Thermogravimetric Studies of Some Lanthanide Complexes of Curcumin I

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***Abstract*— Thermograms of curcumin I and its lanthanide complexes with Pr(III), Nd(III), Sm(III), Gd(III), Er(III) and Tb(IV) ions were studied. The results confirmed $[LnL_2(NO_3)(H_2O)_2]$ stoichiometry for all the complexes except for the Tb(IV) complex which conforms to $[TbL_2(NO_3)_2(H_2O)_2]$ stoichiometry.**

***Keywords*— Curcumin I; 1,3-Diketones; Lanthanide complexes; Thermograms and TG analysis.**

I. INTRODUCTION

Thermogravimetric studies of metal complexes provide valuable information regarding the thermal stability, volatility, number of ligands and the nature of bonding in a mixed ligand complex [1]-[4]. Several thermogravimetric investigations on metal complexes of 1,3-diketones have been reported in view of their importance as volatile complexes in gas chromatographic studies [5], [6]. The influence of the factors like substituent on the dicarbonyl group, the nature of the metal ion used and the composition of the complex have been well explored by various investigators and yielded several interesting results [7]-[9]. Many anhydrous lanthanide chelates of 1,3-diketones are volatile at moderate temperatures (100-200^{o}C) [10]. Thermograms of such chelates show smooth curve that approach 100% weight loss. It has been observed that as the radius of the Ln(III) ion decreases, the volatility of the chelates increases [11]. Hydrated lanthanide 1,3-diketones generally decrease the volatility and thermal stability, and decomposition of the chelates occur after losing the water molecules [12], [13]. In continuation of our studies on the structural characterisation of unsaturated 1,3-diketones and their lanthanide complexes [14]-[17], we here report the thermogravimetric analysis of a typical unsaturated 1,3-diketone (curcumin I) and its lanthanide complexes with Pr(III), Nd(III), Sm(III), Gd(III), Er(III) and Tb(IV) ions.

II. EXPERIMENTAL

Materials and Methods

The thermograms were recorded on a Mettler Toledo STARe thermal analysis system (TGA/SDTA 851e) in N_2 atmosphere at a flow rate of 80 mL/minute.

The curcumin I and its lanthanide complexes were synthesized by the methods reported [14]-[19].

III. RESULTS AND DISCUSSION

The observed thermogravimetric data (TABLE I) of the lanthanide complexes are in conformity with Fig. 1 as reported earlier, based on analytical and spectral methods [14]-[17]. The TG curves of curcumin I and its lanthanide chelates are given in Fig. 2.

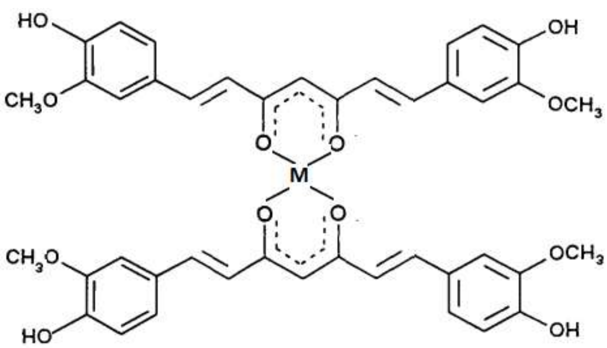

Fig. 1. Structure of the lanthanide complexes of curcumin I; M = Pr(III), Nd(III), Sm(III), Gd(III), Er(III) and Tb(IV); The structure also contains two coordinated water molecules and one bidentate nitrate ion [Tb(IV) complex contains two bidentate nitrate ions].

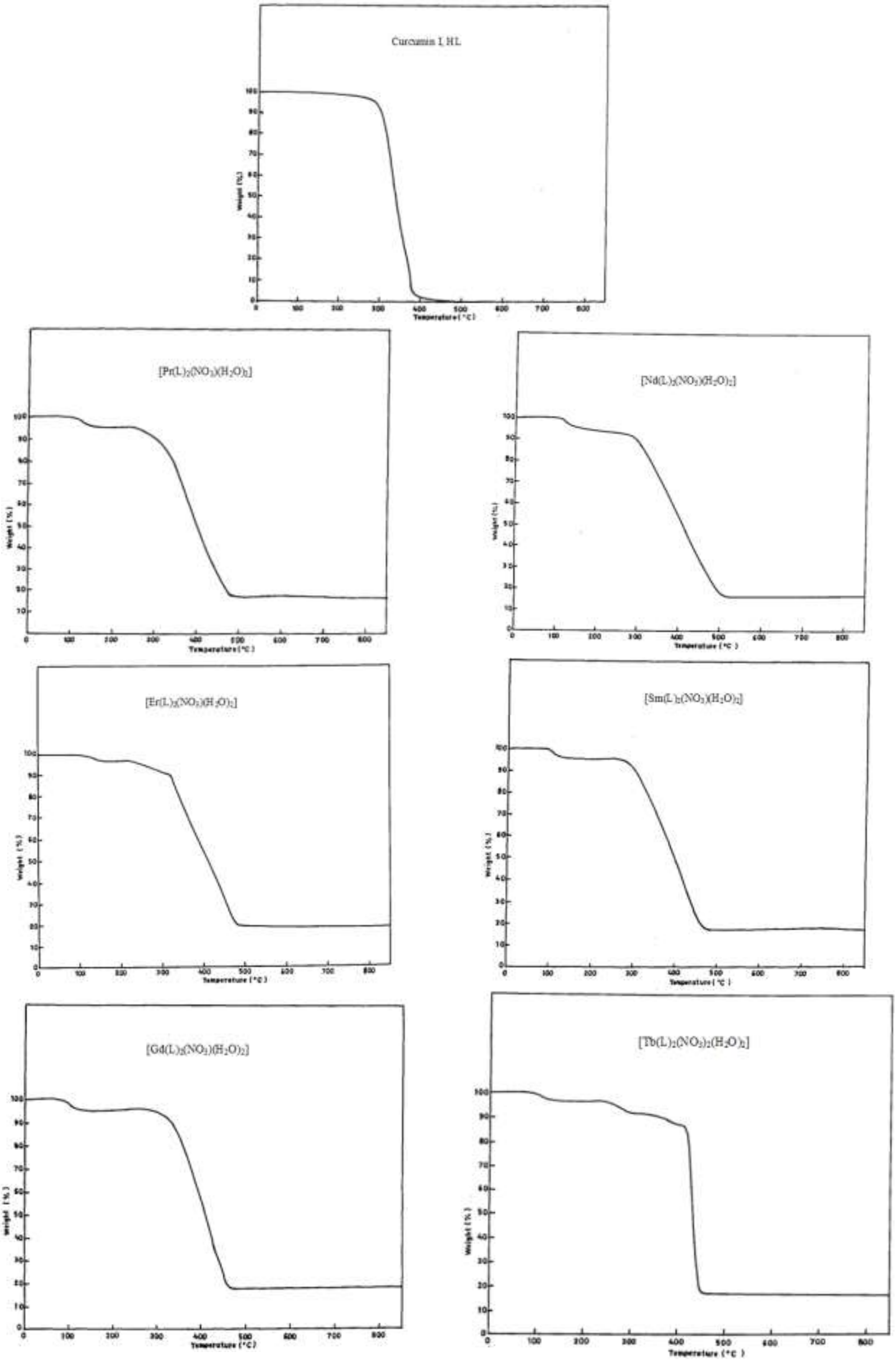

Fig. 2. Thermograms of curcumin I and its lanthanide complexes

TABLE I
THERMAL DECOMPOSITION OF CURCUMIN I AND ITS LANTHANIDE COMPLEXES

Compound (Molecular mass)	Temperature ranges in TG (in ^{0}C)	Mass loss %		Pyrolysis %	Final product
		TG	Theoretical		
Curcumin I, HL (368)	289-390	100	100	100	-
$[Pr(L)_2(NO_3)(H_2O)_2]$ (972.91)	100-150 240-390 300-480	3.4 4.9 75	3.60 4.89 75.44	83.33	Pr_2O_3
$[Nd(L)_2(NO_3)(H_2O)_2]$ (976.24)	100-150 240-280 290-500	3.6 4.89 75	3.6 4.9 73.45	81.85	Nd_2O_3
$[Sm(L)_2(NO_3)(H_2O)_2]$ (982.36)	100-130 220-280 290-460	3.8 4.8 74	3.66 4.9 74.72	83.28	Sm_2O_3
$[Gd(L)_2(NO_3)(H_2O)_2]$ (989.25)	80-120 260-320 320-480	3.7 5 73	3.64 4.9 74.2	82.74	Gd_2O_3
$[Er(L)_2(NO_3)(H_2O)_2]$ (999.26)	100-140 220-300 320-480	3.6 4.7 72	3.6 4.8 73.45	81.85	Er_2O_3
$[Tb(L)_2(NO_3)_2(H_2O)_2]$ (1052.93)	80-120 240-300 325-410 420-500	3.4 4.5 4.7 70	3.5 4.6 4.9 69.71	82.71	Tb_2O_3

The first stage in all thermograms corresponds to the loss of water molecules below 150°C. The observed weight-loss at this stage agrees with the presence of two coordinated water molecules. The weight loss in subsequent stages corresponds to the loss of NO_2 from the complexes followed by the decomposition of the curcumin ligand moiety and formation of Ln_2O_3.

In the thermogram of the Tb(IV) complex, the different well defined stages correspond to the loss of two nitrate groups and two curcumin I moieties.

Although lanthanide chelates of 1,3-diketones are volatile at moderate temperatures, no such behaviour is observed in the lanthanide chelates of curcumin I, probably due to the bulkiness of the ligands and mixed ligand nature of the complexes as in Fig. 1.

IV. CONCLUSIONS

The structure of the complexes of curcumin I with various lanthanide ions [Pr(III), Nd(III), Sm(III), Gd(III), Er(III) and Tb(IV)] has been confirmed by studying their thermal decomposition pattern using TG analysis. The studies unambiguously confirm the proposed $[LnL_2(NO_3)(H_2O)_2]$ stoichiometry of all the complexes except for the Tb(IV) complex which fits into $[TbL_2(NO_3)_2(H_2O)_2]$ stoichiometry. Although lanthanide chelates of 1,3-diketones are volatile at moderate temperatures, no such behaviour is observed in the lanthanide chelates of curcumin I. This may be due to the bulkiness of the ligand moieties and mixed ligand nature of the complexes.

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