Characterisation and Thermal Decomposition of Lanthanide Complexes with 5-C-Prenylgallacatophenone

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Abstract: *Solid complexes of 5-C-prenylgallacatophenone having general formula [M ($C_{13}H_{15}O_4$)$_3$] {Where M = La(III), Pr(III), Nd(III) & Tb(III)} are prepared and characterized by elemental analyses, I R., diffuse reflectance spectra, ^{1}HNMR and thermal decomposition studies. They are found to have octahedral geometries. The complexes undergo thermal decomposition involving random nucleation mechanism. The evaluation of thermal kinetic parameters (E&Z) by using non isothermal method is reported.*
Key words: *Characterization, kinetic parameters, decomposition, complexes.*

I.   Introduction

Lanthanide (III) complexes have biological [1-4] and light emitting [5,6] applications. Keeping in view the applications of complexes, we describe synthesis, spectroscopic characterization and thermal decomposition of the solid complexes of the 5-C- prenylgallacetophenone with La (III), Pr (III), Nd (III) and Tb (III) in the present communication.

Experimental

5-C-Prenylgallacetophenone was prepared by reported method [7]. Purity of the compound was checked by single spot test and its melting point 74 °C (Lit. 73 °C).

The complexes were prepared by refluxing AnalR grade metal chloride, $LnCl_3$ (where Ln = La, Pr, Nd or Tb) with 5-C-prenylgallacetophenone (taken in excess) in 95% methanol on a water bath for two hours. On concentrating the solution, the complexes crystallized out. The excess of ligand was removed by repeated washings with hot benzene. The complexes were dried in vacuum over anhydrous $CaCl_2$.

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The metal contents were estimated gravimetrically as also from the TG curves.

C & H were estimated by using micro analytical combustion method. The infra-red spectra of the complexes were recorded on Perkin-Elmer instrument for the region 4000 to 400 cm^{-1} using KBr pellets while the electronic spectra of the complexes were recorded as diffuse reflectance spectra on VSU2P (Carl-Zeiss) spectrophotometer from 50,000 to 10,000 cm^{-1}.

^{1}HNMR spectra of ligand and complexes recorded on Bruker–400 MHz using DMSO as solvent.

The derivatograms of the complexes were recorded on Paulik-Paulik Erdey MOM derivatograph (Hungary) automatic instrument at the rate of 10^0/min in static air atmosphere using α- Alumina as the reference material.

II.   Results and Discussion

The main IR spectral bands [8,9] of the ligand and complexes are recorded in Table. In case of ligands, the band at 3500 cm^{-1} is assigned to υ(0-H) stretching mode and the shoulder at 3180 cm^{-1} is due υ(O-H) stretching of the intra-molecularly hydrogen bonded hydroxyl group in the molecule. The strong band at 1630 cm^{-1} is assigned to υ (C=O) stretching vibration. A band at 1750 cm^{-1} shows the presence of the ethylene group of the prenyl side chain. The shoulders at 1605 and 1500 cm^{-1} are assigned to OH…O=C hydrogen bonding interaction of the carbonyl group and the adjacent hydroxyl group. The band at 1075 cm^{-1} is assigned to the dimethyl group of the prenyl side chain. A shoulder at 1145 cm^{-1} is because of the presence of the adjacent double bond.

The spectra of the complexes in comparision show significant shifts in the above mentioned bands due to coordination to the metal ions. In the complexes, υ(C=O) and other frequencies get shifted to lower wave numbers (Table I). Additional bands due to υ (M-O) and υ (M-O+ C-C) vibrational modes appear in the complexes are in close agreement to the data reported for many other complexes of these metals with oxygen donors. The shoulders at 1605 and 1500cm^{-1} are missing in the complexes because of the abstraction of proton of the hydroxyl group.

On the basis of available data [10,-12] the main bands of respective transition of diffuse reflectance spectra of the solid complexes are recorded in Table I. The other observed bands are due to electronic transitions (4f→5d), charge transfer (Metal to ligand and ligand to metal) and electronic transitions within the ligand. The presence of the ligands around the metal ion invariably shifts the absorption bands to the higher frequency. Lanthanum (III) has no significant absorption in the visible region. The absorption bands of Praseodymium(III), Neodymium(III) and Terbium(III) in the visible and infrared region appear due to transitions from the ground levels $^3H_4$, $I_{9/2}$, $^7F_6$ to the excited J-levels of 4f configuration, respectively. The d.r. spectra of the solid complexes has been used to elucidate their stereochemistry. The assignments of electronic spectral data suggest octahedral geometries for the complexes [13, 14].

^{1}H NMR spectra of ligand shows two singlet at δ = 7.4 and δ =2.3 for 2H on aromatic ring and 3H of -CH$_3$ proton respectively. The signal for 3OH protons are not found upto δ =10 because of rapid proton exchange. The spectra of the complexes show retention of singlet for aromatic proton between δ =7.35 to 7.40 and for the -CH$_3$ protons between δ =2.30 to 2.40.

The TG curves [Fig.1] have revealed that the complexes are stable upto 140 °C which is indicative of the absence of any solvent molecules. The TG curves of all the complexes show a continuous weight loss from 140°C to 600°C till the formation of oxide La$_2$O$_3$, Pr$_2$O$_3$, Nd$_2$O$_3$, or Tb$_2$O$_3$ as end product. The curves do not feature any stable intermediate state which could be isolated for characterization. The final weight of the residues in all cases correspond to the weights of the metal oxides (Table I).

Non- isothermal kinetic studies of the complexes (Table-II) [15] show the values of kinetic parameters and the mechanism of decomposition. The values of α (fractional weight loss) at different temperatures were obtained from TG curves, corresponding $(1-α)^n$ values were calculated, where n depends upon the reaction model. Various plots with different values of n were tried. The best linear fit plots: Fig. 2 & Fig. 3 were found for piloyan –Novikova [16] and Coats-Redfern [17,18] method respectively. These models suggest random nucleation mechanism [19] of decomposition which is also supported by α-T (K) plot (Fig. 4). Plots (2-3) were analysed for the values of slope, intercept and the energy of activation. From these values, the corresponding values of Z were obtained by applying equations:

$$\text{Intercept} = \frac{\log ZR}{\beta E}; \qquad Z = \frac{E}{RT_m} \beta \exp\left(\frac{E}{RT_m^2}\right)$$

Where R represents the molar gas constant and β the rate of heating (KS^{-1}).

It is concluded that 5-preny-2,3,4-trihydroxy acetophenone acts as a bidentate chelating ligand. The presence of prenyl side chain seems to restrict the coordination number to six only on account of steric hindrance. The decomposition of the complexes is regular and continuous with the formation of the respective oxides as the end products. The decomposition in all cases involving random nucleation mechanism.

S. No	Complex	Colour	Elemental Analysis (Calc/Found)				IR Spectra bands (cm^{-1})					Electronic Absorption (cm^{-1})	
			C	H	M	M$_2$O$_3$	υ(C=O)	(CH$_3$C=O)	υ(C$_6$H$_5$)	(M-O)	(M-O+C)	Major Bands	Assignment
1	[La(C$_{13}$H$_{15}$O$_4$)$_3$]	Dark Brown	55.45/56.0	5.33/5.83	16.46/17.10	19.30/18.89	1600	1400	1080	600	450	22727	Intra-ligand Charge transfer
2	[Pr(C$_{13}$H$_{15}$O$_4$)$_3$]	Brown	55.32/55.93	5.32/5.86	16.65/17.15	19.49/18.93	1600	1380	1090	580	440	25000 21739 15384	^{3}H4→^{3}P$_2$ →^{3}P$_1$ → D$_2$
3	[Nd(C$_{13}$H$_{15}$O$_4$)$_3$]	Brown	55.11/55.82	5.30/5.70	16.98/17.4	19.81/18.23	1600	1380	1090	580	440	23889 16129	^{4}I$_{9/2}$→^{2}P$_{1/2}$ → ^{4}G$_{7/2}$
4	[Tb(C$_{13}$H$_{15}$O$_4$)$_3$]	Brown	54.17/54.96	5.20/5.62	18.4/18.9	21.17/20.94	1600	1425	1085	570	450	26666	^{7}F$_6$ →^{5}D3 →^{5}L$_{10}$ →^{5}D$_2$
5	C$_{13}$H$_{17}$O$_4$ (ligand)	---	-----	----	---	---	3500, 3180	2910,1750,	1630, 1609 (Sh),	1500			

Table-I
Elemental Analysis, colour, IR spectral and electronic Absorption spectra of complexes.

Table-II: Thermal decomposition kinetic parameters.

Complex	Equation	Slope	Intercept	E kJmol^{-1}	Z S^{-1}	Model
[La(C$_{13}$H$_{15}$O$_4$)$_3$]	Piloyan Novikova	-2444.00	- 1.66	46.90	20.52	-
	Coats- Redfern	-222.22	- 2.25	42.55	4.79	R.N.
[Pr(C$_{13}$H$_{15}$O$_4$)$_3$]	Piloyan-Novikova	-1909.09	- 2.24	36.55	4.37	-
	Coats-Redfern	-1214.28	- 3.69	23.25	0.11	R.N.
[Nd(C$_{13}$H$_{15}$O$_4$)$_3$]	Piloyan-Novikova	-1142.85	- 3.90	21.88	0.05	-
	Coats-Redfern	-1105.26	- 3.92	21.16	0.05	R.N.
[Tb(C$_{13}$H$_{15}$O$_4$)$_3$]	Piloyan-Novikova	-1785.71	- 2.56	34.19	1.88	-
	Coats-Redfern	-4800.00	-3.72	91.90	0.03	R.N.

R.N. = Random Nucleation Mechanism.

Legends of Figure

Fig. 1. Derivatograms for La (III) complex [–·–], Pr(III) complex [- -], Tb (III) complex[–] and Nd (III) complex [-o-]

Fig.2.. Piloyan –Novikova plots: La(III) complex [•],1Pr (III) complex [×], Tb (III)complex [0] and Nd (III) complex [-].

Fig.3. Coats –Redfern plots: La(III) complex[•], Pr(III) complex(×), Tb (III) complex [0] and Nd (III) complex (*)

Fig.4. α –T(K) plots: La (III) complex[•], Pr(III) complex (×), Tb (III) complex [0], and Nd (III) complex (*).

Fig. 1
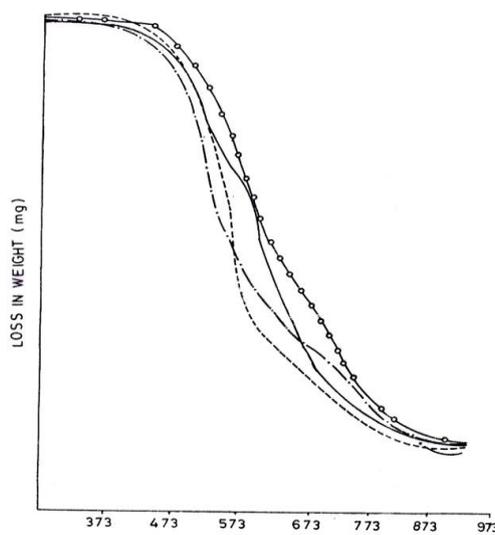
Fig. 2
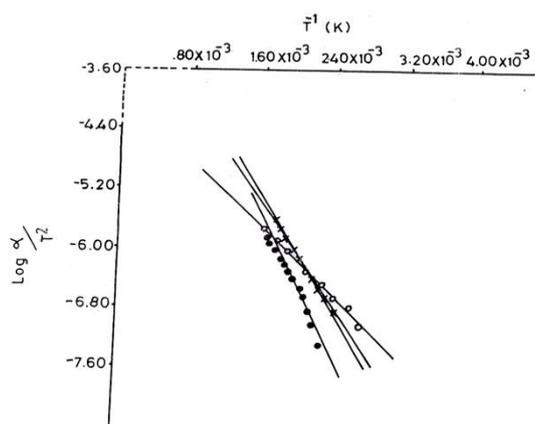
Fig. 3
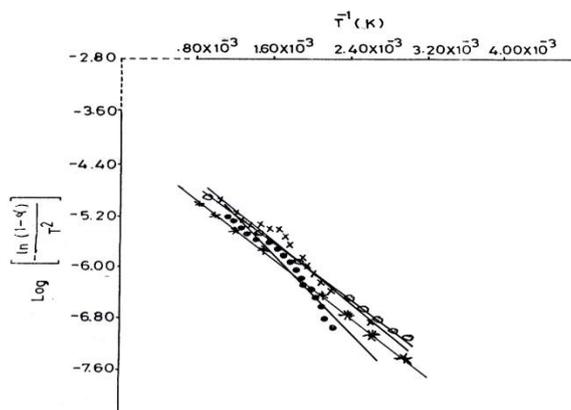
Fig. 4
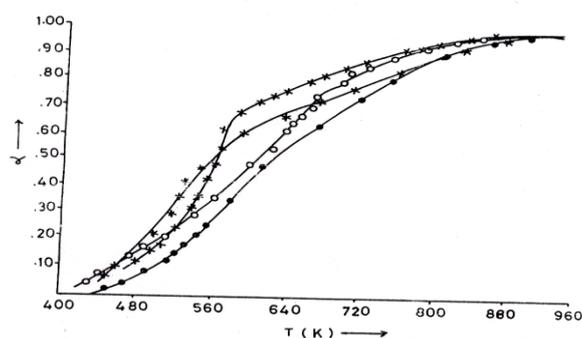
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