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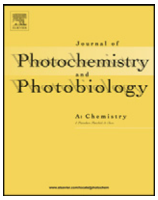

First crystal structures of lanthanide-hydrocinnamate complexes: Hydrothermal synthesis and photophysical studies

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ABSTRACT

Five new lanthanide(III) complexes of hydrocinnamic acid (Hcin), $[Ln(cin)_3(H_2O)_3]\cdot 3Hcin$ (Ln = Tb(III) (**1**), Dy(III) (**2**), Er(III) (**3**), Eu(III) (**4**) and Gd(III) (**5**)) have been synthesized and characterized. The X-ray structures of **1**–**5** reveal that all compounds are isostructural and that each lanthanide ion is nine – coordinated by oxygen atoms in an overall distorted tricapped trigonal-prismatic geometry. Six oxygen atoms are provided by carboxylate moieties, and the other three by water molecules. The supramolecular architectures of **1**–**5** show the presence of uncoordinated hydrocinnamic acid molecules which induce the formation of numerous hydrogen bonds. The photophysical properties of these complexes in the solid state at room temperature were studied using diffuse reflectance (DR), fluorescence excitation and emission spectra. An energy level diagram was used to establish the most relevant channels involved in the ligand-to-metal energy transfer, indicating that cin^- ligands can act as intramolecular energy donors for Tb(III), Dy(III) and Eu(III) ions.

1. Introduction

Although the sensitized emission of lanthanide chelates was first observed in 1942 [1], they are still in the front of the investigation and development. Photoluminescence of lanthanide metal complexes has been the subject of intensive investigation due to unique photophysical features such as narrow emission bands, large stokes shift, and long decay time [2,3]. These highly desirable properties are actively sought for numerous applications, including display devices, chemical and biological sensors, and optical communications [4–6]. However, the usual impediment to the use of such lanthanide ions systems is that the direct absorption of the f–f excited states is very inefficient. In the case of the lanthanide ions, the f–f transitions are parity forbidden which results in very low absorption coefficients. In order to overcome this drawback, suitable chromophores have been employed as antennas or sensitizers that have the capability of transferring energy indirectly to the lanthanide ions [7]. The photophysical properties of Ln(III) ions therefore depend critically on their ligand environments. In this context, numerous ligands have been shown to serve as "antenna" and the list includes β-diketones [8–11] and aromatic carboxylic acids [12–14]. In the recent past, the lanthanide compounds containing carboxylate groups, constitute an important family since they combine supramolecular chemistry principles. [15] In the case of lanthanide monocarboxylate complexes, the carboxylate groups can bind to the lanthanide ion in monodentate, chelating, bridging, and bridging – chelating modes. As a consequence, such complexes can exhibit mononuclear, dinuclear, polymeric chain, or network structures. In especial, the 3-phenylpropanoic acid also known as hydrocinnamic acid (Hcin) is an analog of phenylalanine [16] and can be synthesized from cinnamaldehyde [17]. Despite its structural simplicity, there are very few studies of complexes with the hydrocinnamic acid [18,19]. To gain more knowledge about the hydrocinnamate complexes chemistry, we describe the hydrothermal synthesis, crystal structures and photophysical studies of five hydrocinnamate lanthanide complexes $[Ln(cin)_3(H_2O)_3]\cdot 3Hcin$; (Ln = Tb(III) (**1**), Dy(III) (**2**), Er(III) (**3**), Eu(III) (**4**) and Gd(III) (**5**) and Hcin = hydrocinnamic acid).

2. Experimental

2.1. Materials and measurements

All synthetic work was performed in air and at room temperature. $LnCl_3\cdot 6H_2O$ (Ln = Tb, Dy, Er and Gd) and hydrocinnamic acid (Hcin) were obtained either from Aldrich® or Fluka® and used

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Table 1
Crystal data of [Ln(cin)$_3$(H$_2$O)$_3$]·3Hcin complexes, where Ln = Tb(III) **1**, Dy(III) **2**, Er(III) **3**, Eu(III) **4** and Gd(III) **5**.

Compound	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{54}H_{63}O_{15}Tb$	$C_{54}H_{63}O_{15}Dy$	$C_{54}H_{63}O_{15}Er$	$C_{54}H_{63}O_{15}Eu$	$C_{54}H_{63}O_{15}Gd$
Formula weight/g mol^{-1}	1110.96	1154.54	1119.30	1104.00	1109.29
Temperature/K	298(2)	298(2)	298(2)	150(2)	298(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	1.5418
Crystal system	Rhombohedral	Rhombohedral	Rhombohedral	Rhombohedral	Rhombohedral
Space group	*R*3	*R*3	*R*3	*R*3	*R*3
a/Å	27.3686(6)	27.3455(2)	27.3680(13)	27.3703(4)	27.3771(2)
b/Å	27.3686(6)	27.3455(2)	27.3680(13)	27.3703(4)	27.3771(2)
c/Å	6.0525(2)	6.03840(10)	6.0247(5)	6.06930(10)	6.06150(10)
α/°	90	90	90	90	90
β/°	90	90	90	90	90
γ/°	120.00	120.00	120.00	120.00	120.00
Volume/Å^3	3926.18(18)	3910.43(8)	3908.0(4)	3937.57(10)	3934.46(8)
Z	3	3	3	3	3
Density/g cm^{-3}	1.410	1.420	1.427	1.397	1.405
Crystal size/mm^3	0.47 × 0.18 × 0.16	0.30 × 0.19 × 0.16	0.32 × 0.18 × 0.11	0.17 × 0.16 × 0.13	0.27 × 0.19 × 0.12
Collected reflections	20,737	58,394	16,409	30,274	55,536
Independent reflections	4321	4675	3541	3576	3106
S	1.044	0.982	0.998	1.064	1.075
R [I > 2sigma(I)]	0.0310	0.0208	0.0444	0.0205	0.0266
wR	0.541	0.0449	0.0699	0.0497	0.0670

as received. EuCl$_3$·6H$_2$O were prepared by dissolving europium oxide in hydrochloric acid and then dried. Elemental analyses for C and H were carried out using a Perkin–Elmer 2400CHN analyzer. IR spectra were recorded with a Bomem Michelson 102 FTIR spectrophotometer using KBr pellets in the wavenumber range of 4000–400 cm^{-1} with an average of 128 scans and 4 cm^{-1} of spectral resolution. Thermal analysis was obtained on a Shimadzu TG-60 equipment. 6–10 mg sample were heated at 10 °C min^{-1} from room temperature to 800 °C in a dynamic nitrogen atmosphere (flow rate = 100 mL min^{-1}). Diffuse reflection (DR) spectra were acquired with a Cary 500 spectrophotometer from 200 to 1500 nm with spectral resolution of 1 nm. The luminescence excitation and emission spectra were obtained with a Jobin-Yvon Model Fluorolog FL3-22 spectrophotometer equipped with a R928 Hamamatsu photomultiplier and 450 W xenon lamp as excitation source, the spectra were corrected with respect to the Xe lamp intensity and spectrometer response. Measurements of emission decay were performed with the same equipment by using a pulsed Xe (3 μs bandwidth) source.

2.2. Synthesis of [Ln(cin)$_3$(H$_2$O)$_3$]·3Hcin

A mixture of LnCl$_3$·6H$_2$O (0.13 mmol), Hcin (0.40 mmol, 60 mg), NaOH aqueous solution (0.40 mL, 1 mol L^{-1}) and deionized water (20 mL) was sealed in a 25 mL Teflon-line Parr acid digestion bomb, which was heated up to 160 °C and kept at this temperature for 72 h under hydrothermal conditions. After this time, the reaction vessel was cooled to room temperature at 3.7 °C per hour rate.

2.2.1. [Tb(cin)$_3$(H$_2$O)$_3$]·3Hcin (**1**)

Colorless single crystals were obtained. Yield: 47%. Anal. Calc. for $C_{54}H_{63}O_{15}Tb$: C: 53.1, H: 5.70%; Found: C: 53.6, H: 5.53%.

2.2.2. [Dy(cin)$_3$(H$_2$O)$_3$]·3Hcin (**2**)

Colorless single crystals were obtained. Yield: 51%. Anal. Calc. for $C_{54}H_{63}O_{15}Dy$: C, 52.9, H, 5.67%; Found: C, 52.3, H, 5.71%.

2.2.3. [Er(cin)$_3$(H$_2$O)$_3$]·3Hcin (**3**)

Light pink single crystals were obtained. Yield: 52%. Anal. Calc. for $C_{54}H_{63}O_{15}Er$: C, 52.6, H, 5.64%; Found: C, 53.1, H, 5.73%.

2.2.4. [Eu(cin)$_3$(H$_2$O)$_3$]·3Hcin (**4**)

Colorless single crystals were obtained. Yield: 54%. Anal. Calc. for $C_{54}H_{63}O_{15}Eu$: C, 53.6, H, 5.75%; Found: C, 53.9, H, 5.78%.

2.2.5. [Gd(cin)$_3$(H$_2$O)$_3$]·3Hcin (**5**)

Colorless single crystals were obtained. Yield: 51%. Anal. Calc. for $C_{54}H_{63}O_{15}Gd$: C, 58.4, H, 5.72%; Found: C, 58.5, H, 5.76%.

2.3. X-ray data collection and structure determination

Single crystal X-ray data were collected using a Oxford GEMINI A Ultra diffractometer with Mo Kα (λ = 0.71073 Å) for compounds **1**–**4** and Cu Kα (λ = 1.5418 Å) for compound **5**. Compounds **1**, **2**, **3** and **5** measurements were performed at room temperature (298 K) and compound **4** at 150 K. Data collection, reduction and cell refinement were carried out by CrysAlis RED, Oxford diffraction Ltda – Version 1.171.32.38 software [20]. The structures were solved and refined using SHELXL-97 [21]. An empirical isotropic extinction parameter x was refined, according to the method described by Larson [22]. A Multiscan absorption correction was applied [23]. The structures were drawn by ORTEP-3 for windows [24] and Mercury softwares [25]. Crystal and structural refinement data for all compounds are displayed in Table 1.

3. Results and discussion

3.1. Crystal structures of [Ln(cin)$_3$(H$_2$O)$_3$]·3Hcin

Single crystal X-ray diffraction reveals that **1**–**5** are isostructural and crystallize in rhombohedral system and space group *R*3. Thus, only the crystal structure of Eu(III) complex will be described herein as a representative example. The ORTEP drawing of a structural fragment of [Eu(cin)$_3$(H$_2$O)$_3$]·3Hcin with atom numbering schemes is shown in Fig. 1, while a selection bond distances and angles for all complexes are displayed in Table 2. All complexes are formed by one lanthanide center, three cin$^-$ ligands, three *aqua* ligands and three uncoordinated Hcin molecules. The hydrocinnamate anions act in a chelating coordination mode, as indicated by IR results. The Eu(III) ion is coordinated by six oxygen atoms (O1, O2, O1^{i}, O2^{i}, O1^{ii} and O2^{ii}) from three cin$^-$ ligands and three oxygen atoms (O3, O3^{i} and O3^{ii}) (Symmetry Code: $i(1-y, -1+x-y, z)$ and $ii(2-x+y, 1-x, z)$) from water molecules. The coordination geometry for the nine-coordinated Eu(III) can be described as a distorted tricapped trigonal prism (Fig. 1), in which O2, O2^{i} and O2^{ii} act as the capping atoms. The Eu—O bond lengths range from 2.4131(18) to 2.5152(19) Å, which are similar to other Eu–O bond distances reported in the literature [26,27]. Data on the synthesis