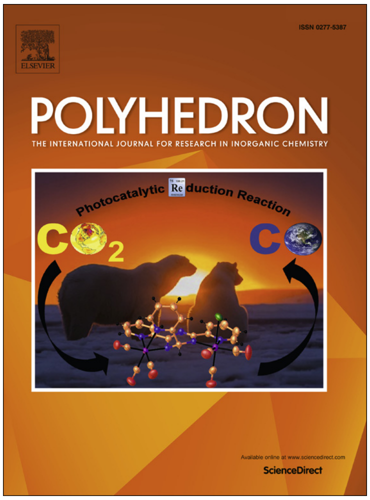

Two types of Lanthanide Schiff base complexes: synthesis, structure and spectroscopic studies

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Two types of Lanthanide Schiff base complexes: synthesis, structure and spectroscopic studies

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Abstract

A series of five Ln(III) salen type complexes, with La(III), Eu(III), Tb(III), Er(III) and Tm(III) cations, were obtained by a template reaction between 5-methylsalicylaldehyde and 4-methyl-1,3-phenylenediamine in the presence of the appropriate Ln(III) nitrate. Two types of complexes of the general formulae $[Ln(H_2L)_3(NO_3)_3]$ (**type I**) [Ln = La (**1**), Eu (**2**), Tb (**3**)] and $[Ln(H_2L)_2(NO_3)_3EtOH]MeOH$ (**type II**) [Ln = Er (**4**), Tm (**5**)], where H_2L is *N,N'*-bis(5-methylsalicylidene)-4-methyl-1,3-phenylenediamine, were characterized by elemental analysis, FT-IR, ESI-MS, TG-DTA analysis, UV-Vis luminescence and ^{1}H and ^{13}C NMR spectroscopy. Single-crystal X-ray diffraction revealed that the **type I** complexes crystallize in the monoclinic $P2_1/n$ space group, while **type II** complexes crystallize in the monoclinic Cc space group. The central cations for both type of complexes are nine-coordinated, exclusively by oxygen atoms, and the coordination resembles a distorted tricapped trigonal prism. In the case of **type 1** complexes, the central cations are coordinated with three nitrate groups and three H_2L neutral molecules, while for **type 2** complexes, one of the ligand molecule is replaced by an ethanol molecule. In the latter case, the methanol molecule plays an important role in the crystal packing, taking part in hydrogen bonding which connects the complex molecules into infinite chains. The structural change is due to a decrease of the ionic radii of the lanthanide ions.

Keywords
Lanthanide contraction, Schiff base, Self-assembly, Salicylaldimines, Spectroscopy

1. Introduction

Salen-type Schiff bases derived from salicylaldehyde and diamines have numerous applications, for instance as pesticides, fluorgenic and herbicidal agents [1], and as ion-selective electrodes for the determination of anions in analytical samples [2]. The interest in Schiff base ligands has grown recently because of findings that their antitumor, antibacterial, antivirus and antifungal activity can be significantly improved by coordinating to a metal ion [3,4]. Transition metal complexes with salen-type ligands have also found application in heterogenous and homogenous catalysis [5-8], diagnostic pharmaceuticals and laser technology [9]. In addition, the unique properties of lanthanide complexes cause them to be used as magnetic materials, e.g. lanthanide ions have proven to be particularly suitable for the synthesis of 4f Single Molecule Magnets (SMM) [10-19].

Lanthanide ions offer high coordination numbers as well as variable and flexible coordination environments, and therefore they have great potential in the design of novel, unusual supramolecular structures [20,21]. One of the main factors contributing to the structural changes experienced by lanthanide ions is the well-known *lanthanide contraction*. This phenomenon is associated with the systematic decrease of an ionic radius with increasing atomic number of a lanthanide. As a result the