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Preparation and properties of complexes between rare earth trifluoroacetates and hexamethylphosphoramide (HMPA)

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Abstract

Complexes of composition $[Ln(TFA)_3(HMPA)_3]$ (Ln=La, Nd, Eu, Gd, Dy, Ho and Er, TFA=trifluoroacetate) were prepared and characterized by complexometric analyses with EDTA and CHN microanalytical procedures. IR spectra show that HMPA's are linked to the central ions through the P=O oxygen and that the trifluoroacetate ions are also coordinated. The visible absorption spectrum of the neodymium compound in a silicone mull, at room temperature, allows us to calculate the nephelauxetic parameter $\beta=0.990$, the covalent factor $b^{1/2}=0.070$ and Sinha's parameter $\delta=1.01$. They are suggestive of an essentially electrostatic interaction between lanthanide and ligands. The emission spectra of the europium complex at room temperature and at 77 K were also determined. Thermogravimetry show that HMPA molecules are totally evaporated at ca. 260°C and that the residues are the corresponding rare earth oxyfluorides.

Keywords: Lanthanides; Trifluoroacetate; Hexamethylphosporamide

1. Introduction

Hexamethylphosphoramide (HMPA), is a liquid miscible with water and other polar and non-polar organic solvents. It presents a pyramidal structure with a high dipolar moment and donor capacity [1,2]. Complexes between HMPA and lanthanide salts have been under study since 1968 [3].

The motivation for undertaking this work was centered in the properties of the trifluoroacetate group. This counter-ion may not be coordinated to the central ion, behave either as a mono or bidentade group, or act as a bridge between neighbouring metal ions. It shows moderate donor strength and the steric hindrance is large, due to the bulky trifluoromethyl groups [4].

In this paper the complexes of composition $[Ln(TFA)_3(HMPA)_3]$ (Ln=La, Nd, Eu, Gd, Dy, Ho and Er) are described. The compounds were characterized by microanalyses, titration of the lanthanides with EDTA, IR spectra, absorption spectrum of the neodymium compound, fluorescence spectra of the europium compound and thermogravimetric studies.

2. Experimental

The compounds were prepared by mixing the hydrated salts dissolved in absolute ethanol with HMPA (in acetone), in a 1:3 molar proportion. The solvents were partially evaporated on a water bath and the solution kept in the refrigerator (~24 h) in order to precipitate the complexes which were separated and dried in vacuum over anhydrous calcium chloride.

Lanthanide ions were titrated by a complexometric method, using EDTA and xylenol orange as indicator [5]. Carbon and hydrogen were determined by microanalytical procedures.

IR spectra were recorded on a MIDAC Prospect R FT-IR using Nujol mulls between KBr plates or KBr pellets. TG curves were made, under dynamic nitrogen atmosphere (50 ml min^{-1}), using a Perkin-Elmer TGA-7 system at a heating rate of 5°C min^{-1}.

The absorption spectrum of the neodymium compound was recorded on a Zeiss DMR-10 spectrophotometer,

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Table 1
Summary of analytical results (%) for the compounds with general formula [Ln(TFA)$_3$(HMPA)$_3$]

Compounds Ln	Ln		C		H		N	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
La	13.7	13.9	28.4	28.6	5.4	5.5	12.4	12.8
Nd	14.1	14.3	28.2	28.0	5.3	5.1	12.4	12.4
Eu	14.8	15.3	28.0	28.0	5.3	5.3	12.3	12.6
Gd	15.2	15.6	27.9	28.0	5.3	5.5	12.2	12.6
Dy	15.6	15.1	27.7	27.6	5.2	5.3	12.1	12.4
Ho	15.8	14.9	27.7	27.4	5.2	5.0	12.1	12.4
Er	16.0	15.6	27.6	28.3	5.2	5.5	12.1	12.8

using a silicone mull on a 0.5 mm quartz path cell at room temperature.

The emission spectra of the solid europium compound at room temperature and at 77 K were registered on a Hitachi Perkin-Elmer spectrofluorimeter, using 396 nm excitation radiation.

3. Results and discussion

Analytical results, presented in Table 1 are in good accordance with the stoichiometry proposed: [Ln(TFA)$_3$(HMPA)$_3$].

The important IR data are given in Table 2. The P=O stretching band appears at 1193 cm^{-1} in free HMPA. In the lanthanide complexes this vibration is shifted to lower frequencies, ca. 50 cm^{-1}, indicating coordination through the phosphoryl oxygen. The ν_{as} and ν_s PNC stretching modes of the free ligand were shifted to higher frequencies. The local symmetry of the trifluoroacetate anion is low [6]. All the fifteen vibration modes are IR active even in the free ion and a lowering of the symmetry due to coordination is not expected to increase the number of IR bands. However, the COO$^-$ ($\nu_{as_{COO^-}}$, $\nu_{s_{COO^-}}$ and δ_{COO^-}) modes are expected to be more sensitive to coordination and the frequencies due to them could be shifted on complexation [4]. Several criteria have been established in an attempt to distinguish between different coordination modes [4,7]. Table 2 contains the most important IR data (cm^{-1}). The La and Nd complexes present two bands (1688 and 1665 cm^{-1}) attributed to $\nu_{as_{COO^-}}$ and only one (1462) attributed $\nu_{s_{COO^-}}$. The Δ values are 226 and 200 cm^{-1}, respectively. The existence of these doublets suggests two types of coordination of the trifluoroacetate group. Compounds of Eu and Gd show one $\nu_{as_{COO^-}}$ (1671) and $\nu_{s_{COO^-}}$ (1463) band and the $\nu_{as} - \nu_s$ is 220 cm^{-1} difference in both cases. The ν_{as} bands are non symmetric and may contain an unresolved peak. Dy, Ho and Er clearly present two medium bands attributed to ν_{as} (1711 and 1675 cm^{-1}) and $\nu_{as_{COO^-}}$ (1463 and 1416 cm^{-1}) with Δ values of ~250 cm^{-1}. In all cases only one band, the δ_{COO^-} band, was formed. However, as a distinction between the different trifluoroacetate coordination modes is not unambiguously clear, a monodentate coordination cannot be totally excluded [8]. According to preliminary X-ray structural studies of the erbium complex, this ion is present in two coordination centers: (a) octahedral with four HMPA molecules, two monodentate trifluoroacetate groups and one trifluoroacetate out of the coordination sphere; (b) trigonal bipyramidal with two HMPA, two monodentate and one bidentate trifluoroacetates. Nevertheless, the crystals are sensitive to X-rays and further refinements will be necessary. Detailed X-ray single-crystal diffraction studies are clearly necessary in order to definitely establish a correlation between stretching frequency shifts and structural parameters.

Table 2
Infrared data (cm^{-1}) for the compounds with general formula [Ln(TFA)$_3$(HMPA)$_3$]

Attributions						
Compounds	ν_{PO}	$\nu_{as_{PNC}}$	$\nu_{s_{PNC}}$	$\upsilon_{as_{COO^-}}$	$\nu_{s_{COO^-}}$	δ_{COO^-}
La	1134m[a]	991s	754m	1688w–1662w	1462w	721w
Nd	1137m	991s	754m	1687w–1665w	1463w	724w
Eu	1140m	992s	754m	1671m	1463w	724w
Gd	1140s	991s	754m	1674s	1464m	721w
Dy	1137m	993s	755m	1711w–1676w	1463w–1416w	712m
Ho	1137m	992s	755m	1712w–1678w	1462w–1416w	712m
Er	1136m	991s	754m	1711w–1678w	1462w–1416w	712w
HMPA	1193s	983s	749s			
TFA				1666w	1469m	728m

[a] s = strong; m = medium; w = weak.

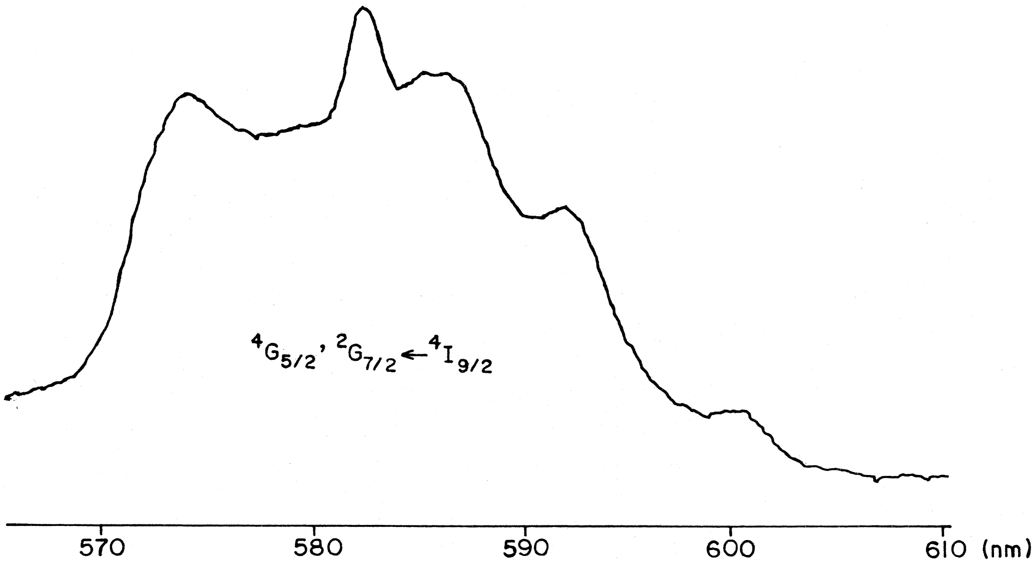

Fig. 1. Absorption spectrum of the compound of formula [Nd$(TFA)_3(HMPA)_3$] at room temperature.

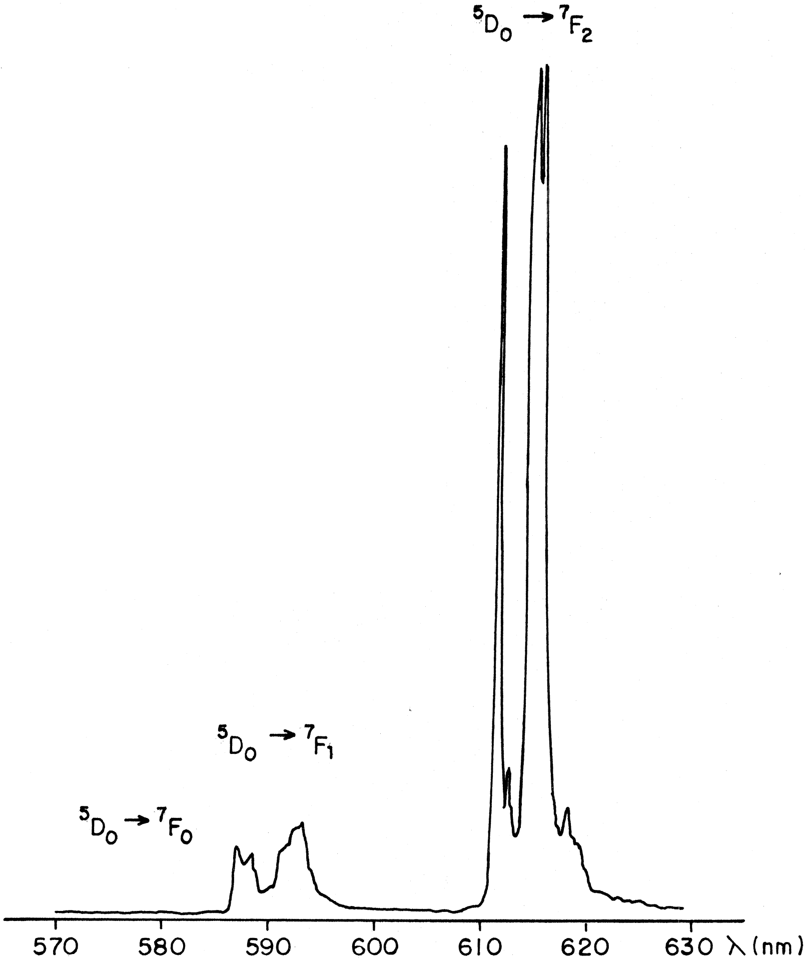

Fig. 2. Emission spectrum of compound of formula [Eu$(TFA)_3(HMPA)_3$] at 77 K.

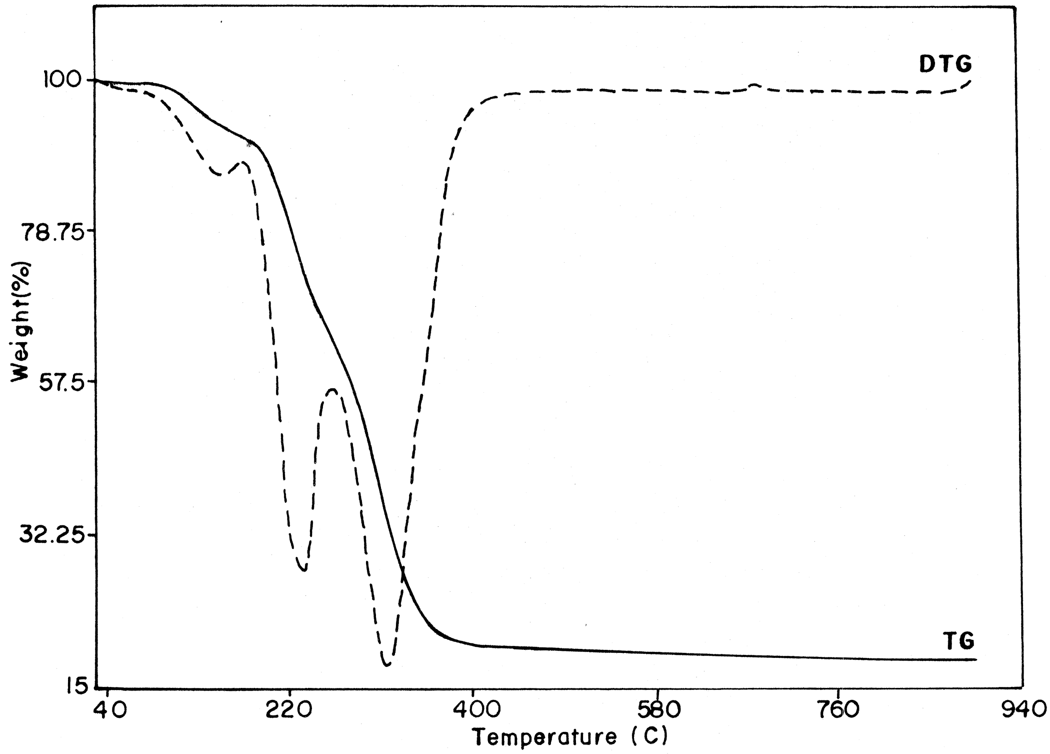

Fig. 3. Thermogravimetric curve obtained of the erbium compound under dynamic nitrogen atmosphere (50 ml $\min^{-1}$) and 5°C $\min^{-1}$ heating rate. (TG)----(DTG).

Fig. 1 shows the absorption spectrum of the neodymium compound at room temperature for the transitions $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{912}$ transitions. The baricenter was calculated by applying Simpson's rule [9] and the value obtained (17 156 cm^{-1}) was compared to that of the standard Nd^{3+}: LaF_3 (17 329 cm^{-1}) [10] in order to calculate the nephelauxetic parameter [11], $\beta = 0.990$. The covalent factor [12], $b^{1/2} = 0.070$, and Sinha's parameter [13] $\delta = 1.01$ were also calculated. They are all indicative of an essentially ionic character of the bonds between the central ion and the ligands.

Fig. 2 contains the emission spectrum of the europium compound. The $^5D_0 \rightarrow {}^7F_0$ band is extremely weak and the several peaks attributed to the $^5D_0 \rightarrow {}^7F_1$ transition are indicative of more than one symmetry site. For the $^5D_0 \rightarrow {}^7F_2$ transition there are also several bands confirming the above statement.

Fig. 3 contains a typical TG curve obtained for the erbium compound. It is possible to detect that approximately two HMPA molecules are lost up to 260°C. After that the remaining molecule leaves and decomposition of the salt occurs with liberation of several gaseous products [14] the final residue is LnOF. This behaviour was observed for all complexes. Table 3 shows the results obtained for the final residues. In some cases small carbonization occurs and some LnF_3 may still be present.

Table 3
Residues obtained in the thermogravimetric analyses (%), final temperature 897°C

Ln	Theor.	Exp.
La	17.1	17.3
Nd	17.6	19.6
Eu	18.2	19.7
Gd	18.6	21.5
Dy	19.0	16.3
Ho	19.3	18.3
Er	19.4	19.2

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