

FORMATION AND DISSOCIATION OF LANTHANUM COMPLEXES OF NAPHTHOATE WITH HYDRAZINE

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Abstract— Metal Complexes of Pr (III), Gd(III) and Sm (III) with substituted naphthoic acid and hydrazine ligand were prepared. Thermal behavior (TGA/DTA) of the complexes was studied and kinetic parameter was determined by Coats-Redfern method. **The TG and DTA data indicated that all complexes are thermo stable up to 91.9 K.** The data from thermo gravimetric analysis clearly indicates that decomposition of the complexes proceeds in two or three steps. The decomposition of all the complexes ended with the metal oxide. The tentative mechanism for the thermal decomposition has been proposed.

Keywords— *Coats-Redfern; Kinetics; Lanthanum; Decomposition; Thermo gravimetric*

I. INTRODUCTION

Co-ordination chemistry of lanthanides is one of the more active research fields in inorganic chemistry¹⁻⁴. Lanthanides and actinides ion generally present a high coordination number and the type of polyhedron obtained influences the nature of the coordinating ligands.

The hexagonal structure phase of La₂O₃ is stable up to 2050 °C. It is an important component of automobile exhaust gas conversion and it is a catalyst support in the formation of gas conversion catalyst [3]. The interest in paramagnetic and radioactive metal ions is largely driven by advances in magnetic resonance imaging (MRI) contrast agents (mostly Gd³⁺ complexes), nuclear medicine diagnostic agents and therapeutic radiopharmaceuticals.⁴

Thermogravimetry is the one of the oldest method to provide the information about the sample composition, thermal stability as well as the kinetic data relating the chemical changes occur on heating [2]. In the present work, we studied the thermogravimetric analysis and the kinetics of the thermal decomposition of the naphthoate complexes of lanthanum with hydrazine.

II. EXPERIMENTAL

Preparation of [Pr(N₂H₄){1&2-C₁₀H₇(COO)}₃].2H₂O & [Pr(N₂H₄)₂{C₁₀H₆(1&2-O)(2&1-COO)}_{1.5}].nH₂O where n = 0 & 3

Praseodymium oxide (0.325g, 1mmol) was dissolved in a minimum quantity of 1:1 HNO₃, evaporated to eliminate excess of acid, and dissolved in 20 mL of water. This was added slowly to a

Special Issue on Proceedings of International Conference on Newer Trends and Innovation in Nanotechnology, Materials Science, Science and Technology March 2021. International Journal of Aquatic Science, Vol 12, Issue freshly prepared aqueous solution (60 mL) of the ligand containing naphthoic and hydroxy naphthoic acid (0.188 g, 1 mmol) and hydrazine hydrate (0.2 g, 4 mmol) at 70 °C, stirring the reaction mixture at pH 6. Immediately turbidity developed which turned out to be micro-crystalline solid. Crystalline product obtained was washed with water, alcohol and then with ether and dried in a desiccators over anhydrous CaCl₂. A similar procedure was adopted for obtaining the other lanthanides with the molar ratio Metal: Acid: Base = 1:1:4.

III. RESULT AND DISCUSSION

The elemental analysis, Thermal analysis, magnetic moments, infrared and electronic and spectra show that the five complexes have the formulae: $[\text{Pr}(\text{N}_2\text{H}_4)(1\text{-C}_{10}\text{H}_7\text{COO})_3] \cdot 2\text{H}_2\text{O}$, $[\text{Pr}(\text{N}_2\text{H}_4)_2(2\text{-C}_{10}\text{H}_7\text{COO})_3] \cdot 2\text{H}_2\text{O}$, $[\text{Pr}(\text{N}_2\text{H}_4)_2\{\text{C}_{10}\text{H}_6(1\text{-O})(2\text{-COO})\}_{1.5}] \cdot 3\text{H}_2\text{O}$, $[\text{Pr}(\text{N}_2\text{H}_4)_2\{\text{C}_{10}\text{H}_6(2\text{-O})(1\text{-COO})\}_{1.5}]$. A neutral bidentate ligand hydrazine bonded to the central metal ion. The compositions of the intermediate and the final products are those which best fit with the observed weight loss in the TG studies. Thermogravimetric results are in good agreement with the DTA data. The TG and DTA curves of all four complexes are given in Figs. 1-4. Simultaneous TG-DTA data of the naphthoate and hydroxy naphthoate complexes are summarized in Table.1.

The hydrated complex of Praseodymium 1- naphthoate $[\text{Pr}(\text{N}_2\text{H}_4)\{1\text{-C}_{10}\text{H}_7(\text{COO})\}_3] \cdot 2\text{H}_2\text{O}$ is thermally stable up to 98 °C and undergoes decomposition into three stages (Table 1) as represented by the DTA peaks at 85.6, 263.9 and 657.1 °C. The first stage of endothermic dehydration corresponds to a weight loss of 7.3%, which may be attributed to the loss of two molecules of water. The second stage with a mass loss of 25.4 % may be due to the exothermic decomposition of $\text{Pr}(\text{N}_2\text{H}_4)\{1\text{-C}_{10}\text{H}_7(\text{COO})\}_3$ in to unstable oxy carbonate intermediate $[\text{Pr}_2\text{O}_2\text{CO}_3]$ (4). The third stage intermediate oxy carbonate decomposition in to lanthanum oxide and the corresponding weight loss is 66.4%. The decomposition temperatures of these intermediates agree with the values reported.

In Praseodymium 2- naphthoate complex $[\text{Pr}(\text{N}_2\text{H}_4)\{2\text{-C}_{10}\text{H}_7(\text{COO})\}_3] \cdot 2\text{H}_2\text{O}$ undergoes decomposition in three stages giving the stable lanthanum oxide as the final residue. In the first step of endothermic decomposition starts at about 65 °C to form $[\text{Pr}(\text{N}_2\text{H}_4)\{2\text{-C}_{10}\text{H}_7(\text{COO})\}_3]$ and the corresponding weight loss of 5.1%, implying loosely bound lattice water. In the second step weight loss (9.8%) is due to the formation of unstable intermediate $[\text{Pr}\{2\text{-C}_{10}\text{H}_7(\text{COO})\}_3]$ showing exotherms decomposition in the range 152-280. The final step of decomposition occurs with a weight loss of 75.4% which may be due to the decomposition of intermediate to metal oxide. The formation of final products was confirmed their pXRD patterns.

The thermal analysis of Praseodymium complex of 1- hydroxy -2-naphthoic acid evinces the decomposition in three stages. The hydrated complexes of 1 - hydroxy - 2- naphthoates are stable in air upto 63 °C, and are then dehydrated by showing endothermic peaks in the temperature range of 63 - 140 °C and the weight loss is 10.2%, followed by decomposition in the second step forming an unstable intermediate, probably $\text{Pr}_2(\text{C}_2\text{O}_4)_3$, with a display of an exothermic peak in the range of 140-625 °C in DTA . During last step of decomposition of the complexes (weight loss 68%), the intermediate degrades to the respective metal oxide showing a strong exothermic peak in the range of 625-790 °C.

Praseodymium 2- hydroxy -1-naphthoate complex $[\text{Pr}(\text{N}_2\text{H}_4)_2\{\text{C}_{10}\text{H}_6(2\text{-O})(1\text{-COO})\}_{1.5}]$ undergoes decomposition in four stages as indicated by the DTA peaks obtained at 70 , 386 and 427 °C (5) and weight loss corresponds to 13.2, 43.2 and 64.3% respectively. In the second stage unstable intermediate $[\text{Pr}_2\text{O}(\text{C}_2\text{O}_3)_4]$ are formed [6]. In the final stage this intermediate undergoes exothermic decomposition to form corresponding metal oxide as final product.

From the thermal studies, the nature of the decomposition changes with the anion, even though all the complexes contain same ligand. Except 2-hydroxy -1-naphthoic acid all the complexes show two stage decompositions. In all the complexes of praseodymium contain two bridged hydrazine molecules and bidentate nature of carboxylate ions present in inside the coordination sphere. Hence, their thermal stability is more or less the same. The thermal stabilities of the naphthoic acid complexes are less than those of the hydroxy naphthoic acid complexes, because the strain at the

Special Issue on Proceedings of International Conference on Newer Trends and Innovation in Nanotechnology, Materials Science, Science and Technology March 2021. International Journal of Aquatic Science, Vol 12, Issue central atom is more in hydroxy naphthoic acid complexes.

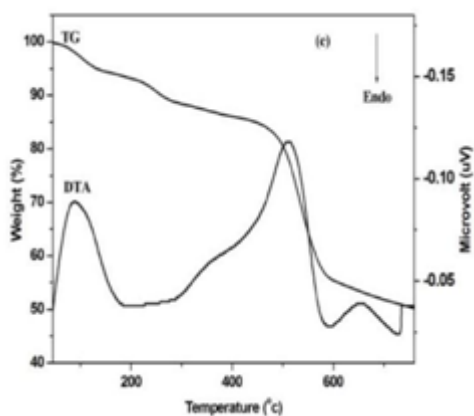


Fig. 1. TG and DTA curves of $[Pr(N_2H_4)(1-C_{10}H_7COO)_3].2H_2O$ complex

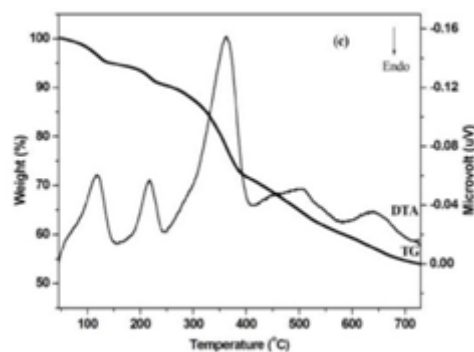


Fig. 2. TG and DTA curves of $[Pr(N_2H_4)_2(2-C_{10}H_7COO)_3].2H_2O$

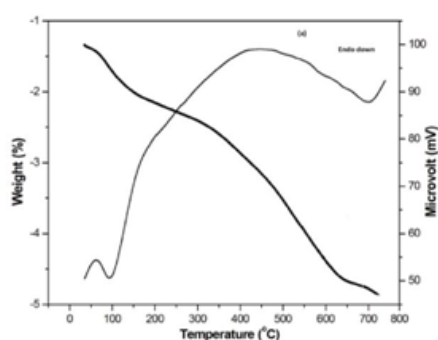


Fig. 3. TG and DTA curves of $[Pr(N_2H_4)_2\{C_{10}H_6(1-O)(2-COO)\}_{1.5}].3H_2O$ complex

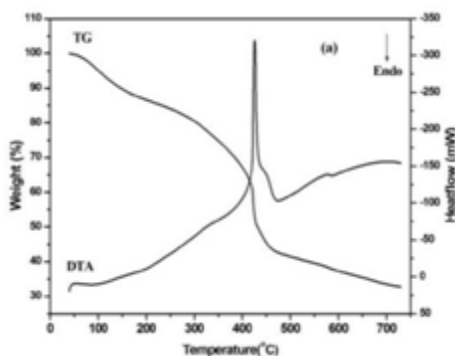


Fig. 4. TG and DTA curves of $[Pr(N_2H_4)_2\{C_{10}H_6(2-O)(1-COO)\}_{1.5}]$

Table 1 Thermal analysis data of Lanthanum naphthoate & Hydroxy naphthoate complexes

Molecular formula of the complexes	DTA peak Temp (°C)	T G		Intermediate/End product	
		Temp. Range (°C)	Observed		Calculated
$[Pr(N_2H_4)\{1-C_{10}H_7(COO)\}_3].2H_2O$	85.6(+) 263(-) 513(-) 657(-)	98-201 201-500 500-700	7.3 25.4 66.4	7.2 25.5 66.2	$[Pr(N_2H_4)\{1-C_{10}H_7(COO)\}_3]$ $[Pr_2O_2CO_3]$ Pr_6O_{11}
$[Pr(N_2H_4)\{2-C_{10}H_7(COO)\}_3].2H_2O$	116(+) 217(-) 364(-) 639(-)	65-152 152-280 280-730	5.0 9.7 75.3	5.1 9.8 75.4	$[Pr(N_2H_4)\{2-C_{10}H_7(COO)\}_3]$ $[Pr\{2-C_{10}H_7(COO)\}_3]$ Pr_6O_{11}

Special Issue on Proceedings of International Conference on New Trends and Innovations in Nanotechnology, Materials Science, and Technology, 09-10 March 2021, International Journal of Aquatic Science, Vol 12, Issue 01 (2020)	350(-) 720(+)	140-625 625-790	49.2 68.1	49.3 68.4	[Pr(N ₂ H ₄) ₂ {C ₁₀ H ₆ (2-O)(1-COO)} _{1.5}] Pr ₂ (C ₂ O ₄) ₃ Pr ₆ O ₁₁
[Pr(N ₂ H ₄) ₂ {C ₁₀ H ₆ (2-O)(1-COO)} _{1.5}]	70 (+) 386 (-) 427(-)	65-353 353-430 430-700	13.2 43.2 64.9	13.1 43.0 64.2	[Pr{C ₁₀ H ₆ (2-O)(1-COO)} _{1.5}] [Pr ₂ (C ₂ O ₃) ₄] Pr ₆ O ₁₁

Computation of Kinetic Parameters

The kinetic studies of the thermal decomposition of the lanthanum complexes were carried out using a computer program. Dehydration and decomposition were selected for the study of the kinetics of decomposition of the complexes. Coats and Redfern developed an integral method which is applied to TG data [7]. The correct order is assumed to lead to the best linear plot from which activation energy (E) is also determined. Coats and Redfern equation is

$$\log \left[\frac{1-(1-\alpha)^{n-1}}{(1-n)T^2} \right] = \log \left[\frac{AR}{\phi E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT} \right]$$

This is Coats-Redfern equation.

Plotting $\left[\frac{1-(1-\alpha)^{n-1}}{(1-n)T^2} \right]$ vs $\frac{1}{T}$ gives a straight line for a parameter, n.

From the slope and intercept, E and A are calculated.

The best of fit was assessment by correlation coefficient method. The entropy of activation ΔS can

$$A = \frac{kT}{h} e^{\frac{\Delta S}{R}}$$

be calculated using the equation.

where k is Boltzmann's constant, h Planck's constant, and S the entropy of activation.

The kinetic parameters of the decomposition reactions of the complexes of lanthanum are given in Table 2. There is no regular variation carried out in the values of the kinetic parameters of decomposition of the lanthanum complexes as with other common physical constants and melting point, etc.,

The activation energy is similar with the activation energy of dehydration of the hydrated salts. This indicates that the ligands are loosely bond to the central metal ion through electrostatic forces, because 4f electrons shielded by the 5s²5p⁶ octet are not available for covalent bonding. There is no definite trend in the values of the energy of activation or the entropy of activation.

The calculated parameters of all the lanthanum of 1& 2-naphthoic acid, 1-hydroxy-2-naphthoic acid and 2-hydroxy-1- naphthoic acid that the entropy of activation of the second stage is found to be greater than that of the first stage in all the complexes. These values suggest that the activated complex has a less ordered structure than the reactants [8]. There is no significant trend is followed in the values of A, E and n.

Table 2 Kinetic parameters of the thermal decomposition of lanthanum complexes

Comple x	Stages	E _a in KJ/mole	A (s ⁻¹)	ΔS in KJ/kelvin
[Pr(N ₂ H ₄)(1- C ₁₀ H ₇ COO) ₃].2H ₂ O	I	22.49	1.33x10 ⁵	0.040 3
	II	58.45	6.61x10 ²	0.066 2
[Pr(N ₂ H ₄) ₂ (2- C ₁₀ H ₇ COO) ₃].2H ₂ O	I	11.79	1.89x10 ⁹	0.067 8
	II	20.18	1.13x10 ⁹	0.049 2
[Pr(N ₂ H ₄) ₂ {C ₁₀ H ₆ (1-O) (2- COO)} _{1.5}].3H ₂ O	I	33.27	40.23 ×10 ¹³	0.018 9
	II	37.18	62.93 × 10 ¹⁵	0.033 4
[Pr(N ₂ H ₄) ₂ {C ₁₀ H ₆ (2-O)(1- COO)} _{1.5}]	I	46.19	9.12 x10 ⁷	0.056 0
	II	52.12	14.10x10 ⁴ 2	0.080 6

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