

Structural and spectroscopic studies of lanthanide complexes with S(+)-mandelic acid

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ABSTRACT

Lanthanide (Gd^{3+} , Tb^{3+} , Dy^{3+} , Er^{3+}) complexes with S(+)-mandelic acid were synthesized in the form of powders and were characterized by elemental and thermal analyses, XRPD method, FTIR, Raman and UV–vis–NIR spectroscopy. It was found that all the complexes were isostructural with the erbium $R(-)$ mandelate, $Er(Man)_3(H_2O)_2$, for which the crystal structure was previously determined. Photophysical studies carried out on the solid samples have revealed that the mandelate ligand is a better sensitizer for Tb^{3+} than Dy^{3+} ion. The luminescence quantum yields of these compounds were estimated as 95% and 6%, respectively.

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1. Introduction

Lanthanide complexes with aromatic carboxylic acids have been of increasing interest due to their potential applications as optical materials or biological sensors [1–3]. The use of this type of ligands strongly affects the photophysical properties of lanthanide ions. The presence of the phenyl ring in these ligands may contribute to the efficient energy transfer, called the antenna effect [4–7]. Owing to this effect the weak luminescence of lanthanide ions is strongly enhanced. Moreover the carboxylic group from the ligand strongly binds the lanthanide ion, giving rise to various coordination geometries around the metal cation. One of such ligands, which also contains the hydroxyl group, is 2-hydroxy-2-phenylacetic acid (mandelic acid – hereinafter ManH). The compound exists in two enantiomeric forms (one of them is shown in Scheme 1) as well as the racemic mixture what gives an opportunity to form various spatial motifs [8–10].

The crystal structures of lanthanide complexes with all optical forms of the mandelic acid are known [11,12]. For instance, a Pr^{3+} complex of the formula $Pr(Man)_3(ManH)$ was obtained from racemic acid [11], a Nd^{3+} compound, $(Nd_2(Man)_6(H_2O)_4 \cdot 3H_2O)_\infty$ – from S(+)-mandelic acid [12], and an Er^{3+} compound, $Er(Man)_3(H_2O)_2$ – from R(–)-enantiomer [11]. While the Pr^{3+} and Er^{3+} mandelate crystals form monomeric species with eight-coordinate Ln^{3+} ions, the coordination number of two symmetry independent Nd^{3+} cations in polymeric chains is nine. The Pr^{3+} and Er^{3+} ions are chelated by three mandelate anions. Each of the chelate rings is formed by a carboxylate oxygen atom and the oxygen atom from a hydroxyl group. The

inner sphere of the Pr^{3+} ion is completed by two oxygen atoms from the carboxylic and hydroxyl groups of the mandelic acid molecule, whereas in the case of erbium by two water molecules. The coordination spheres of Nd^{3+} ions are filled by two water molecules and four mandelate anions. Two of them chelate each Nd^{3+} ion in the same fashion as in the case of Pr^{3+} and Er^{3+} complexes, while the carboxyl groups from the remaining two mandelate ligands are connected with Nd^{3+} ions in bi- and tridentate modes. One of the hydroxyl groups of these anions is not bounded to the Nd^{3+} ion, namely that with a bridging-bidentate carboxyl coordination.

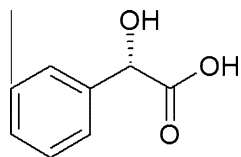
Since luminescence properties of lanthanide mandelates in the solid state were examined for Eu^{3+} ion only [13], therefore the aim of this work was to study photophysical properties of Gd^{3+} , Tb^{3+} and Dy^{3+} complexes in the form of powders. The structural characteristic of these compounds was performed on the basis of elemental and thermal analyses, XRPD method, FTIR, Raman and NIR spectroscopy.

2. Experimental

Solutions of $LnCl_3$ (Gd^{3+} , Tb^{3+} , Er^{3+}) and $Dy(NO_3)_3$ were prepared by dissolving Ln_2O_3 (99.9% Merck) in 2 M hydrochloric or nitric acid. The solutions were standardized with EDTA using xylenol orange as an indicator. A stock solution of S(+)-mandelic acid (>98% Fluka AG) with the concentration of 0.2 M was also prepared. Lanthanide complexes with S(+)-mandelic acid were obtained by slow evaporation of aqueous solutions prepared by mixing solutions of $LnCl_3$ or $Dy(NO_3)_3$ with S(+)-mandelic acid and NaOH in molar ratios of 1:1:1. The Ln^{3+} concentration in the resulting solutions was 0.03 M.

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Scheme 1. The S(+)-mandelic acid (2-hydroxy-2-phenylacetic acid) hereafter referred as ManH.

Elemental analyses for C and H contents in the products were performed on a 2400 CHN Elemental Analyzer (Perkin–Elmer) and allowed to predict the chemical formula for the studied compounds. They corresponded to the $C_{24}H_{25}LnO_{11}$ or $Ln(Man)_3(H_2O)_2$. The experimental and calculated (in parentheses) contents of C and H for each complex are as follows: Gd – 44.30, 3.73 (44.57, 3.89); Tb – 44.21, 3.48 (44.45, 3.88); Dy – 44.10, 3.64 (44.21, 3.86); Er – 44.06, 3.52 (43.89, 3.83).

Thermogravimetric analysis was carried out from 30 to 500 °C under nitrogen atmosphere on a SETSYS 16/18 Setaram thermogravimetric analyzer.

X-ray powder diffraction (XRPD) patterns were obtained on a D8 ADVANCE diffractometer with Cu $K\alpha$ radiation and Vantec detector in the 2θ of 2–40° range with a step size of 0.008° and a counting time of 0.1 s per step.

FTIR spectra were measured on a Bruker 113v FTIR spectrometer using KBr pellets, whereas Raman spectra were recorded on a Nicolet Magna 860 FTIR/FT Raman spectrometer.

UV–vis reflectance spectra were obtained on a Cary 5 UV/vis/NIR spectrophotometer and absorption spectra of solid samples dispersed in Nujol were recorded on a Cary 500 UV/vis/NIR spectrophotometer at room and 4.2 K temperatures in a continuous flow helium cryostat (Optistat, Oxford).

The luminescence and excitation spectra as well as luminescence lifetime measurements of lanthanide complexes in the form of powders were performed at room temperature on a FLS 920-Edinburgh Instruments Ltd with a Xenon lamp as a light source. All recorded spectra were corrected accordingly to the spectrometer characteristic. Measurements of emission quantum yields of powdered samples were carried out on a Hamamatsu Absolute PL Quantum Yield Measurement System C9920-03G fluorescence spectrofluorometer with an integrating sphere under λ_{exc} of 369 and 350 nm for Tb^{3+} and Dy^{3+} , respectively. Quantum yield values ($\Phi_{Tb} = 9.8\%$, $\Phi_{Dy} = 1.5\%$) were calculated directly from measurements using Hamamatsu PLQY U6039-05 software. These values allowed to estimate the overall quantum yields under ligand excitation ($\lambda_{exc} = 270$ nm) by using emission intensities of the lowest energetic component of the $\pi \rightarrow \pi^*$ and appropriate $f-f$ transitions from the excitation spectra recorded in the range 235–400 nm.

3. Results and discussion

All the studied compounds are composed of the lanthanide ion, two water molecules and three mandelate anions.

The results obtained with the use of thermogravimetric analysis for dysprosium and erbium mandelate complexes indicated that the first stage of weight loss in the range 100–170° corresponds to the loss of two water molecules (exp. 5.91%, calc. 5.52%).

The powder X-ray diffraction patterns of the complexes revealed that all of them are isostructural and crystalline. The patterns of the studied complexes shown in Fig. 1 are in good agreement with the simulated diffractogram based on X-ray analysis for the $Er(Man)_3(H_2O)_2$ single crystal [11], indicating that the surrounding of the Ln^{3+} ion in the studied complexes is similar to that found in the erbium crystal.

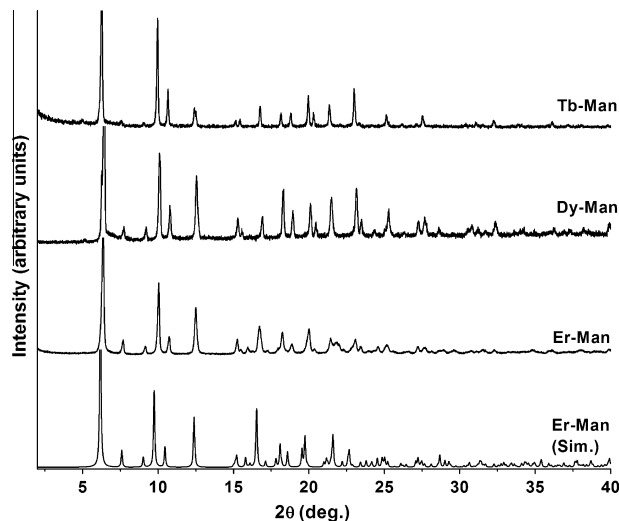


Fig. 1. XRPD diffractograms of Ln^{3+} mandelates. Er-Man (Sim.) is simulated diffractogram for the monocrystal of $Er(Man)_3(H_2O)_2$ [11].

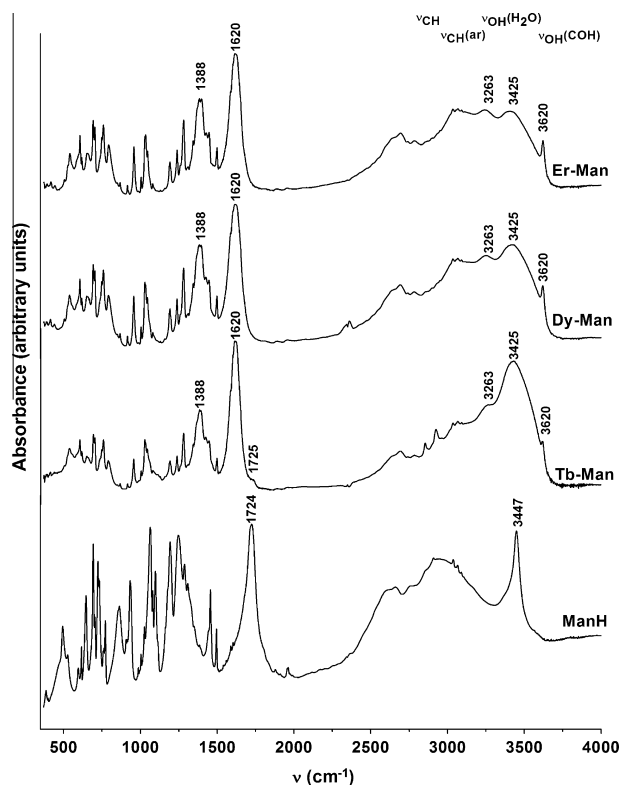


Fig. 2. FTIR spectra of Ln^{3+} mandelates ($Ln-Man$) and S(+)-mandelic acid (ManH).

3.1. FTIR, Raman and NIR spectroscopy

Similarity between the FTIR spectra of lanthanide complexes (Fig. 2) confirms the results obtained from the XRPD method. The spectrum of ManH, included in Fig. 2 for comparison purposes, shows an intense band at 1724 cm^{-1} , corresponding to the $\nu_{C=O}$ vibrations of protonated carboxylic group and a wide absorption band in the range $2750\text{--}3250\text{ cm}^{-1}$ attributed to the ν_{OH} vibrations of the COOH group. In this region one can find also some peaks of the methylenic and aromatic CH stretches. As it was revealed previously [14–16], the sharp peak at 3447 cm^{-1} belongs to the ν_{OH} vibration of alcoholic group, indicating the absence of intermolecular

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