazan, Russia

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ABSTRACT

Four new tetranuclear complexes, $[Ln_4(dbm)_4(O\text{-}btd)_6(OH)_2]$ **1a** (Ln = Yb), **1b** (Ln = Dy) and $[Ln_4(dbm)_6(O\text{-}btd)_4(OH)_2]$ **2a** (Ln = Yb), **2b** (Ln = Dy) (O-btd = 4-hydroxo-2,1,3-benzothiadiazolate and dbm = dibenzoylmethanide), and their solvates with toluene and tetrahydrofuran were synthesized. The magnetic properties of the complexes **1a**, **1b**, **2a** and **2b** have been studied, revealing different magnetic susceptibility patterns for the Yb(III) and Dy(III) complexes in the temperature range 80–300 K. Upon lowering the temperature, a weak antiferromagnetic ordering is observed for both Yb compounds, while the Dy derivatives are assumed to show weak ferromagnetic interactions. The Yb complexes **1a** and **2a** demonstrate strong NIR luminescence at ~1000 nm in CH_2Cl_2 solution upon excitation of the $(O\text{-}btd)^-$ ligand. This observation suggests the $(O\text{-}btd)^-$ ligand to be an efficient antenna ligand for lanthanide-based NIR luminescence.

1. Introduction

Lanthanide-based compounds attract significant attention due to their unique photophysical [1,2] and magnetic properties [3,4]. For example, NIR-emitting ions have recently gained much popularity due to their application in the telecommunications industry, sensors technology [5,6], solar energy conversion [7,8] and biomedical analysis [1,9]. Slow-relaxing lanthanide ions, possessing single-molecule-magnet behaviour, display magnetic memory effects and can potentially be used as high-density information-storage media [10–12]. For these reasons, lanthanide complexes with organic ligands have been intensively investigated. Given the wide opportunities provided by smart selection and functionalization of the ligands, one can precisely tune the coordination environment and crystal structure of lanthanide compounds, thus strongly influencing the resulting properties.

β-Diketonates are among the most popular ligands for the design of lanthanide complexes [2,13–24] and have several important features: (1) they form a wide variety of derivatives which influence the properties; (2) they form stable complexes; (3) they are able to act as chelating-bridging ligands and form complexes with different nuclearities; (4) some of them can be efficient antenna ligands for lanthanides emitting in the visible and NIR regions; (5) other uncharged and/or negatively charged species can additionally be included to form heteroligand compounds.

Recently, we have reported on the synthesis, structural characterization and luminescence and magnetic properties of new tetranuclear erbium complexes containing the dibenzoylmethanide (dbm^-) and 4-hydroxy-2,1,3-benzothiadiazolate ($O\text{-}btd^-$) ligands (Fig. 1): $[Er_4(dbm)_6(O\text{-}btd)_4(OH)_2]$ and $[Er_4(dbm)_4(O\text{-}btd)_6(OH)_2]$ [25]. The thiadiazole derivative has been shown to be an efficient antenna ligand for the erbium ion. This paper presents the synthesis of the Yb and Dy analogues of these complexes and their photophysical and magnetic properties.

2. Results and discussion

In this work, two types of tetranuclear complexes containing $(O\text{-}btd)^-$ and $(dbm)^-$ ligands are discussed, $[Ln_4(dbm)_4(O\text{-}btd)_6(OH)_2]$ and $[Ln_4(dbm)_6(O\text{-}btd)_4(OH)_2]$. They were prepared by the

* Corresponding author at: Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, 630090 Novosibirsk, Russia.
E-mail address: konch@niic.nsc.ru (S.N. Konchenko).

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