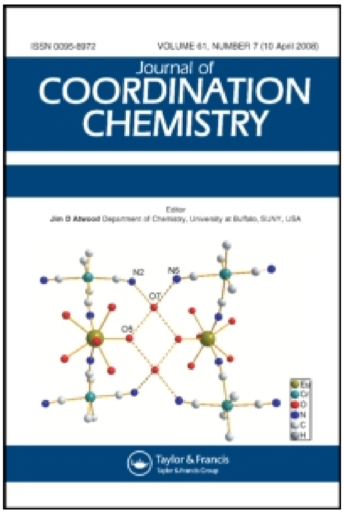

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SYNTHESIS AND CHARACTERIZATION OF LANTHANIDE R-(+)- AND S-(–)-α-METHOXY-α-(TRIFLUOROMETHYL) PHENYLACETATES (MTPA)

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The lanthanide salts with MTPA were obtained by reaction of the acid with the respective basic carbonates. The compounds with composition $\{Ln[R\text{-}(+)\text{-}MTPA]_3OH\}^-H_3O^+$ and $\{Ln[S\text{-}(-)\text{-}MTPA]_3OH\}^-H_3O^+$ (Ln = Eu, Nd, Tb) were characterized by microanalysis, IR spectra, ^1H NMR spectroscopy, absorption spectra of the neodymium salts, emission spectra of the europium and terbium compounds and TG analysis. Circularly polarized luminescence was observed in the Eu salts.

Keywords: Lanthanide; R-(+)-; S-(–)-α-methoxy-α-(trifluoromethyl) phenylacetates

INTRODUCTION

The objective of this research is to prepare lanthanide coordination compounds containing optically active anions or neutral ligands. In this article the synthesis and characterization of salts derived from R-(+)- and S-(–)-α-methoxy-α-(trifluoromethyl) phenylacetic acids are described.

EXPERIMENTAL

The salts were prepared by addition, under stirring and gentle heating, of a lanthanide basic carbonate to a dilute aqueous solution of the respective acids; the pH was maintained around 4. The solutions were filtered to remove the small excess of basic carbonate and evaporated in a water bath for crystallization of the salts, which were dried and dissolved in acetone. The solutions were filtered and left to evaporate in a dessiccator for crystallization. The final product was separated and dried *in vacuo* over anhydrous calcium chloride.

The compounds were characterized by lanthanide titration with EDTA[1] and C, H microanalysis.

IR spectra were recorded on a Nicolet FTIR-510 spectrophotometer, using Nujol mulls between KBr plates. The absorption spectra of the neodymium compound were determined on a Zeiss DMR-10 spectrophotometer, using silicone mulls for the solids, in cells of 0.500 mm optical path, and solutions of *ca.* 0.02 M in 10.00 mm optical path cells. The emission spectra of the europium salts, and also those of the terbium salts at 77K, were recorded on a modified Hitachi Perkin-Elmer MPF-4 spectrofluorimeter. High-resolution emission spectra were studied in a Jobin-Yvon U-1000 double monochromator, with 1800 grooves/mm diffraction gratings and a Coherent Radiation Innova 90 krypton ion laser at 406.7 nm and 30 mW power for excitation. Refractive indexes were determined at 298K in an Abbé-type Bausch and Lomb refractometer. TG analyses were performed on a Perkin-Elmer TGA-7 apparatus, under a dynamic air atmosphere, using a 10°C min^{-1} heating rate.

Circularly polarized luminescence (CPL) emissions were studied in a Perkin-Elmer MPF-4 spectrofluorimeter modified by the addition of an electrooptical modulator (Hinds) and a Glan-Taylor polarizer (Melles-Griot). Signals were detected in a lock-in amplifier (PAR mod. 121).[2]

RESULTS AND DISCUSSION

Table I presents a summary of the analytical results. They are in accordance with the general composition $Ln(MTPA)_3.2H_2O$.

TABLE I Summary of analytical results

	Analysis (%)					
	Lanthanide		*Carbon*		*Hydrogen*	
Ln	*Theor.*	*Exp.*	*Theor.*	*Exp.*	*Theor.*	*Exp.*
Nd[a]	16.4	16.3	41.0	41.3	3.2	3.4
Eu[a]	17.5	17.5	40.6	41.1	3.2	3.2
Tb[a]	17.8	18.1	40.3	40.7	3.2	3.2
Nd[b]	16.4	16.5	41.0	41.1	3.2	3.0
Eu[b]	17.5	17.6	40.6	41.2	3.2	3.1
Tb[b]	17.8	18.0	40.3	40.7	3.2	3.1

a = $\{Ln[S\text{-}(-)\text{-}MTPA]_3OH\}\ H_3O+$;b = $\{Ln[R\text{-}(+)\text{-}MTPA]_3OH]\}^{-}H_3O^{+}$

IR spectra show clearly the existence of νOH at 3635 cm^{-1} in all salts, as well as H_3O^+ bands at 2956 and 2923 cm^{-1} and a shift of νCOO from 1735 cm^{-1} (free acid) to *ca.* 1586 cm^{-1} (salts), thus showing bidentate coordination of the anions through the carboxyl groups. Thus, the proposed formulation for these compounds is $[Ln(MTPA)_3OH]^-H_3O^+$ for both R-(+) and S-(−) isomers.

In order to obtain further evidence of the presence of an OH group, the Tb S-(−) salt was synthesized in D_2O. The peak at 3635 cm^{-1} decreased as expected and a new peak at 2615 cm^{-1} appeared in the region expected for the OD stretching frequency.

Proton **NMR** spectra were recorded for both free acids and their Tb salts, the latter dissolved in deuteroacetone. Both acids have resonances at *ca.* 2.05, 3.6, 6.7 and 7.5 ppm (TMS). Both salts have only one peak at 1.99 ppm (methoxyl protons), indicating that all other protons were exchanged (OH^-, H_3O^+ and the phenylic protons). This is further support for the proposed formulation for these compounds.

The absorption spectra of the neodymium salts in the solid state and in acetone (Figure 1) at room temperature are very similar, indicating the existence of the same species (25°C). The parameters: nephelauxetic β_1 = 17252/17329 = 0.996, β_2 = 23299/23468 = 0.993 and $\bar{\beta}$ = 0.995[3] and covalent factor $b^{1/2}$ = 0.0500[4] were calculated from the transitions $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ (using Simpson's rule)[5] and $^2P_{1/2} \leftarrow {}^4I_{9/2}$ (using the more intense peaks), respectively. They indicate the electrostatic nature of the metal-ligand bonds.

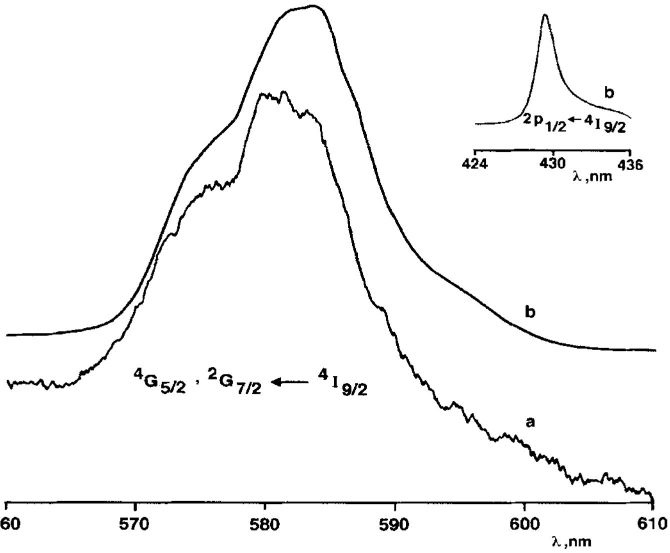

FIGURE 1 Absorption spectra of the Nd salt: a) solid state, b) acetone solution, both at 298K.

The emission spectra of the europium (Figure 2) and terbium (Figure 3) salts are identical for both enantiomers. The europium compounds show a very weak peak, with a shoulder at 578.5 nm due to the $^5D_0 \rightarrow {}^7F_0$ transition. This may be interpreted as a lower symmetry around the central ion, or a distortion of the coordination polyhedron. On the other hand, this peak with a shoulder may signify that the central ion has more than one center of symmetry. Unfortunately, no single crystals were obtained for X-ray structural determinations. The $^5D_0 \rightarrow {}^7F_1$ transition shows one peak at 588 nm followed by poorly resolved shoulders. The $^5D_0 \rightarrow {}^7F_2$ transition presents two more intense peaks at 612 nm and 613 nm and two medium peaks at 618 and 622.5 nm. Due to the facts above, it was impossible to make a correct attribution of the symmetry around the central ion. The transitions $^5D_4 \rightarrow {}^7F_{6,5,4,3}$ were observed for the terbium salt (Figure 3).

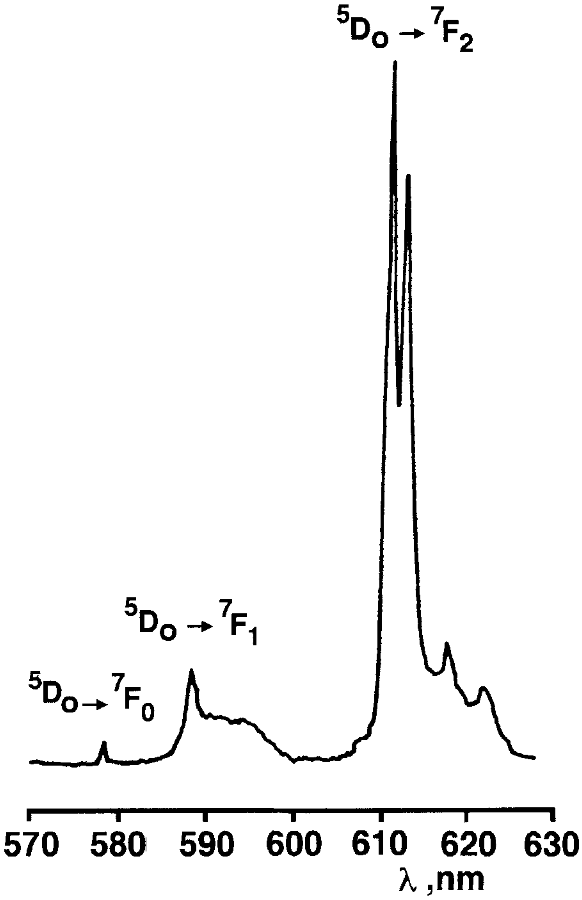

FIGURE 2 Emission spectrum of the Eu S-(−) salt, solid state, at 77K.

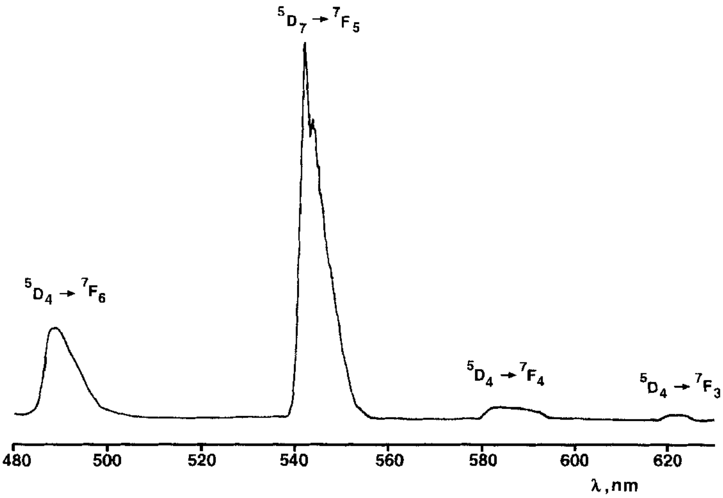

FIGURE 3 Emission spectrum of the Tb R-(+) salt, solid state, at 77K.

High-resolution spectra for the $^5D_0 \rightarrow {}^7F_0$ band of the Eu S-(−) salt (Figure 4) showed three peaks for this transition, at 578.696, 578.838 and 579.105 nm. This clearly suggests the presence of three different coordination environments, or, possibly polymeric character of the compound.[6]

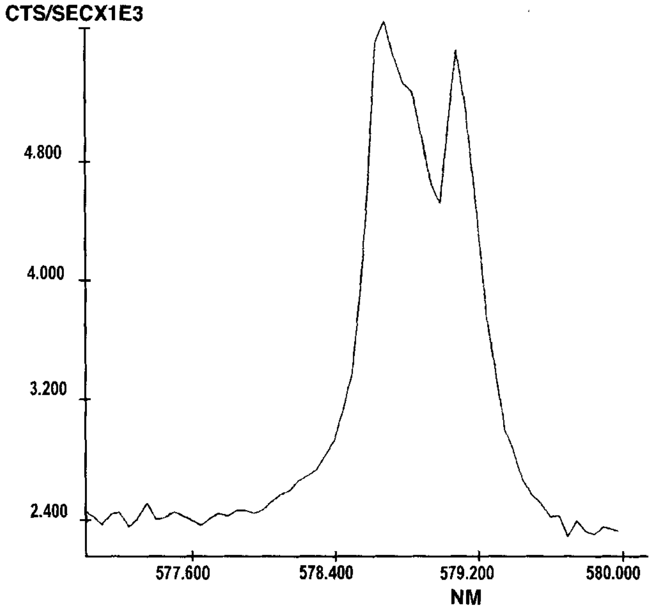

FIGURE 4 High-resolution emission spectrum, $^5D_0 \rightarrow {}^7F_0$ band, of the Eu S-(−) salt, at 298K.

Circularly polarized luminescence (CPL) emissions[7] were observed for the Eu salts both in acetone and DMSO solutions. The signal of CPL was positive for the R-(+) and negative for the S-(−) compounds, for the $^5D_0 \rightarrow {}^7F_1$ transition, with identical lineshapes for both solvents. Since the selection rules for optical activity of this transition predict large CPL intensities when this transition is both electric dipole and magnetic dipole allowed,[8] the above results suggest the absence of an inversion center (in order for this transition to be electrically allowed) and an alignment of both transition dipole moments.

No CPL emission was observed in the Tb salts. This is possibly due to a non-alignment between the transition dipole moments in these compounds, or even solvation effects.[9]

Figure 5 presents the TG curve of the terbium S-(−) compound as representative of the general thermal behavior that these compounds exhibit. All the compounds lose water up to *ca.* 190°C, followed by total decomposition, yielding LnF_3 as final residue at 900°C.

One point that must be mentioned is the inertness of these compounds with respect to further complexation. Unsuccessful attempts to prepare complexes with sulfoxides (dibenzyl and *t*-butylbenzyl), phosphine oxides (triphenyl and tripiperidino) and hexamethylphosphoramide, all of which readily form stable complexes with lanthanide (III) ions[10–11] illustrate this point. The existence of OH^- and H_3O^+, probably hydrogen bonded, and the bulk of the coordinated anions, probably saturating the coordination sphere, may be responsible for that. Another point is that the presence of OH^- and H_3O^+, strongly bonded to the central ion, explain the loss of two water molecules at *ca.* 190°C, as shown by TG studies.

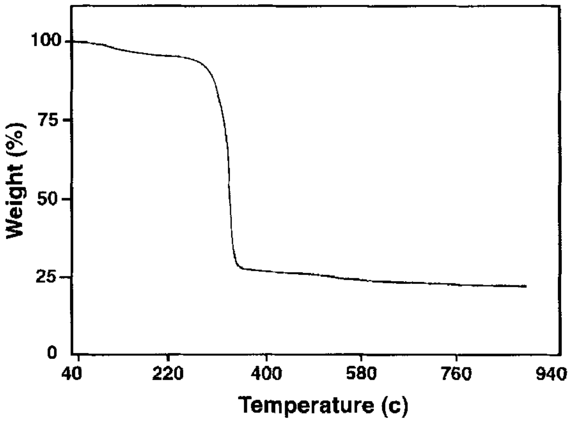

FIGURE 5 TG curve of the Tb S-(−) salt. Heating rate, 10°C min^{-1} in a dynamic air atmosphere.

Acknowledgments

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