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THERMOGRAVIMETRIC STUDIES ON LANTHANIDE COMPLEXES OF NEW DERIVATIVES OF 1,5-DIARYL-3-ACETYLFORMAZAN

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ABSTRACT

Solid complexes of two new derivatives of 1,5-diaryl-3-acetylformazan with lanthanide metal ions were prepared and characterized by elemental and thermogravimetric analyses. The suggested formula of the complexes is $ML_2(H_2O)_x \cdot yH_2O$ where L = formazan, $x = 0–2$, $y = 1–4$ and M = trivalent lanthanide ion. Information about the water of hydration, the coordination chemistry and the thermal stability of these complexes was obtained. A general mechanism for the thermal decomposition of the complexes is suggested. A coordination number of ten is proposed for the lanthanide ions in these complexes which decreases from La to Lu due to the lanthanide contraction.

INTRODUCTION

Formazans form a distinct class of organic compounds with characteristic properties. Such compounds have received great attention due to their use in analytical chemistry, biology, agriculture and industry [1–9]. The use of formazans as ligands or metal extractants has received little attention particularly with the lanthanide ions.

In this study, the thermogravimetric (TG) analysis of the solid lanthanide complexes with 1,5-bis(*o*-carboxyphenyl)-3-acetyl-formazan (**I**) and 1-(*o*-carboxyphenyl)-5-(*o*-hydroxyphenyl)-3-acetylformazan (**II**) was undertaken in order to throw some light on the coordination chemistry of the lanthanides, to obtain some information about the thermal stability of these new complexes and to suggest a general scheme for their thermal decomposition.

Since the water content is variable in the complexes under investigation, several specific stoichiometries may be obtained. This problem deserves special emphasis by considering the location of the water molecules in the complexes. It is not possible to distinguish between the hydrated and coordinated H_2O molecules from the spectral data.

EXPERIMENTAL

All chemicals and solvents used were pure BDH products. 1,5-Bis(*o*-carboxyphenyl)-3-acetylformazan (**I**) was prepared by coupling of *o*-carboxybenzenediazonium chloride with acetylacetone in a molar ratio of 2 : 1 in an alkaline medium of sodium hydroxide [10]. The asymmetric formazan (**II**) was prepared by coupling of *o*-hydroxybenzenediazonium chloride with acetylacetone(2-carboxyphenyl)hydrazone in a molar ratio of 1 : 1 in an alkaline medium of sodium hydroxide [10]. The red formazans produced were then washed with doubly distilled water and recrystallized from the appropriate solvents.

Preparation and analysis of the lanthanide complexes

Lanthanide perchlorate (0.3–0.5 g) was dissolved in about 10 ml of boiling ethanol. It was then added slowly with stirring to about 70 ml of

TABLE 1

Analytical data of lanthanide complexes with formazans **I** and **II**

Ligand H_2L	Metal ion	Tentative formula	C (%)		H (%)		M (%)	
			Calc.	Found	Calc.	Found	Calc.	Found
I	Y	$YL(HL)2H_2O$	49.16	49.30	3.52	4.00	10.71	10.20
	La	$LaL(HL)4H_2O$	44.55	44.30	3.63	3.40	15.17	15.30
	Ce	$CeL(HL)2H_2O$	46.31	47.00	3.32	3.50	15.90	16.00
	Pr	$PrL(HL)4H_2O$	44.47	44.70	3.62	3.70	15.35	15.10
	Nd	$NdL(HL)3H_2O$	45.17	45.30	3.46	3.80	15.97	15.70
	Sm	$SmL(HL)3H_2O$	44.86	44.80	3.44	3.80	16.54	16.10
	Gd	$GdL(HL)6H_2O$	42.05	41.50	3.84	3.60	16.21	16.60
	Dy	$DyL(HL)6H_2O$	41.82	41.80	3.79	3.40	16.66	17.10
	Ho	$HoL(HL)4H_2O$	43.34	43.30	3.33	4.00	17.47	17.80
	Er	$ErL(HL)2H_2O$	44.92	44.70	3.22	3.90	18.41	18.00
	Tm	$TmL(HL)2H_2O$	44.84	44.60	3.21	3.80	18.51	18.10
	Yb	$YbL(HL)4H_2O$	42.95	42.90	3.47	3.70	18.21	18.50
	Lu	$LuL(HL)2H_2O$	44.54	44.60	3.20	4.00	19.10	18.80
II	Y	YL(HL)	52.04	52.50	3.42	3.60	12.05	11.40
	La	LaL(HL)	48.74	48.70	3.20	3.20	17.63	18.40
	Pr	$PrL(HL)H_2O$	47.53	47.60	3.37	4.00	17.44	16.40
	Nd	$NdL(HL)2H_2O$	46.31	46.60	3.53	3.90	17.39	17.70
	Sm	$SmL(HL)H_2O$	46.97	46.60	3.32	3.30	18.40	18.80
	Gd	$GdL(HL)H_2O$	46.58	46.10	3.30	3.30	19.08	19.50
	Ho	$HoL(HL)H_2O$	46.16	46.20	3.27	3.40	19.82	19.40
	Er	$ErL(HL)H_2O$	46.03	46.40	3.26	3.40	20.05	19.00
	Tm	TmL(HL)	46.94	46.90	3.08	3.60	20.65	19.50
	Yb	YbL(HL)	46.71	47.40	3.07	3.50	21.05	19.80
	Lu	LuL(HL)	46.61	47.50	3.06	3.60	21.23	20.10

boiling ethanol containing the corresponding formazan in a molar ratio of 1 : 2 (M : L) to produce the required complex. The reaction mixture was stirred on a water bath for 30 min with the addition of concentrated ammonia solution until pH 7–8 was reached. The product was left overnight, filtered and then washed several times with cold ethanol until the filtrate became colourless. The 1 : 1 complexes could not be isolated in the solid state.

Elemental analysis of carbon, hydrogen and metal in the formazans and their complexes was performed in the microanalytical centre of Cairo University. The metal content of the complexes was determined after decomposition of the complex using the method described by Macdonald and Sirichanya [11]. The results are given in Table 1.

Thermogravimetric analysis of the lanthanide–formazan complexes was carried out using a Du Pont 1090 thermal analyser. Weight losses of 10–25 mg were measured from ambient temperature up to 600–700 ° C at a heating rate of $10\,^{\circ}\mathrm{C\ min}^{-1}$.

RESULTS AND DISCUSSION

Formulation of the solid complexes

The formulation of the complexes as hydrated 1 : 2 species gives good agreement with the carbon, hydrogen and metal analyses (Table 1). The complex formation reaction is considered to proceed as

$$M(ClO_4)_3 + 2H_2L \rightarrow [ML(HL)] + 3HClO_4$$

The analytical results show that these complexes have the general formula $[ML(HL)(H_2O)_n] \cdot xH_2O$, where M = trivalent lanthanide and yttrium metal ions, L = deprotonated formazan, $n = 0$–2 and $x = 1$–4. According to this formula the lanthanide metal ion is expected to have a coordination number of 8–10 if the formazans **I** and **II** are considered to be tetradentate ligands.

TG of the solid complexes

The thermograms of the samarium and praseodymium complexes (Fig. 1) are considered as representatives for the investigation. The thermal stability of the lanthanide–formazan complexes (Table 2) is slightly higher than that reported for the lanthanide carboxylates [12]. This similarity in thermal stability indicates that the donor nitrogens of the formazans have a slight effect on the thermal stability of the lanthanide complexes. Some complexes show an additional inflection in the temperature range 350–450 ° C. Such inflection may be attributed to the formation of an unstable intermediate product (e.g. 1 : 1 complex, aryl-carboxylate, carbonate, etc.). Accordingly,

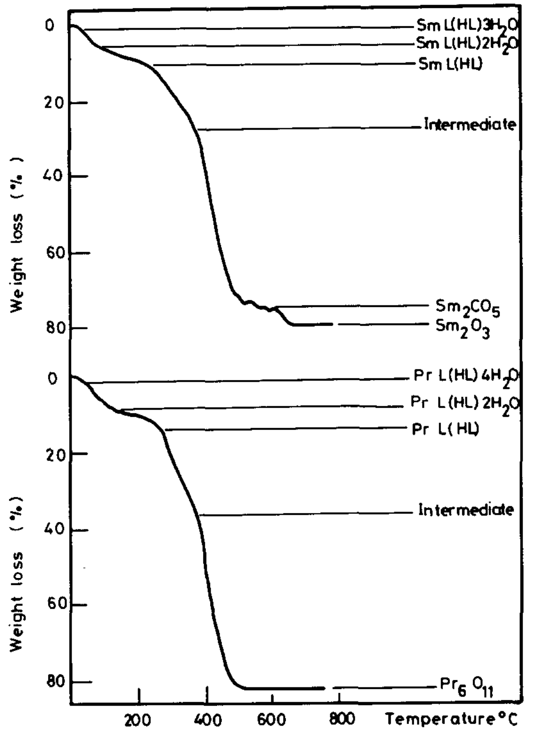

Fig. 1. TG curves of formazan I complexes with Sm(III) and Pr(III) ions.

the final stage at 450–650 °C includes the conversion of such intermediates to the stoichiometric oxide M_2O_3 or to the non-stoichiometric oxide Pr_6O_{11} as end product. The small inflection observed near 550 °C is attributed to the formation of M_2CO_5 (oxycarbonate) in a very short stage before oxide formation. The formulation of this product as M_2CO_5 gives acceptable agreement with the observed percentage on the curve at this inflection. The product M_2CO_5 has previously been observed at the same temperature during the decomposition of lanthanide glutarates and oxyglutarates [13].

Based on the above observations, the following scheme of thermal decomposition may be proposed for the lanthanide–formazan complexes

$$\text{Solid complex} \xrightarrow{\text{drying}} \text{dry complex} \tag{1}$$

$$[ML(HL)(H_2O)_n]\cdot xH_2O \xrightarrow{\text{dehydration}} [ML(HL)(H_2O)_n] \tag{2}$$

$$[ML(HL)(H_2O)_n] \xrightarrow{\text{decoordination}} [ML(HL)] \tag{3}$$

$$\left.\begin{aligned} &[ML(HL)] \xrightarrow{\text{partial decomposition}} \text{intermediate} \\ &\text{Intermediate} \xrightarrow{\text{partial decomposition}} M_2CO_5 \\ &M_2CO_5 \xrightarrow{\text{final decomposition}} M_2O_3 \end{aligned}\right\} \tag{4}$$

TABLE 2

TG results of the lanthanide complexes with formazan I

Metal ion	Suggested formula	Drying stage (°C)	Dehydration stage			Decoordination of water			Start of decom-position (°C)	Oxide formation		
			Temp. range (°C)	H_2O loss (%)		Temp. range (°C)	H_2O loss (%)			Temp. (°C)	Oxide (%)	
				Calc.	Found		Calc.	Found			Calc.	Found
La	$LaL(HL)2H_2O\cdot 2H_2O$	25–80	80–125	3.93	4.0	125–280	3.93	4.0	280	600	17.8(La_2O_3)	18.0
Ce	$CeL(HL)2H_2O$	25–85	85–140	2.04	2.0	140–270	2.04	2.0	270	550	19.5(CeO_2)	19.2
Pr	$PrL(HL)2H_2O\cdot 2H_2O$	25–70	70–125	3.92	4.2	125–265	3.92	4.2	265	550	18.5(Pr_6O_{11})	18.0
Sm	$SmL(HL)2H_2O\cdot H_2O$	25–80	80–120	1.98	2.0	120–250	3.96	4.0	250	675	19.5(Sm_2O_3)	20.0
Dy	$DyL(HL)2H_2O\cdot 4H_2O$	25–70	70–140	7.3	7.2	140–250	3.7	4.0	250	650	19.1(Dy_2O_3)	19.8
Ho	$HoL(HL)H_2O\cdot 3H_2O$	25–70	70–170	5.73	5.4	170–230	1.91	2.0	230	650	20.1(Ho_2O_3)	20.0
Er	$ErL(HL)H_2O\cdot H_2O$	25–75	75–120	2.0	2.4	120–200	2.0	2.4	200	675	21.1(Er_2O_3)	21.0
Y	$YL(HL)H_2O\cdot H_2O$	25–90	90–125	2.17	2.4	125–210	2.17	2.4	210	650	13.6(Y_2O_3)	13.6

Looking at Fig. 1, Table 2 and the scheme, some trends and conclusions may be drawn.

(1) The decomposition of cerium and praseodymium complexes shows no inflection at 500–600 °C indicating that M_2CO_5 is not formed in this exceptional case due to the oxidation of trivalent Ce and Pr ions [14]. Accordingly, the complexes can be classified into the following three groups: group I, complexes of Ce and Pr; group II, complexes of La and Sm; group III, complexes of Dy, Ho, Er and Y. The TG curves of the first group show no inflections corresponding to the M_2CO_5 intermediate. The complexes of the other groups are decomposed to M_2O_3 via M_2CO_5 as indicated from the inflections at 550 °C. Such inflections are more horizontal in the second group, indicating that M_2CO_5 is more stable than in the third group.

(2) On going from La to Er, as the ionic radii decrease, the temperature of decomposition decreases gradually from 280 to 200 °C. The same finding has been reported by Nabar and Barave [15], suggesting a decrease in the thermal stability of the lanthanide–formazan complexes from lanthanum to erbium.

(3) As a conclusion, the real coordination number of the lanthanide metal ions is likely to be ten in these complexes if the formazans **I** and **II** are considered to be tetradentate ligands. However, other apparent coordination numbers cannot be excluded. It is also interesting to note that the complexes of yttrium, holmium and erbium (of relatively small ionic radii) have a coordination number of nine (two tetradentate formazans + H_2O). This decrease in coordination number from ten to nine with decreasing ionic radii may illustrate, once more, the effect of the "lanthanide contraction" on the number of ligands around the tripositive lanthanide metal ions. This finding indicates that the coordination sphere of these metal ions decreases on going from the lighter to the heavier lanthanides, which is in good agreement with previously reported findings [16,17].

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