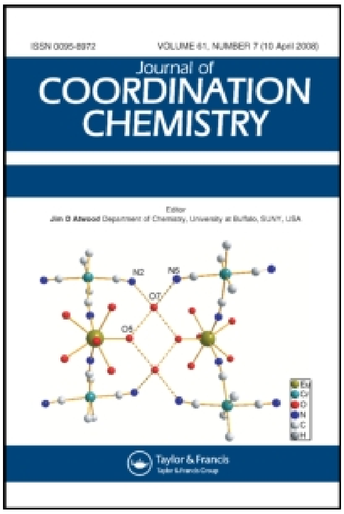

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Dulce M. De A. Melo[a]; Patrícia M. Pimentel[a]; Ótom A. De Oliveira[a]; Zelma R. Da Silva[a]; Robson F. De Farias[b]
[a] Departamento de Química, Universidade Federal do Rio Grande do Norte, Natal, Rio Grande do Norte, Brasil [b] Departamento de Química, Universidade Federal de Roraima, Boa Vista, Roraima, Brasil

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Synthesis, characterization and tg-dsc study of lanthanide trifluoroacetate-2-azacyclononanone compounds

DULCE M. DE A. MELO†, PATRÍCIA M. PIMENTEL†,
ÓTOM A. DE OLIVEIRA†, ZELMA R. DA SILVA† and
ROBSON F. DE FARIAS*‡

†Departamento de Química, Universidade Federal do Rio Grande do Norte,
Cx. Postal 1662, 59078-970, Natal, Rio Grande do Norte, Brasil
‡Departamento de Química, Universidade Federal de Roraima,
Cx. Postal 167, 69301-970, Boa Vista, Roraima, Brasil

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The synthesis, characterization and tg-dsc study of $Ln(tfa)_3 \cdot 3aza$ where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb and Er, tfa = trifluoroacetate and aza = 2-azacyclononanone are reported. The obtained X-ray powder diffraction patterns show that the compounds are divided in two isomorphous groups: La, Pr, Nd and Eu, Sm, Gd, Tb and Er. For all compounds, the thermodegradation under nitrogen gave the respective oxifluorides (LnOF) as the final product. The melting temperature intervals are 105–110°C, 100–112°C, 90–95°C, 79–101°C, 65–70°C, 75–90°C, 64–76°C and 50–65°C for the La, Pr, Nd, Sm, Eu, Gd, Tb and Er compounds, respectively, and it is verified that the lanthanide contraction induces a weaker intermolecular interaction between adjacent molecules in the solid state.

Keywords: Cycloazanonanone; Lanthanides; Thermogravimetry

1. Introduction

Lanthanide complexes with organic ligands are efficient Light Conversion Molecular Devices (LCMD), constituting an important theme in coordination chemistry [1–2]. There are, however, relatively few thermochemical works dealing with this class of compounds, with lanthanide 2,2,6,6-tetramethyl-3,5-heptanedione [3] and lanthanide trifluoromethanesulphonates [4] as examples.

This publication reports the synthesis and characterization of the compounds $Ln(tfa)_3 \cdot 3aza$ where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb and Er, tfa = trifluoroacetate and aza = 2-azacyclononanone. A thermogravimetric and dsc study are also performed.

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*Corresponding author. Email: robsonfarias@pesquisador.cnpq.br

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2. Experimental

All reagents were of analytical grade (Aldrich or Merck) and were employed without further purification.

The lanthanide fluoroacetates were synthesized as follows: The respective oxides were treated with a 6.0 mol dm^{-3} HCl aqueous solution until complete dissolution. Then, urea was added until pH 7.0 and the obtained solution was heated for three days until complete precipitation of the respective basic carbonate, $Ln(OH)CO_3 \cdot xH_2O$. The obtained carbonates were filtered off, washed with distilled water (until the complete removal of the Cl^- ions) and then dried at 80°C in a water bath. The prepared carbonates were suspended in water and then trifluoroacetic acid was added promoting dissolution of the carbonates (a small amount of the carbonate was not dissolved in order to guarantee that all acid was consumed. The solution was then filtered off and the solvent was evaporated in a water bath. The formed crystals (lanthanide fluoroacetates) were ground and stored on calcium chloride.

The compounds with 2-azacyclononanone (aza) were prepared by the reaction between the lanthanide trifluoroacetate and aza, both in ethanolic solutions. The resulting solution was then aged for 20–30 days until precipitation of the compounds. After crystallization, the compounds were washed with carbon tetrachloride and dried under vacuum over calcium chloride.

Carbon, hydrogen and nitrogen elemental analyses were performed in a Perkin-Elmer microanalyser model 240. The lanthanide content was determined through EDTA complexometric titration. Infrared spectra were obtained on a Midac Corporation FTIR apparatus by using KBr discs, in the 4000–400 cm^{-1} range. The melting point measurements were performed on MQAPF-301 equipment from Microquimica. X-ray powder diffraction patterns were obtained for all compounds in Miniflex-Rigaku equipment (Cu Kα radiation).

The thermogravimetric curves were obtained on a Perkin-Elmer TGA-7 instrument. The DSC curves were obtained on DSC-50 Shimadzu equipment. Both groups of curves were obtained under nitrogen with a gas flux of 50 cm^3 min^{-1}and a heating rate of 10°C min^{-1}.

3. Results and discussion

The obtained CHN elemental analysis results are summarized in table 1 and are in good agreement with the proposed formulas: $La(tfa)_3 \cdot aza$, $Pr(tfa)_3 \cdot 3aza$, $Nd(tfa)_3 \cdot 3aza$, $Sm(tfa)_3 \cdot 3aza$, $Eu(tfa)_3 \cdot 3aza$, $Gd(tfa)_3 \cdot 3aza$, $Tb(tfa)_3 \cdot 3aza$ and $Er(tfa)_3 \cdot 3aza$; tffa = trifluoroacetate and aza = azacyclononanone. The compounds can be obtained as powders or crystals. The powders are hygroscopic whereas the crystals are not. The compounds are soluble in ethanol, methanol, acetone, ether and acetonitrile, but exhibit low solubility in benzene, chloroform and carbon tetrachloride.

The melting temperature intervals are 105–110°C, 100–112°C, 90–95°C, 79–101°C, 65–70°C, 75–90°C, 64–76°C and 50–65°C for the La, Pr, Nd, Sm, Eu, Gd, Tb and Er compounds, respectively. When the melting temperature (105°C, 100°C, and so on) are plotted as function of the atomic number, a straight line correlation ($r = -0.97$) is obtained, as shown in figure 1. Such lowering of the strength of the intermolecular forces with the increase of the atomic number (and the consequent decrease of the ionic radii) indicates that the lanthanide contraction induces a weaker intermolecular interaction between adjacent molecules in the solid state.

The infrared data summarized in table 2 are in agreement with coordination through oxygen for aza. It was not possible to assign the νC=O band of aza in the complex (in the "free" ligand it is located at 1647 cm^{-1}) due to the superimposition with the ν_{as}COO$^-$ of tfa. However, the observed positive shifts of the νCN band are also indicative of coordination through oxygen for aza. The presence of three bands in the range 1760–1630 cm^{-1} is indicative of the presence of two or even three coordination features of tfa. The magnitude of $\Delta\nu_1 = \nu_{as}\mathrm{COO}^- - \nu_s\mathrm{COO}^-$ and $\Delta\nu_2 = \nu\mathrm{C{=}O}$–$\nu$C–O, is a criterion to identify the possible coordinative features of acetate groups, such as tfa [5, 6]. The $\Delta\nu_1$ and $\Delta\nu_2$ found for the studied compounds indicate that the tfa anions are behaving as both monodentate and bidentate ligands. The bridge-coordinating feature is also possible.

Table 1. Metal and CHN elemental analysis results for lanthanide fluoroacetate compounds with aza, Ln(tfa)$_3\cdot$3aza. Calculated values are in parenthesis.

Ln	Metal	C	H	N
La	(15.4) 15.2	(39.9) 39.0	(5.0) 4.9	(4.7) 4.6
Pr	(15.6) 15.2	(39.9) 40.0	(5.0) 5.1	(4.6) 4.7
Nd	(15.9) 16.0	(39.7) 40.5	(5.0) 5.2	(4.6) 4.7
Sm	(16.5) 16.1	(39.5) 39.0	(5.0) 5.0	(4.6) 4.5
Eu	(16.6) 17.0	(39.0) 39.0	(4.9) 4.7	(4.6) 4.7
Gd	(17.1) 17.1	(39.2) 38.7	(4.9) 5.0	(4.6) 4.6
Tb	(17.2) 17.2	(39.1) 39.5	(4.9) 5.1	(4.6) 4.8
Er	(18.0) 18.1	(38.7) 38.3	(4.9) 5.0	(4.5) 4.3

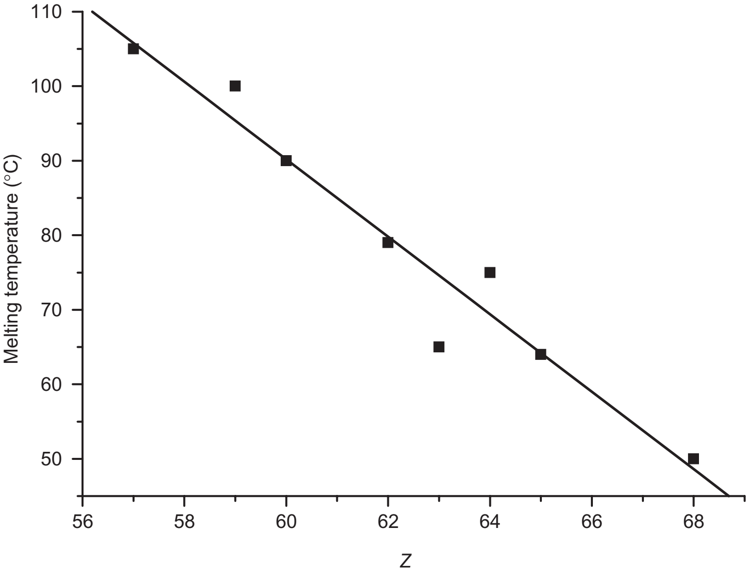

Figure 1. Melting temperatures (°C) as function of the atomic numbers (Z) for Ln(tfa)$_3\cdot$3aza compounds.

The obtained X-ray powder diffraction patterns (not shown) verify that, from the structural point of view, the eight synthesized compounds are divided in two isomorphous groups: La, Pr, Nd and Eu; Sm, Gd, Tb and Er. The radius of the respective cation may play a prominent role is such behavior, since, with the exception of Eu, all the other cations in the series exhibit a cationic radius larger than 100 pm, and with exception of Sm, all the other cations in its series exhibit a radius smaller than 100 pm.

The main thermogravimetric data are summarized in table 3. For all compounds, the first mass loss step is related to release of aza molecules, followed by release of the

Table 2. Infrared data (cm^{-1}) for lanthanide fluoroacetate (tfa) compounds with aza, $Ln(tfa)_3 \cdot 3aza$.

	$\nu C{=}O$	$\nu_{as}COO^- + \nu C{=}O$	$\nu_s COO^-$	$\nu C–O$	$\Delta\nu_2$	$\Delta\nu_1$	$\nu C–N$
aza	–	1647s	–	–	–	–	1287w
tfa	1737vs	1672vs–1621vs	1476m	1453m	284	196–145	–
La	1746vs	1687vs–1633vs	1497m	1453s	293	190–136	1300w
Pr	1751s	1688s–1634vs	1498m	1453s	298	190–136	1302w
Nd	1753s	1685vs–1632vs	1493w	1452m	301	192–139	1300w
Sm	1755s	1685vs–1635vs	1502m	1448s	307	183–133	1298w
Eu	1756m	1687s–1636s	1502m	1453m	303	185–134	1298w
Gd	1760m	1692s–1637vs	1495w	1453m	307	197–142	1300w
Tb	1756s	1685s–1637vs	1502m	1450s	306	183–135	1297w
Er	1761s	1681vs–1630vs	1500w	1448m	313	181–130	1298w

vs = very strong; s = strong; w = weak; m = medium 1287w.
$\Delta\nu_1 = \nu_{as}COO^- - \nu_s COO^-$.
$\Delta\nu_2 = \nu C = O - \nu C–O$.

Table 3. TG data summary for the thermal degradation of $Ln(tfa)_3 \cdot 3aza$ under nitrogen.

Ln	ΔT (°C)	Mass loss (%)	Final residue (%)
La	104–278	33.8	
	278–395	38.2	
	395–897	10.1	18.2
Pr	98–281	35.1	
	281–394	37.1	
	394–897	10.5	18.4
Nd	117–283	33.0	
	283–412	38.6	
	412–897	9.9	18.7
Sm	120–283	31.5	
	283–400	38.2	
	400–897	10.8	19.2
Eu	120–277	29.6	
	277–400	38.6	
	400–987	10.9	19.3
Gd	113–284	34.9	
	284–412	37.4	
	412–897	8.4	19.8
Tb	105–281	34.8	
	281–394	36.8	
	394–897	9.6	19.9
Er	70–280	33.0	
	280–396	37.9	
	396–897	8.6	21.8

Table 4. DSC data summary for thermal degradation of the compounds $Ln(tfa)_3 \cdot 3aza$ under nitrogen.

	Peak I		Peaks II + III		Peak IV	
Ln	ΔT	ΔH	ΔT	ΔH	ΔT	ΔH
La	105–135	33.9	225–335	−130.0	418–470	−27.2
Sm	78–108	25.3	252–327	−100.9	417–443	−15.0
Gd	74–112	36.0	254–344	−119.4	352–452	−19.2
Tb	66–94	37.3	249–342	−128.3	371–464	−28.3
Er	54–83	30.7	265–341	−137.1	400–461	−13.6

$\Delta T = {}^\circ C$,
$\Delta H = kJ\,mol^{-1}$.

remaining aza and tfa. Based on the mass of the final residues, can be concluded that the oxifluorides (LnOF) are formed.

The DSC data are summarized in table 4. For all compounds four peaks are observed in the DSC curves: the first one is endothermic and associated with the melting of the compounds and the beginning of the thermal decomposition process. The other three are exothermic and are associated with the release/thermal degradation of aza and tfa molecules. Since the rupture of the chemical bonds between the lanthanides and aza and tfa molecules will require some energy (endothermic), the resulting exothermic process could be related with the rearrangement of the crystalline structure of the lanthanide fluoroacetate and formation of the LnOF crystalline network.

References

[1] J.-M. Lehn. *Angew. Chem. Int. Ed. Engl.*, **29**, 1304 (1990).

[2] J.-C.G. Buzli. In *Lanthanides Probes in Life, Chemical and Earth Sciences. Theory and Practice*, J.-C.G. Buzli, G.R. Choppin (Eds), Chap. 7, Elsevier, Amsterdam (1989).

[3] L.S. Santos Jr, G.P. Petrucelli, C. Airoldi. *Polyhedron*, **18**, 969 (1999).

[4] D.M.A. Melo, Z.R. da Silva, J.D.G. Fernandes, C.P.F. dos Santos, H.E.B. da Silva, L.B. Zinner. **328**, 183 (1999).

[5] B.S. Manhas, A.K. Trikha. *J. Indian Chem. Soc.*, **59**, 315 (1982).

[6] E. Spinner. *J. Chem. Soc.*, 4218 (1964).