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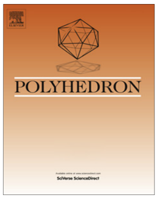

Europium (III) complexes with new N-donor ligand: A comparative study in solid state and solution

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ABSTRACT

In this paper a pyridine-based racemic ligand [*N*,*N*′-bis(2-pyridylmethylidene)-1,2-(*R*,*R* + *S*,*S*)-cyclohexanediamine], **1**, and its new trifluoromethansulfonate ($CF_3SO_3^-$, triflate) and nitrate Eu(III) complexes were studied, both in the solid state and in acetonitrile (AN) solution. In the case of the triflate complexes, a combination of structural and spectroscopic evidences, revealed the different nature of the species in solution and in the solid state. On the contrary, the nitrate adduct in the solid state presented similar features as the complex present in AN solution. All triflate and nitrate complexes detected in solution are highly stable.

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1. Introduction

Luminescent lanthanide complexes possess peculiar photophysical properties mainly due to the spectroscopic features of the metal ion. In particular, the emission spectra of lanthanide ions consist of sharp and narrow bands corresponding to the *f*–*f* transitions that are characteristic of the metal ion. Although Ln(III) ions show weak absorption intensities, due to the parity forbidden nature of these intraconfigurational transitions, this disadvantage can be overcome by indirect sensitization through the absorption bands of an organic ligand coordinated to the Ln(III) ion in the UV region (antenna effect). A suitably designed ligand also provides the advantage of protecting the Ln(III) ions from the intrusion of solvent molecules (i.e. H_2O) into the inner coordination sphere. These coordinated solvent molecules are in fact often responsible for radiationless deactivation processes that occur upon interaction of OH, NH, and to a lesser extent CH oscillators with the lanthanide ions. This phenomenon is extremely detrimental for the efficiency of the rare earth ion luminescence, even if lanthanide ions such as Eu(III) and Tb(III) are less affected by this deactivation processes. For this reason, Eu(III) and Tb(III) complexes are more suitable for application in biological (aqueous) fluids as efficient fluorophores [1–4].

As far as applications in the biomedical field are concerned, Eu(III) and Tb(III) complexes exhibit several additional desirable and unusual characteristic when compared with conventional organic fluorophores, such as long excited state lifetimes (usually in the milliseconds range), large energy shift between absorbed and emitted radiations (in the case of ligand sensitization) and very narrow emission bands; these two effects allow the separation between Ln(III) luminescence and short-lived background fluorescence [5].

Recently, the interest in Ln(III) compounds possessing chiral properties increased, as a result of the possibility to take advantage of the chiral feature introduced in the design of the complex [6]. In particular, Ln(III) compounds, where the chirality is "introduced" through the use of chiral ligands, has led to the development of new chiral sensing/recognition applications, such as luminescence sensing of anions [7–10] and of chiral biological substrates [8,11–13].

In the former case, Yamada et al. [7] showed how the introduction of a stereogenic carbon in the skeleton of tris(2-pyridilmethyl)amine can enhance the sensitivity of the ligand in the luminescence anion sensing.

In order to design efficient and reliable sensors based on Ln(III) coordination compounds, the detailed knowledge of the Ln(III) speciation in solution is desirable. Thermodynamic studies have been widely run for this purpose and also to gain information on the nature of the Ln(III) coordinated species in aqueous solution [14] and organic solvent [15–19].

Even if the nature of the species in solution is often different from the one in the solid state, we believe that a combined study of the molecular structure and of the luminescence spectroscopy

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in the solid state should give a complete overview of the investigated subject. Recently, the structure and the luminescence spectroscopy in the solid state of a new family of chiral nitrate Eu(III) complexes with some pyridine-based chiral ligands have been presented [20].

Due to the aforementioned advantages of chirality, in the present contribution, the racemic mixture of pyridine-based chiral ligand *N,N′*-bis(2-pyridylmethylidene)-1,2-(*R,R* + *S,S*)-cyclohexanediamine,1, and its novel trifluoromethansulfonate ($CF_3SO_3^-$, triflate) and nitrate Eu(III) complexes are presented both in the solid state and in acetonitrile (AN) solution. A careful characterisation of the species in solution and in the solid state is performed exploiting different techniques such as single crystal X-ray diffraction, Eu(III) luminescence spectroscopy, spectrophotometric UV–Vis titration and IR spectroscopy.

2. Material and methods

$Eu(CF_3SO_3)_3$ (Aldrich, 98%) and $Eu(NO_3)_3{\cdot}5H_2O$ (Aldrich, 99.9%) have been stored in glove box, absolute ethanol (Aldrich, 99.9%) was used without further manipulation, anhydrous acetonitrile used for all the experiments in solution has been obtained by refluxing AN (Aldrich, 99%) for 2 h in presence of CaH_2 and then distilled. The central fraction was transferred in a MB 150 glove box and stored in presence of molecular sieves (4 Å). The concentration of water (<5 ppm) was checked by Karl Fischer instrument (Metrohm).

FT-IR spectra were recorded under nitrogen purge at room temperature on Nicolet, Magnet-IR 760 with a spectral resolution of 2 cm^{-1} and 256 scans. For the solution measurements a single cell with KBr windows was used. For the measurements of the spectra of the powder, the samples were dispersed in KBr (3 wt.%) and pressed to obtain a pellet.

Complex **2**: Elemental *Anal.* Calc. for $C_{20}H_{23}N_4F_6S_2O_8Eu$ (MW 777.50): C, 30.90; H, 2.98; N, 7.21; O, 16.46. Found: C, 30.85; H, 2.96; N, 7.26; O, 16.48%. IR (KBr pellet, cm^{-1}): 3450 (broad), 2933, 2856, 1595, 1490, 1440, 1310, 1280, 1248, 1160, 1026 (ν_sSO_3), 1023 (ν_sSO_3), 778, 631, 571, 510.

Complex **2**: IR (1 mM in anhydrous AN, cm^{-1}): 2305 ($\nu_3 + \nu_4(CH_3CN)$ upon complexation), 1599 ($\nu_{C=N}$), 1270 (ionic $\nu_{as}SO_3$), 1226 (ionic ν_sCF_3), 1156 (ionic $\nu_{as}CF_3$), 889, 780, 640, 573, 518. $\lambda_{max} = 284$ nm, $\varepsilon = 15992$ $mol^{-1}cm^{-1}dm^3$ (acetonitrile solution).

Complex **3**: Elemental *Anal.* Calc. for $C_{39}H_{44}N_8F_9S_3O_{11}Eu$ (MW 1219.96) C, 38.40; H, 3.64; N, 9.19; O, 14.43. Found: C, 38.38; H, 3.58; N, 9.12; O, 14.37. IR (KBr pellet, cm^{-1}): 3405 (broad), 2932, 2856, 1595, 1490, 1441, 1310, 1282, 1248, 1160, 1029(ν_sSO_3), 1023(ν_sSO_3),779, 631, 573, 510.

Complex **3**: IR (1 mM in anhydrous AN, cm^{-1}): 3610 (very weak), 2307 ($\nu_3 + \nu_4(CH_3CN)$ upon complexation), 1599 ($\nu_{C=N}$), 1271 (ionic $\nu_{as}SO_3$), 1226 (ionic ν_sCF_3), 1156 (ionic $\nu_{as}CF_3$), 888, 833, 778, 640, 573, 518. $\lambda_{max} = 286$ nm, $\varepsilon = 29759$ $mol^{-1}cm^{-1}dm^3$ (acetonitrile solution).

Complex **4**: (0.02 mM in anhydrous AN). ESI-MS(Scan ES+; *m/z*): 669 ($[M + K]^+$), 653 ($[M + Na]^+$), 568 (($[M{-}NO_3]^+$). IR (1 mM in anhydrous AN, cm^{-1}): 3611 (broad), 1643, 1596 ($\nu_{C=N}$), 1283, 1244, 1230, 1159, 1107, 894, 832(very weak, ionic nitrate), 818 (bonded (bidentate) nitrate), 780, 637, 586, 531, 511. $\lambda_{max} = 286$ nm, $\varepsilon = 20338$ $mol^{-1}cm^{-1}dm^3$ (acetonitrile solution).

Elemental analyses were carried out by using a EACE 1110 CHNO analyzer.

The ESI-MS spectra were obtained by single-quadrupole mass spectrometer: for complexes **2** and **3** in AN solution are not informative because a complex pattern of signals were detected. For this reason, it is not possible to get clear information about the molecular weight of the species in solution.

The molar conductivity of $Eu(NO_3)_3$ in AN solutions was measured with a Metrohm 712 conductometer at 25.0 + −0.1 °C.

2.1. Spectroscopic measurements

$Eu(CF_3SO_3)_3$ (Aldrich, 98%) and $Eu(NO_3)_3{\cdot}5H_2O$ (Aldrich, 99.9%) have been stored under vacuum for several days at 80 °C and then transferred in glove box. Stock solutions of the salt were prepared by dissolving weighed amounts of them in anhydrous AN and then standardized by complexometry with EDTA [21].

Spectrophotometric titrations were performed by adding a solution of Eu(III) salt to a ligand solution prepared with anhydrous AN. Typically the concentration of the ligand was in the range 2–5 × 10^{-5} mol dm^{-3} and a ratio of the ligand to metal concentration up to 4 were reached. The stability constants values were calculated by simultaneous fit of the absorbance values at different wavelengths for two titrations using the program HypSpec [22].

Photoluminescence measurements were carried out using a tunable dye laser pumped by a Nd:YAG laser. The emission signal was analyzed by a half-meter monochromator (HR460, Jobin Yvon) equipped with a 1200 lines/mm grating and detected with a CCD detector (Spectrum One, Jobin Yvon) or with a photomultiplier. The spectral resolution of the emission spectra is 0.15 nm. The emission decay curves were recorded upon pulsed laser excitation using a water cooled GaAs photomultiplier (Hamamatsu) as a detector and a 500 MHz digital oscilloscope (WaveRunner, LeCroy) to collect the emission decay curves.

2.2. X-ray crystallography

The X-ray intensity data for **2** were measured on a Bruker SMART Apex II CCD area detector diffractometer. The cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. For all crystals, a full sphere of reciprocal space was scanned by 0.3°ω steps. The software SMART [23] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by the SAINT [23] program, and an empirical absorption correction was applied using SADABS [24]. The structures were solved by direct methods (SIR 97) [25] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL) [26], using anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms, except the ones bound to oxygens that were refined isotropically, were added in calculated positions, included in the final stage of refinement with isotropic thermal parameters, $U(H) = 1.2\ Ueq(C)$ and allowed to ride on their carrier carbons. Molecular graphics were generated using SCHAKAL [27].

3. Results and discussion

The synthesis of *N,N′*-bis(2-pyridylmethylidene)-1,2-(*R,R* + *S,S*)-cyclohexanediamine (**1**) (racemic mixture) was performed as reported in literature [20,28].

The synthesis of Eu(III) complexes was performed in absolute ethanol (20 mL), by adding the desired amount of the ligand and of the triflate or nitrate europium(III) salt: the synthetic protocol is drawn in Scheme 1.

In particular for the synthesis of the triflate europium(III) complex (**2**), 0.49 mmol of the ligand (**1**) and 0.49 mmol of $Eu(CF_3SO_3)_3$. (L:Eu = 1:1) were mixed together and the mixture was stirred for 3 h at room temperature. Crystals suitable for a single crystal X-ray diffraction study were obtained by slow diffusion of diethyl

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