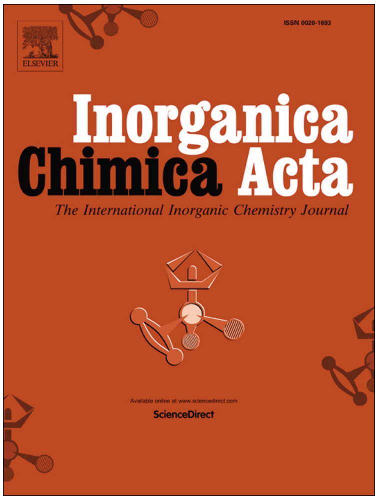

Research paper

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Felix Braun, Peter Comba, Laura Grimm, Dirk-Peter Herten, Bianca Pokrandt, Hubert Wadepohl

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Ligand-sensitized lanthanide(III) luminescence with octadentate bispidines

Felix Braun,[a] Peter Comba,[b] Laura Grimm,[b] Dirk-Peter Herten,[a] Bianca Pokrandt,[b]*
and Hubert Wadepohl[b]
a) Universität Heidelberg, Physikalisch-Chemisches Institut, INF 229,
D-69120 Heidelberg, Germany
b) Universität Heidelberg, Anorganisch-Chemisches Institut and Interdisciplinary Center for
Scientific Computing (IWR), INF 270,
D-69120 Heidelberg, Germany

Dedicated to Prof. Rabindranath (Rabi) Mukherjee on the occasion of his 65th birthday

Correspondence:
E-mail: peter.comba@aci.uni-heidelberg.de

Abstract

The octadentate bispidine ligand L (bispidine = 3,7-diazabicyclo[3.3.1]nonane) with two pyridine groups at C2 and C4 and two picolinates at N3 and N7, providing two tertiary amines, four pyridines and two carboxylates to metal ions, has been coordinated to lanthanide(III) ions (Sm^{III}, Eu^{III}, Tb^{III}, Dy^{III}, Ho^{III}). The single crystal X-ray structures of $[Tb^{III}(L)(NO_3)]$ and $[Ho^{III}(L)(OH_2)](TFA)$ (TFA = trifluoracetate) have been determined and define the complexes as 9-coordinate with a monodentate nitrate or a water molecule completing the coordination sphere. Spectroscopy indicates that in solution all complexes are 9-coordinate with an OH_2 coordinated to the lanthanide(III) center. Absorption and emission spectra show that the ligands function as antennas with UV excitation (260 nm) leading to relatively high intensity emission in the visible region (500-600 nm) with millisecond lifetimes of the excited states.

Keywords

bispidine, lanthanide, luminescence, antenna effect

Introduction

Due to relatively long-lived excited states and large Stokes shifts, the luminescence properties of molecular lanthanide complexes are attractive for applications in biology and medicine (sensors and immunoassays), spintronics (light-emitting diodes) and energy conversion.[1-7] Due to the Laporte-forbidden f-f transitions ($\varepsilon < 10\ M^{-1}cm^{-1}$) indirect excitation of the f-orbital based excited states by organic chromophores (antennas) is required for all these purposes. We have recently reported a novel octadentate bispidine-based ligand L (bispidine = 3,7-diazabicyclo[3.3.1]nonane, see Chart 1) that forms very stable complexes with a range of lanthanide and actinide ions.[8] In the last two decades, the bispidine scaffold with its diaza-adamantane-derived backbone has been used extensively in coordination chemistry, with tetra-, penta-, hexa-, hepta- and octadentate ligands and applications involving bio-inspired and medicinal chemistry, molecular catalysis and