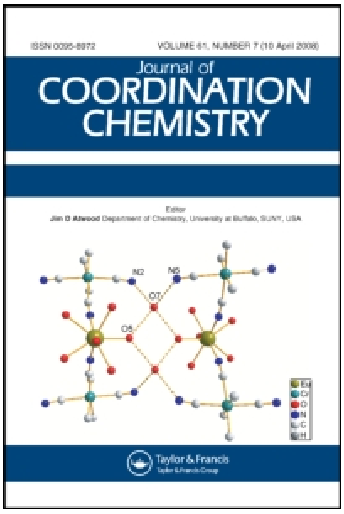

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and thermogravimetric study of Dy and Sm 12-crown-4 bipy, terpy and phen complexes

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To cite this Article De Farias, Robson F. , Belian, Mônica F. , Alves Jr, Severino , De Sá, Gilberto F. , Silva, Wagner E. and Refat, Moamen S.(2007) 'Synthesis, characterization and thermogravimetric study of Dy and Sm 12-crown-4 bipy, terpy and phen complexes', Journal of Coordination Chemistry, 60: 24, 2695 — 2702, First published on: 19 September 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701304384

URL: http://dx.doi.org/10.1080/00958970701304384

Journal of Coordination Chemistry
Vol. 60, No. 24, 15 December 2007, 2695–2702

Synthesis, characterization and thermogravimetric study of Dy and Sm 12-crown-4 bipy, terpy and phen complexes

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(*Received 24 August 2006; revised 27 October 2006; in final form 14 March 2007*)

The synthesis, characterization and thermogravimetric study of $[Sm(12C4)(H_2O)_4]Cl_3$, $[Dy(12C4)(H_2O)_4]Cl_3$, $[Sm(12C4)(bipy)(H_2O)_2]Cl_3$, $[Dy(12C4)(bipy)(H_2O)_2]Cl_3$, $[Sm(12C4)(bipy)(phen)]Cl_3$, $[Dy(12C4)(bipy)(phen)]Cl_3$, $[Sm(12C4)(phen)_2]Cl_3$, $[Dy(12C4)(phen)_2]Cl_3$, $[Sm(12C4)(terpy)(H_2O)]Cl_3$ and $[Dy(12C4)(terpy)(H_2O)]Cl_3$ (12C4 = 12-crown-4; bipy = bipyridine; phen = 1,10-phanathroline; terpy = terpyridine) are reported. All compounds exhibit CN = 8 and four oxygen–lanthanide bonds of the crown ether provide a very stable (from the thermal point of view) chemical environment, since the crown ether molecules are the last organic moiety to be released under heating.

Keywords: Crown ethers; Thermogravimetry; Rare earths

1. Introduction

Crown ethers are promising ligands, due to their polydentate and ring nature, making them possible selective (taking into account their different radius) coordinating agents, as verified in the well known use of crown-5, crown-6 and crown-7 for coordination with alkaline metal cations [1]. They are able to promote the solubility of alkali salts in organic solvents as a result of the large hydrophobic organic ring. The ability to form complexes with alkali metals is affected by the ‘‘crown’’ radius. However, complexes with transition metal cations are not so well explored, with the preparation of compounds with Pd(II) and Pt(II) [2], as well as their use as agents for solvent extraction of trivalent lanthanoids [3] as recent examples.

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970701304384

Thermogravimetry is a reliable tool to study the physico-chemical behavior of coordination compounds since there is a very close relation between thermogravimetric, reaction calorimetric and spectroscopic data for coordination compounds [4]. In a previous study [5] we investigated the effects of the counter ions (F, Cl, Br, SCN, ClO_4 and NO_3) on the thermal degradation profiles of Eu 12-crown-4-1,10-phenanthroline complexes. The present work reports the synthesis, characterization and thermogravimetric study of $[Sm(12C4)(H_2O)_4]Cl_3$, $[Dy(12C4)(H_2O)_4]Cl_3$, $[Sm(12C4)(bipy)(H_2O)_2]Cl_3$, $[Dy(12C4)(bipy)(H_2O)_2]Cl_3$, $[Sm(12C4)(bipy)(phen)]Cl_3$, $[Dy(12C4)(bipy)(phen)]Cl_3$, $[Sm(12C4)(phen)_2]Cl_3$, $[Dy(12C4)(phen)_2]Cl_3$, $[Sm(12C4)(terpy)(H_2O)]Cl_3$ and $[Dy(12C4)(terpy)(H_2O)]Cl_3$ (12C4 = 12-crown-4; bipy = bipyridine; phen = 1,10-phanathroline; terpy = terpyridine).

2. Experimental

All used reagents were analytical grade and employed without further purification. Dy and Sm chlorides were prepared from the respective oxides, by reaction with aqueous HCl.

The complexes were synthesized as follows: 5.0×10^{-4} mol of the dysprosium or samarium salt and the same amount of 12-crown-4 were added to a 1 : 1 (v : v) mixture of acetone/ethanol with magnetic stirring. After precipitation of the crown complexes (3 h) and evaporation of the solvent, the complexes were isolated, washed with cold acetone, and dried under vacuum at room temperature. The 12C4 complexes with bipy, terpy or phen were prepared by reaction of stoichiometric amounts of those molecules with $[Dy(12C4)(H_2O)_4]Cl_3$ or $[Sm(12C4)(H_2O)_4]Cl_3$ under similar conditions. The formulas for all synthesized compounds are shown in table 1.

C, H and N elemental analyses were performed in a Perkin–Elmer 2400 analyzer. Infrared spectra were recorded in a Gengis II FTIR apparatus in the 4000–400 cm^{-1} range, with a resolution of 4 cm^{-1}. All IR spectra were obtained from powders in KBr discs. Thermogravimetric curves were obtained using a Shimadzu TG-50H apparatus under N_2 with a heating rate of 15°C min^{-1}.

Table 1. Elemental analysis results for Dy and Sm 12-crown-4 complexes.

	%C		%H		%N	
Complex	c	e	c	e	c	e
$[Sm(12C4)(H_2O)_4]Cl_3$	19.01	18.51	4.75	4.63	–	–
$[Dy(12C4)(H_2O)_4]Cl_3$	18.57	18.32	4.64	4.61	–	–
$[Sm(12C4)(bipy)(H_2O)_2]Cl_3$	34.57	34.23	4.48	4.32	4.48	4.35
$[Dy(12C4)(bipy)(H_2O)_2]Cl_3$	33.91	33.87	4.39	4.33	4.39	4.14
$[Sm(12C4)(bipy)(phen)]Cl_3$	42.80	42.45	3.80	3.42	6.66	6.50
$[Dy(12C4)(bipy)(phen)]Cl_3$	42.19	41.95	3.75	3.69	6.56	6.47
$[Sm(12C4)(phen)_2]Cl_3$	44.38	43.99	3.70	3.57	6.47	6.39
$[Dy(12C4)(phen)_2]Cl_3$	43.76	43.65	3.65	3.64	6.38	6.27
$[Sm(12C4)(terpy)(H_2O)]Cl_3$	36.52	36.31	3.84	3.76	5.56	5.49
$[Dy(12C4)(terpy)(H_2O)]Cl_3$	35.94	35.64	3.78	3.68	5.47	5.37

c = calculated, e = experimental.

3. Results and discussion

The obtained CHN elemental analysis results are summarized in table 1 and are in good agreement with the proposed formulas. For all synthesized complexes, negative shifts of the C–O–C (crown ether) band are verified (FTIR spectra), indicating coordination through oxygen. For complexes with bipy, terpy or phen negative shifts of the C$=$N band is observed, in agreement with coordination through nitrogen.

Despite the fact that a structural study was nor performed in this work, taking into account the coordination features of 12-crown-4 and phen, it is possible to propose,

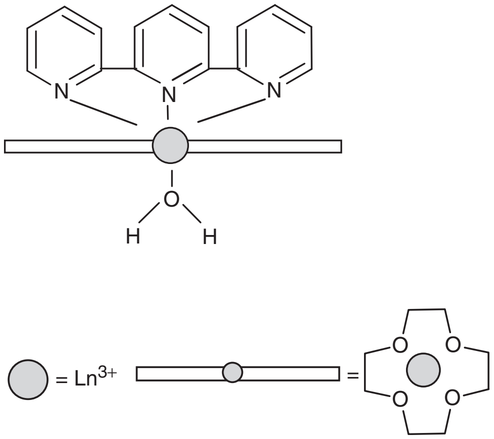

Figure 1. Schematic structure (out of scale) for the complex cations [Ln(12C4)(terpy)(H_2O)]; Ln = Dy or Sm.

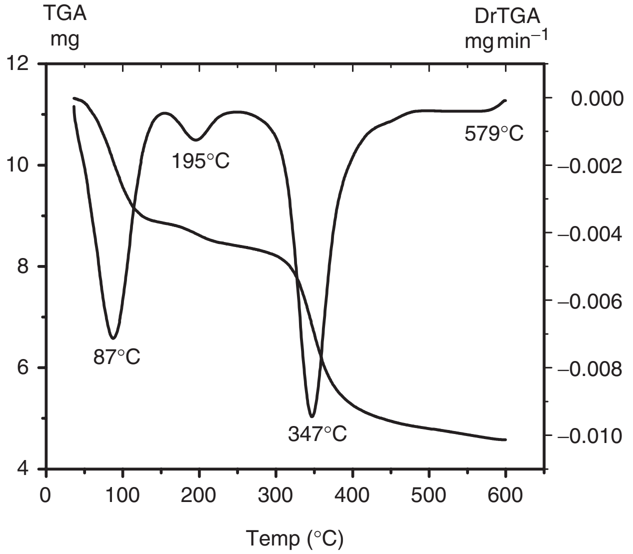

Figure 2. Thermogravimetric and derivative curve for [Sm(12C4)(H_2O)$_4$]Cl_3.

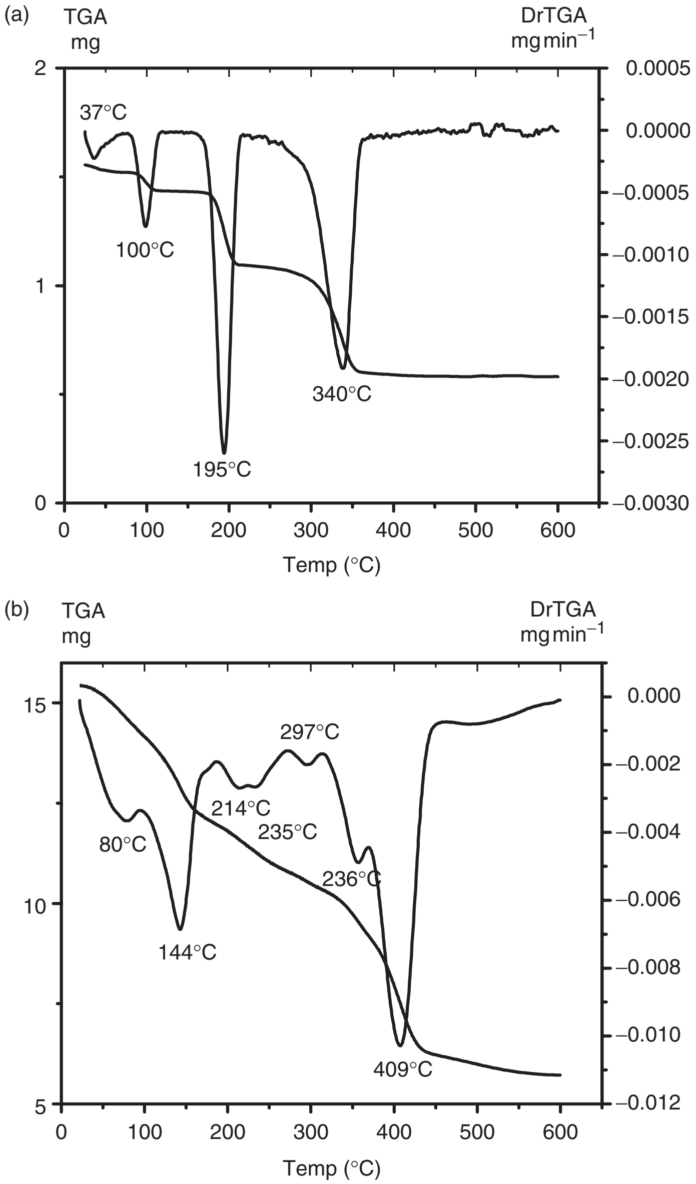

Figure 3. Thermogravimetric and derivative curves for $[Sm(12C4)(bipy)(H_2O)_2]Cl3$ (a) and $[Dy(12C4)(bipy)(H_2O)_2]Cl_3$ (b).

as previously suggested for Eu, Tb and Gd complexes [6] the structure schematically shown in figure 1.

The obtained thermogravimetric curves are shown in figures 2–6. The TG curve for $[Dy(12C4)(H_2O)_4]Cl_3$ was not obtained, since it is very hygroscopic. The complexes $[Ln(12C4)(bipy)(phen)]Cl_3$ and $Ln(12C4)(phen)_2]Cl_3$ are the only ones with no water molecules in the coordination sphere, despite the fact that all complexes exhibit $CN = 8$. This is in contrast with the observed behavior for 15C5 compounds with Eu, Tb and

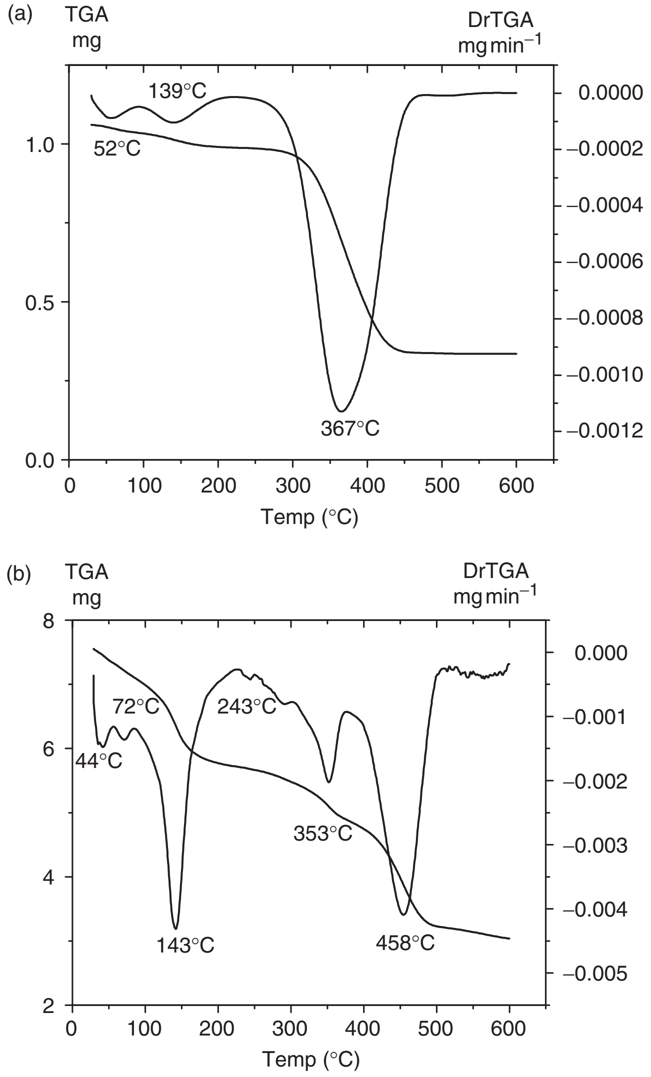

Figure 4. Thermogravimetric and derivative curves for [Sm(12C4)(bipy((phen)]Cl_3 (a) and [Dy(12C4)(bipy)(phen)]Cl_3 (b).

Gd [6] for which the [Ln(15C5)(terpy)]Cl_3 (all of them with CN = 8) are anhydrous and only complexes with 12C4, [Ln(12C4)(terpy)(H_2O)]Cl_3 (all of them with CN = 8) are hydrated. Such observations suggest that not only the CN value but also the number of oxygen atoms on the crown ether ring is important to the presence of water molecules in the coordination sphere. Since the ionic radius of Sm (100 pm) and Dy (91 pm) are, respectively, larger and shorter than the ionic radius of Eu (98 pm), Gd (97 pm) and Tb (93 pm), the cation radius apparently is not responsible for such phenomena.

For all hydrated compounds, the first mass loss step is associated with release of water molecules (the minor initial mass loss steps observed on figures 3(a), 4, 5(a) and 6(a) are due to the release of physisorbed water molecules and not the constitutional

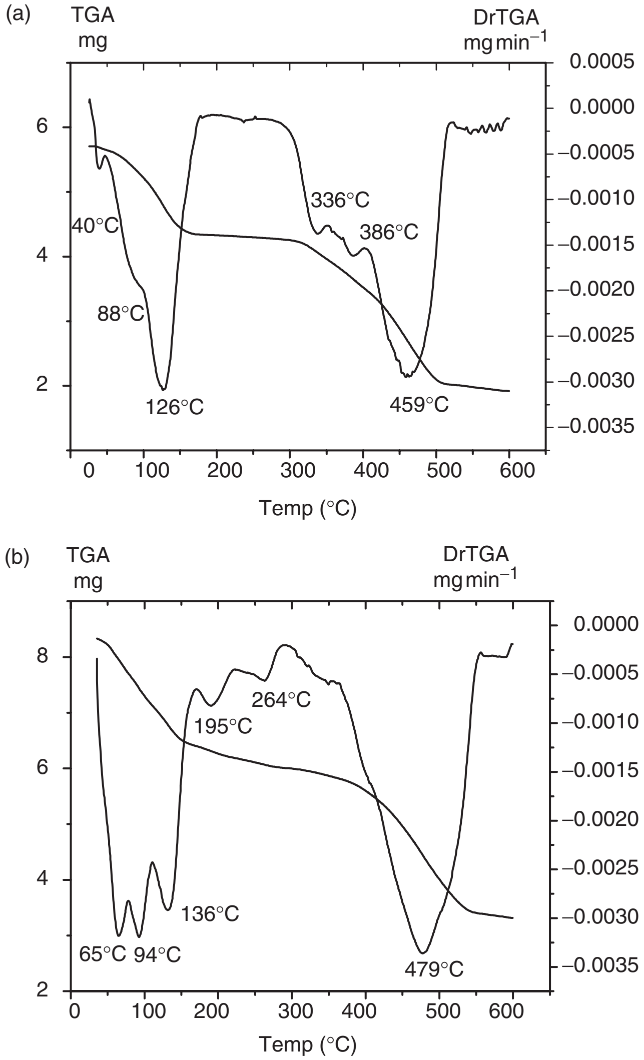

Figure 5. Thermogravimetric and derivative curves for [Sm(12C4)(phen)$_2$]Cl$_3$ (a) and [Dy(12C4)(phen)$_2$]Cl$_3$ (b).

water molecules. As can be observed in figures 3 and 6, the release of water occurs at lower temperatures for Sm compounds. This fact suggests a stronger interaction of water with Dy, in agreement with lower ionic radius of Dy, giving it a larger charge to radius ratio and making it a harder acid. For [Ln(12C4)(bipy)(H$_2$O)$_2$]Cl$_3$ complexes the temperatures for release of water (100°C for Sm and 144°C for Dy) are higher than the temperatures of water release for [Ln(12C4) $\cdot$ terpy $\cdot$ H$_2$O)]3Cl complexes (59°C for Sm and 73°C for Dy) indicating stronger Ln–H$_2$O interaction for the first pair of complexes, in agreement with the fact that terpy has three nitrogen atoms acting

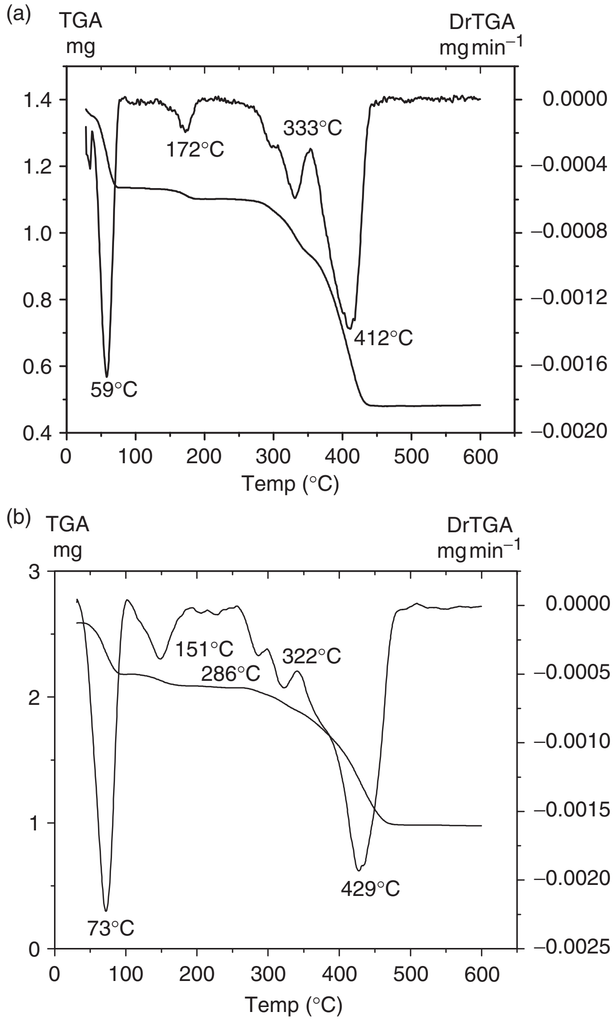

Figure 6. Thermogravimetric and derivative curves for [Sm(12C4)(terpy)(H_2O)]Cl_3 (a) and [Dy(12C4)(terpy)(H_2O)]Cl_3 (b).

as coordination sites and bipy has only two. For bipy complexes the electron affinity of the metal cation is higher than for terpy complexes making them “complete” the coordination number 8 by taking two water molecules and promoting electron neutrality by taking a larger amount of the oxygen electron density, making stronger bonds with water molecules.

After the release of the water molecules, the next mass losses are associated with the release of bipy, terpy or phen molecules, and finally the release of the 12C4 molecule, showing that four oxygen-lanthanide bonds of the crown ring provide a very stable (from the thermal point of view) chemical environment.

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