

Optical properties of heavy lanthanide maleates in solution and crystal form



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ABSTRACT

Monocrystals of $\text{Ln}(\text{C}_4\text{O}_4\text{H}_3)_3 \cdot 8\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$) were grown and spectroscopic investigations were performed to understand their photophysical properties. It was found that all the complexes were isostructural with neodymium maleate, $\text{Nd}(\text{C}_4\text{O}_4\text{H}_3)_3 \cdot 8\text{H}_2\text{O}$, whose crystal structure had been determined previously. Electronic absorption and emission spectra at low temperatures for crystals of the lanthanide maleates (with the splitting of the levels) were allowed for the stated lanthanide ions, with a low symmetry environment, in these systems. The intensities of the electronic lines and the Judd–Ofelt parameters were calculated and compared to those obtained for light lanthanides (i.e. Nd(III) and Sm(III)) maleates. The variation of the spectroscopic parameters (e.g. β , δ) and their correlation with the nature of the Ln^{3+} –L bond are discussed. The nephelauxetic ratio β and Sinha's parameter δ suggested an increase in the 'degree of covalency' of the metal–ligand coordination bond from the Eu^{3+} crystal to the Ho^{3+} crystal and to the Er^{3+} crystal of the title compounds. The $-\text{C}=\text{C}-$ double bond in the carboxylate ions determines the distribution of the charge and the character of the Ln–O coordination bonds, which is very important when considering the potential applications of lanthanide carboxylates. In the low-temperature absorption and emission spectra, relatively strong vibronic lines occur, promoted by both ligand (L) and Ln–L localised vibrational modes. In the vibronic coupling, the role of π electrons is not negligible. The emission from the ${}^5\text{D}_1$ level was detected for the europium maleate in spite of the presence of water molecules in the inner coordination sphere of the lanthanide maleate crystals. On the basis of the europium maleate-excited spectra, a ligand-to-metal charge transfer (LMCT) transition was determined at 345 nm.

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1. Introduction

Metal–organic compounds, especially coordination systems, are a promising class of porous materials with strategic applications in fields such as catalysis, luminescent materials, non-linear optics and others [1,2]. These applications depend on the structure of the material. Therefore, control of ligand structures is considered important in the formation of new structures [3]. For example, malonic acid (H_2mal) as a ligand allows the construction of extended networks with different topologies, dependent on the coordination geometry of the metal ion [4]. The complex of the formula $[\text{Eu}_2(\text{mal})_3(\text{H}_2\text{O})_6]$ created a polymeric three-dimensional compound [4], which is an example of a coordination compound with malonic acid and lanthanide or transition metals. Such systems have rich applications as fluorescence probes [5–8] and molecular magnetic materials as well as precursors for oxides [9].

Lanthanide-based compounds are characterised by weak luminescence, which can be overcome through the coordination of organic ligands that transfer energy to the lanthanide ions (antenna effect), thus generating very efficient luminescent materials [10]. From this point of view, unsaturated dicarboxylate ligands are a good choice since they may contain chromophore groups (for example $-\text{C}=\text{C}-$). These O-donor ligands efficiently coordinate Ln^{3+} ions leading to coordination polymers. The carboxylic group from the ligand strongly binds the lanthanide ion, giving rise to various coordination geometries around the metal cation.

Whereas the use of different saturated aliphatic dicarboxylic acids to form bridges between metal centres has been frequently studied [11], the use of unsaturated ones has been studied only rarely [12]. Maleic acid is the simplest unsaturated aliphatic dicarboxylic acid. In our previous work, we reported on the photophysics, magnetism and crystal structures of light lanthanide (i.e. Nd(III) and Sm(III)) maleates [13]. The crystal structure of $\text{Nd}(\text{C}_4\text{O}_4\text{H}_3)_3 \cdot 8\text{H}_2\text{O}$ was determined. Nd^{3+} creates a ninefold coordination polyhedron, with two carboxyl groups of two independent hydrogenmaleate ions being involved in metal ion coordination

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in a monodentate manner (see Fig. 1). For all the maleic ions there were very strong intramolecular hydrogen bonds (~ 2.45 Å). Absorption studies at 293 and 4.2 K confirmed the presence of one metal site, with a low symmetry, in the structure. In the low-temperature spectra, relatively strong vibronic lines occurred, promoted by both ligand (L) and Nd–L localised vibrational modes. In this vibronic coupling, the role of π electrons was not negligible. From the values of the magnetic data for samarium maleate, one could observe minor interactions between the metal ions in the structure, in which some role was played by π electrons and hydrogen bonds [13].

Qing-Yue Shen et al. [14] determined the crystal structure of europium maleate, which was isostructural with the Nd analogue.

The aim of the present paper is to gain insight into the nature of the Ln^{3+} –ligand bond of unsaturated aliphatic dicarboxylate maleates. Maleic acid has carboxyl groups and a C=C double bond, which comprise chromophoric groups, whose presence in the coordination compounds of lanthanide ions will significantly change the optical properties of those materials. We would like to show how the presence of the $-\text{C}=\text{C}-$ double bond in the carboxylate ion can enhance the sensitivity of the ligand in luminescence anion sensing. The considerations include the structure of the complex

(e.g. the formation of a polynuclear species) and its functionalities, which can dramatically change the usefulness of the compound. Examination of those structures for different rare earth ions, particularly ones towards the end of the series, will enable a closer look at how the Ln–L bond characteristics (ionic or covalent) will impact on the structure of the inner coordination sphere of the Ln^{3+} ion, thereby impacting on its optical properties. We present investigations on the heavy lanthanide maleates, $\text{Ln}(\text{C}_4\text{O}_4\text{H}_3)_3 \cdot 8\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$). The absorption and emission spectra at room and low temperatures for crystals of these rare earth maleates allowed us to determine the photophysical properties of the title compounds as new luminescent materials based on lanthanide ions. The research presented now has the character of a basic investigation, which will be expanded to practical applications in the future.

2. Experimental

2.1. Compound synthesis

Lanthanide maleates of the formula $\text{Ln}(\text{C}_4\text{O}_4\text{H}_3)_3$ ($\text{Ln} = \text{Eu}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$) were synthesised by the slow reaction between the

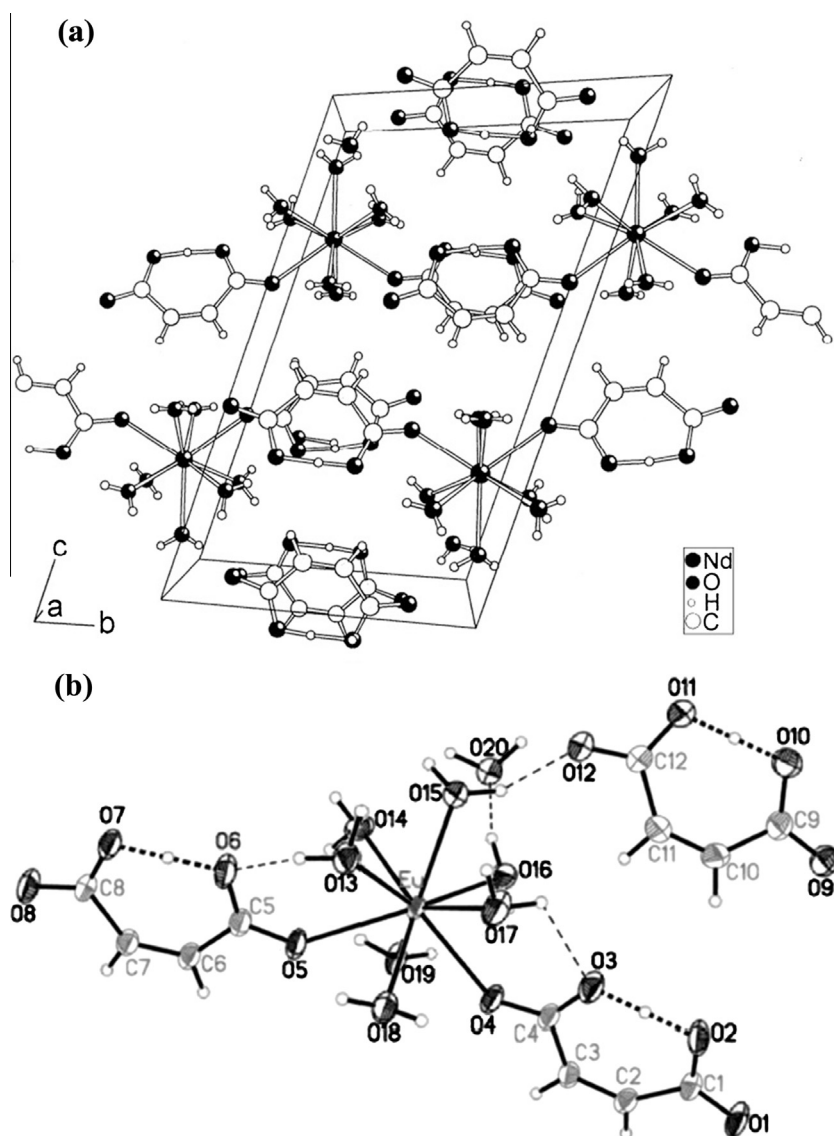


Fig. 1. (a) Crystal structure of $\text{Nd}(\text{C}_4\text{O}_4\text{H}_3)_3 \cdot 8\text{H}_2\text{O}$, showing the packing of $[\text{Nd}(\text{C}_4\text{O}_4\text{H}_3)_2(\text{H}_2\text{O})_7]^+$ cations and non-coordinating hydrogenmaleate anions [13]; (b) The molecular structure of $[\text{Eu}(\text{C}_4\text{H}_3\text{O}_4)_2(\text{H}_2\text{O})_7](\text{C}_4\text{H}_3\text{O}_4)\text{H}_2\text{O}$, dashed lines indicate O–H···O hydrogen bonds [14].

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