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Synthesis, characterization and thermogravimetric study of the complexes [Eu(12-crown-4)·phen$_2$]·X$_3$ (phen = 1,10-phenanthroline; X = F, Cl, Br, SCN, ClO$_4$ and NO$_3$): Effect of the counter-ion on the thermal degradation profile

Mônica F. Belian[a], Severino Alves Jr.[a], Gilberto F. de Sá[a],
Wagner E. Silva[a], Robson F. de Farias[b,*]

[a] Departamento de Química Fundamental, Universidade Federal de Pernambuco, 50670-901 Recife, Pernambuco, Brazil
[b] Programa de Pós-Graduação em Química, Universidade Federal do Rio Grande do Norte, Cx. Postal 1664,
59078-970 Natal, Rio Grande do Norte, Brazil

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Abstract

The complexes [Eu(12-crown-4)·phen$_2$]·X$_3$ (phen = 1,10-phenanthroline; X = F, Cl, Br, SCN, ClO$_4$ and NO$_3$) were synthesized and characterized by elemental analysis, UV–vis and IR spectroscopy. A thermogravimetric study was performed to evaluate the effect of the counter-ion on the thermal degradation profile of the [Eu(12-crown-4)·phen$_2$]$^{+3}$ complex cation. In general, the 1,10-phenanthroline molecules are the first to be released, showing that the crown ether molecule forms more stable bonds with the +3 cation. The fluorine complex sublimes and thus could be employed as a precursor for preparation of luminescent films.

Keywords: Crown ether; Thermogravimetry; Counter-ion; Europium

1. Introduction

Thermogravimetry is a reliable tool to study the physico-chemical behavior of coordination compounds. There is a very close relation between thermogravimetric, reaction calorimetric and spectroscopic data for coordination compounds [1]. The present work describes the synthesis, characterization and thermogravimetry of [Eu(12-crown-4)·phen$_2$]·X$_3$ (phen = 1,10-phenanthroline; X = F, Cl, Br, SCN, ClO$_4$ and NO$_3$) to evaluate the effect of the anion on the thermal degradation of the complex cation.

2. Experimental

All reagents were of analytical grade (Aldrich) and were employed without further purification. With the exception of EuF$_3$, all europium salts were prepared from the respective oxide: EuX$_3$, were X = Cl, Br, NO$_3$ and ClO$_4$ were prepared by reacting stoichiometric amounts of Eu$_2$O$_3$ and HCl, HBr, HNO$_3$ and HClO$_4$, respectively. The europium content was checked by EDTA titration. The Eu(SCN)$_3$ was prepared by reacting an ethanolic solution of EuCl$_3$ with KSCN. The secondary product (KCl) was removed by filtration and the obtained solution of Eu(SCN)$_3$ was used to prepare the respective crown ether complex.

The complexes were synthesized as follows: 5.0×10^{-4} mol of the europium salt and the same amount of 12-crown-4 were added to a 1:1 (v:v) mixture of acetone/

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[*] Corresponding author. Tel.: +55 95 81118206; fax: +55 95 6213137.
E-mail address: robdefarias@yahoo.com.br (R.F. de Farias).

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ethanol with magnetic stirring. After precipitation of the crown complexes (3 h), 1.0 mmol of 1,10-phenanthroline was added. After evaporation of the solvent, the complex was isolated, washed with cold acetone, and dried under vacuum at room temperature.

All complexes were characterized by CHN elemental analysis (Carlo Erba model EA 1110), melting point (Isothermal 9100), UV (Perkin-Elmer lambda 6, W lamp, 800–340 nm, deuterium lamp, 350–190 nm, 10^{-5} to 10^{-6} mol dm^{-3} in ethanol) and IR spectroscopy (KBr discs, Bruker FTIR, model IF66). Thermogravimetric curves were obtained on a TGA 50/50H Shimadzu under N_2 atmosphere at 10 °C min^{-1}.

3. Results and discussion

The CHN elemental analysis are in good agreement with the proposed formulas, as shown in Table 1. The measured melting points are also summarized in Table 1.

With exception of the fluoride complex, the complexes degrade without melting suggesting that the ionic bonds of the crystal lattice are stronger than the intramolecular bonds.

The crown ether molecule is UV silent, hence the absorption is due to phenanthroline only. All absorptions are of the $\pi \rightarrow \pi^*$ type, and the observed shifts, as well as the inversion of the bands at 203 and 226 nm (comparing free phenanthroline and complexes) agree with coordination of phen to the metal ion.

In all the complexes, negative shifts of the C–O–C (crown ether) and C=N (phenanthroline) IR absorption bands are observed, in agreement with coordination through oxygen and nitrogen, respectively. Despite the fact that a structural study was not performed in this work, taking into account the coordination features of 12-crown-4 and phen, we propose the structure shown in Fig. 1.

The thermogravimetric curves are shown in Figs. 2 and 3. Form the experimental mass loss percentages, as a general behavior, the 1,10-phenathroline molecules are released first. The crown ether molecule apparently forms more stable bonds with the +3 cation.

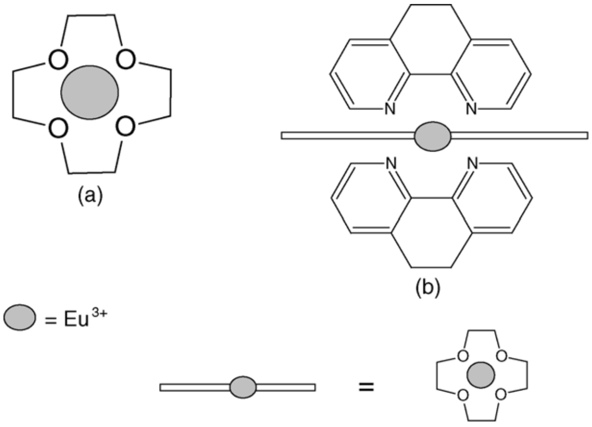

Fig. 1. Schematic representation for the supposed structure of the 12-crown-4/phen prepared complexes. The Eu(III) cation is coordinated to the four O atoms in the crown ether ring, as shown in (a) as well as to four N atoms of two phen molecules, as shown in (b).

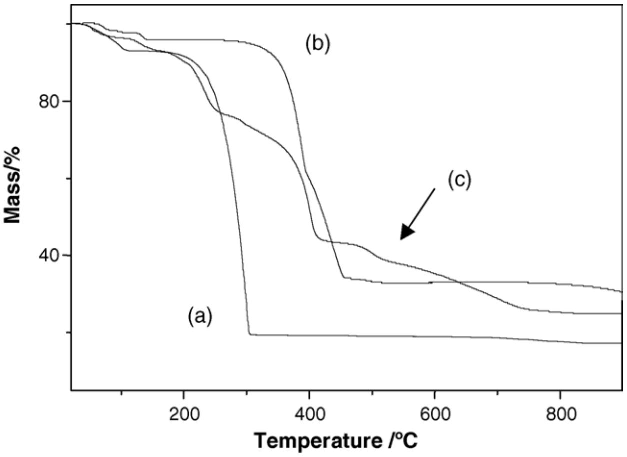

Fig. 2. Thermogravimetric curves for the complexes: (a) [Eu(12-crown-4)·phen$_2$]F$_3$, (b) [Eu(12-crown-4)·phen$_2$]Cl$_3$ and (c) [Eu(12-crown-4)·phen$_2$]Br$_3$.

In the halide complexes, a first mass loss step is associated with the release of physisorbed water molecules. For the fluoride complex, the ligand mass loss corresponds to 73.4%, with a final residue of 26.6%, due to EuF$_3$ (calculated value = 27.8%). This could be employed as a good precursor for the preparation of luminescent films. For the chloride

Table 1
Elemental analysis results (calculated values are between parenthesis) and melting points for the synthesized Eu-(12-crown-4) complexes

Complex	C	H	N	mp (°C)
[Eu(12-crown-4)·phen$_2$]F$_3$	52.3 (52.0)	4.0 (4.2)	8.0 (7.5)	97
[Eu(12-crown-4)·phen$_2$]Cl$_3$	48.2 (48.0)	3.3 (4.0)	7.0 (7.1)	[b]
[Eu(12-crown-4)·phen$_2$]Br$_3$	40.6 (41.0)	3.0 (3.4)	6.6 (6.1)	236[a]
[Eu(12-crown-4)·phen$_2$](ClO$_4$)$_3$	38.6 (38.9)	3.8 (3.3)	6.0 (5.7)	171[a]
[Eu(12-crown-4)·phen$_2$](SCN)$_3$	49.4 (49.0)	3.6 (3.7)	11.9 (11.4)	240[a]
[Eu(12-crown-4)·phen$_2$](NO$_3$)$_3$	44.0 (43.9)	3.7 (3.7)	11.1 (11.2)	259[a]

[a] The complex degrades at the reported temperature.

[b] This complex does not melt, and does not degrade until 300 °C.

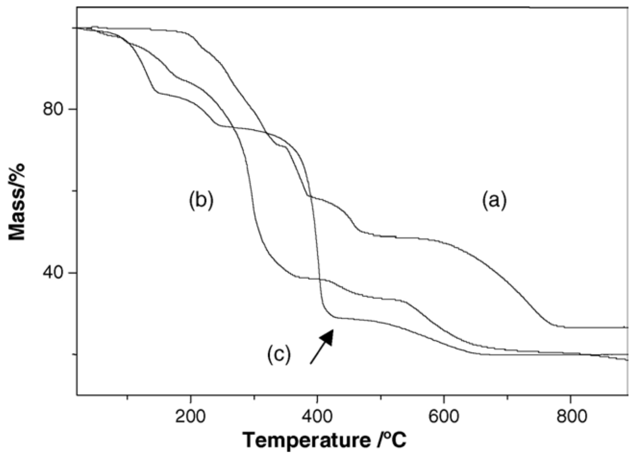

Fig. 3. Thermogravimetric curves for the complexes: (a) [Eu(12-crown-4)·phen$_2$](SCN)$_3$, (b) [Eu(12-crown-4)·phen$_2$](ClO$_4$)$_3$ and (c) [Eu(12-crown-4)·phen$_2$](NO$_3$)$_3$.

complex, a total ligand mass loss of 67.9% is observed. The first ligand mass loss is associated with the release of phenanthroline molecules, and the second one with the release of 12-crown-4. The final residue is 32.2% (calculated value = 32.4% = EuCl$_3$). For the bromide complex, the final residue is 34.2%, due to the formation of europium oxide (calculated value = 36.0%).

The SCN$^-$, ClO$_4$$^-$ and NO$_3$$^-$ complexes release phenanthroline before the crown ether. In these three complexes, the final residue is Eu$_2$O$_3$, within 2–10% of calculated values. The difference between the fluoride and chloride complexes (the F$^-$ complex loses both ligands at 250 °C, whereas the Cl$^-$ complex releases the ligands above 300 °C) is remarkable.

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