

## THERMAL STUDIES ON IONIC DERIVATIVES OF HAFNIUM(IV) INVOLVING MALTOL LIGAND

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### Abstract

A number of ionic chelate complexes of maltol(A) and hafnium(IV) the type  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{MCl}_3]^-$  (B) [*HL*=maltol; *M*=Zn(II), Cd(II), Hg(II), Cu(II)] have been synthesized and characterized by spectral studies (IR, UV, <sup>1</sup>H NMR and <sup>13</sup>C NMR). The stoichiometry of the complexes has been confirmed by conductance measurements. Thermogravimetric (TG) and differential thermal analytical (DTA) studies have been carried out for these complexes and from TG curves, the order, apparent activation energy and apparent activation entropy of the thermal decomposition reactions have been elucidated. The order in each case has been determined to be one and the degree of spontaneity and lability have been inferred from the apparent activation energy and entropy, respectively. Thermal parameters have been correlated with some structural aspects of the complexes concerned. From differential thermal analysis curves, the heat of reaction has been calculated.

**Keywords:** apparent activation energy, apparent activation entropy, heat of reaction, order of thermal reaction, thermal studies

### Introduction

The diverse applications of thermal analysis have contributed to advances made in the fields of explosives, polymers, soil studies, space research, agrochemicals, organometallics, pharmaceuticals etc. [1]. Thermal studies were previously carried out for analogous complexes of titanium(IV), zirconium(IV) and hafnium(IV) chelated to oxine as a ligand [2–4]. Similar thermal effects have been observed in the present case. In this paper an attempt is made to explain the variation in thermal stability of some metal complexes in terms of their structural parameters. This follows from our interest to investigate the thermal behavior of metal-biomolecule complexes [5, 6].

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## Experimental

The following instruments were used: Elico conductivity Bridge, model CM-180 for conductance measurements; Perkin Elmer, FTIR spectrometer, Spectrum 2000 for IR Spectra; Beckman DU-64 spectrophotometer for UV spectra; Bruker Spectrospin advance 300 spectrometer for  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra. Rigaku Thermoflex, model PTC-10A, Rigaku corporation Japan, was used for simultaneous recording of TG-DTA curves in air at a heating rate of  $10^\circ\text{C min}^{-1}$ . For TG, the instrument was calibrated using calcium oxalate while for DTA, calibration was done using indium metal both of which were supplied along with the instrument. A flat bed type Al-crucible was used with  $\alpha$ -alumina (99% pure) as the reference material for DTA. Maltol was procured from Aldrich Sigma, U.S.A and hafnocene dichloride,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{HfCl}_2$  was purchased from Alfa products, Ventron, USA. These were used without further purification.

### *Preparation and characterization of complexes*

A solution of hafnocene dichloride (0.095 g, 0.25 mmol) in 10 mL acetone was slowly added to a solution of maltol (HL, 0.031 g, 0.25 mmol) in 10 mL acetone which was finally added to a solution of metal salt ( $\text{ZnCl}_2$  0.034 g, 0.25 mmol;  $\text{CdCl}_2$  0.046 g, 0.25 mmol;  $\text{HgCl}_2$  0.068 g, 0.25 mmol or  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  0.043 g, 0.25 mmol) in 10 mL acetone. The contents were stirred at room temperature for 4 h and filtered. From the filtrate the solvent was evaporated under vacuum at room temperature so as to reduce the volume of the filtrate to about one-quarter of the original solution. Petroleum ether was added to the concentrated filtrate and the mixture was left to stand overnight. The products thus obtained were washed with petroleum ether. They were then recrystallized from an acetone solution by the addition of petroleum ether.

The complexes were yellow or brown in colour. They were soluble in THF, DMSO, DMF and water. Conductance measurements indicated that these complexes were 1:1 electrolytes in nitrobenzene. Some physical characteristics and elemental analysis data are presented in Table 1.

In IR spectra, the absorption at  $1660\text{ cm}^{-1}$ , in case of the ligand was assigned to  $\nu(\text{C}=\text{O})$  stretching frequency. On complexation, this frequency was further lowered by ca  $45\text{ cm}^{-1}$ , indicating that the carbonyl group chelated to the hafnium(IV) ion. The  $\nu(\text{C}=\text{C})$  stretching frequency observed at  $1600\text{ cm}^{-1}$  for maltol (A) shifted to ca  $1565\text{ cm}^{-1}$  in the complexes (B) [7]. In the free ligand, the band due to phenolic OH stretching occurred at  $3200\text{ cm}^{-1}$  [8] and that due to  $\delta(\text{OH})$  at  $1300\text{ cm}^{-1}$  [7]. These bands were absent in the spectra of the complexes. A weak absorption band around  $490\text{ cm}^{-1}$  had been observed in the spectra of all the complexes which may be due to stretching M-O vibration. Another weak band was observed around  $375\text{ cm}^{-1}$  which was due to M-Cl stretching. The bands at  $1282$  and  $1230\text{ cm}^{-1}$  in the ligand and complexes, respectively, were due to aromatic C-O-C stretching frequency [8].

In the UV spectra of maltol (A), an intense band was observed at  $284\text{ nm}$  ( $\log \epsilon = 7.4$ ) due to  $\pi\text{-}\pi^*$  absorptions of the chromophoric carbonyl group [9]. This

**Table 1** Physical characteristics and elemental analysis

Compound	Colour	Yield/%	Melting point/°C	$\Lambda^a$ (C=1.5·10 <sup>-3</sup> M)	Found/Calc. %		
					C	H	Cl
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{ZnCl}_3]^-$	yellowish brown	40	142	28.5	31.72 (31.75)	2.48 (2.40)	17.59 (17.65)
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CdCl}_3]^-$	yellowish brown	50	139	28.9	29.43 (29.42)	2.30 (2.33)	16.32 (16.35)
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{HgCl}_3]^-$	brown	55	133	26.5	25.93 (25.97)	2.03 (2.05)	14.38 (14.33)
$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CuCl}_3]^-$	light brown	58	122	30.5	31.81 (31.88)	2.49 (2.45)	17.65 (17.63)

<sup>a</sup>=ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>

band shifted to ca 294 nm ( $\log \epsilon$  ca 4.2) in the case of its complexes (B). The shift was attributed to the involvement of C=O group in complexation.

$^1\text{H}$  NMR spectra of maltol complexes (B) showed signals in  $\delta$  2.25 (s, 3H,  $\text{CH}_3$  at C(2)),  $\delta$  6.45 (d, 1H, H(5),  $J=6.0$  Hz) and  $\delta$  8.00 (d, 1H, H(6),  $J=6.0$  Hz) regions. The signal due to H(5) in free maltol (A) has been reported to absorb at  $\delta$  6.30 (d, 1H,  $J=6.0$  Hz) [10]. The downfield shift in the metal complexes may be attributed to the involvement of carbonyl at C(4) in complexation. Another signal around  $\delta$  6.3 was observed in the spectra of all the complexes and was attributed to the cyclopentadienyl ring [11, 12].

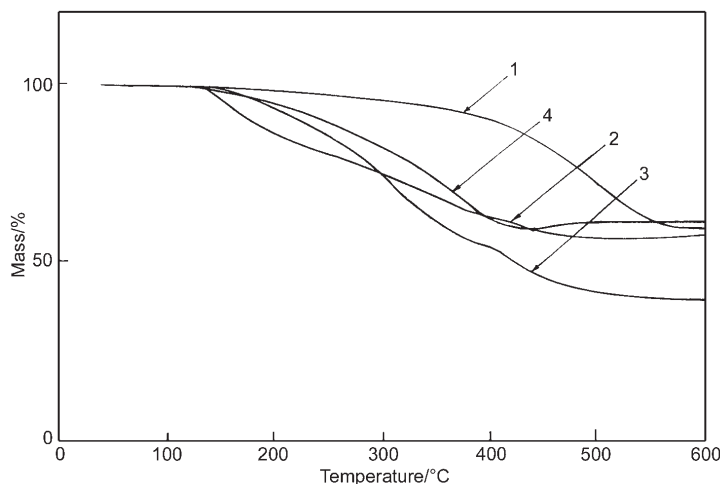
$^{13}\text{C}$  NMR spectrum of maltol (A) showed signals at 149.2 ppm (C(2)), 143.2 ppm (C(3)), 173.2 ppm (C(4)), 113.9 ppm (C(5)), and 155.2 ppm (C(6)) [13]. In the complexes the C(4) absorbed at ca 177.48 ppm while the C(3) absorbed at ca 146.2 ppm. The downfield shifts indicated that the complexes were formed by deprotonation of C(3) hydroxyl and chelation through C(4) carbonyl. The methyl group at C(2) showed a resonance signal at ca 27.1 ppm, while the carbon of the cyclopentadienyl ring gave a resonance signal at 122.2 ppm [14].

## Results

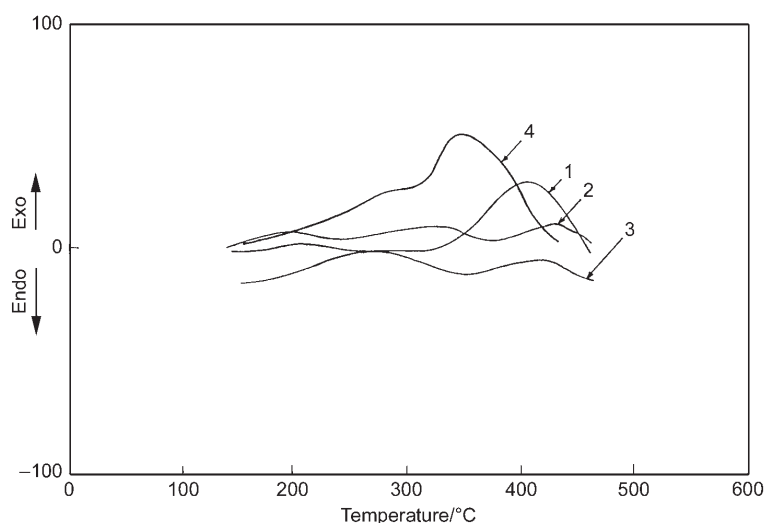
TG and DTA curves are shown in Figs 1 and 2 respectively



The TG curve indicated that the mass change began at 399 K and continued upto 835 K. The observed mass loss (50.7%) corresponded to the formation of a mixture of  $\text{HfO}_2$  and  $\text{ZnO}$ , for which the theoretically calculated mass loss was 51.8%.

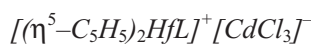


**Fig. 1** TG curves: 1 –  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{ZnCl}_3]^-$ ; 2 –  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CdCl}_3]^-$ ; 3 –  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{HgCl}_3]^-$ ; 4 –  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CuCl}_3]^-$



**Fig. 2** DTA curves: 1 –  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{ZnCl}_3]^-$ ; 2 –  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CdCl}_3]^-$ ; 3 –  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{HgCl}_3]^-$ ; 4 –  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CuCl}_3]^-$

In the DTA profile, an exothermic peak was observed with  $T_{\text{max}}$  485, followed by another exothermic peak with  $T_{\text{max}}$  at 675 K.



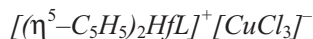
The TG curve recorded a mass change of 52.1% in the temperature range of 412–773 K. This corresponded to the formation of a mixture of  $\text{HfO}_2$  and  $\text{CdO}$  for which the theoretically calculated mass loss was 48%.

The DTA curve showed three thermal effects, all in the form of exothermic peaks with  $T_{\text{max}}$  465, 615 and 695 K.



From the TG curve, it was observed that the complex was stable upto 407 K. Beyond this temperature, the TG curve showed a mass loss upto 793 K, which corresponded to the formation of  $\text{HfO}_2$ .  $\text{HgO}$  volatilizes at such high temperatures. The observed mass loss of 69% was in close agreement with the theoretically calculated mass loss of 71.6%.

Two exothermic peaks were observed in the DTA curves of the complexes. The first had a  $T_{\text{max}}$  545 while the second had  $T_{\text{max}}$  690 K.



From the TG curve, it was observed that the mass change began at 395 K and continued upto 710 K. A mass change of 48% was observed over this temperature range

**Table 2** Thermal data

Compound	Thermogravimetry			Differential thermal analysis			
	Temperature range/K	<i>n</i>	<i>E<sub>a</sub></i> /kJ mol <sup>-1</sup>	<i>S<sup>‡</sup></i> /J K <sup>-1</sup> mol <sup>-1</sup>	Thermal effect	<i>T<sub>max</sub></i> /K	$\Delta H$ /J g <sup>-1</sup>
[( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> HfL] <sup>+</sup> [ZnCl <sub>3</sub> ] <sup>-</sup>	399–835	1	5.02	16.86	Exothermic	485	20.8
					Exothermic	675	127.6
[( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> HfL] <sup>+</sup> [CdCl <sub>3</sub> ] <sup>-</sup>	412–773	1	6.42	16.81	Exothermic	465	20.5
					Exothermic	615	15.3
					Exothermic	695	18.4
[( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> HfL] <sup>+</sup> [HgCl <sub>3</sub> ] <sup>-</sup>	407–793	1	21.69	16.85	Exothermic	545	50.2
					Exothermic	690	23.8
[( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> HfL] <sup>+</sup> [CuCl <sub>3</sub> ] <sup>-</sup>	395–710	1	1.835	16.94	Exothermic	620	146.8

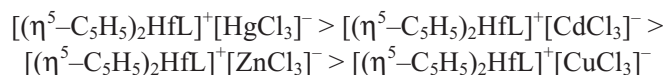
which corresponded to the formation of a mixture of  $\text{HfO}_2$  and  $\text{CuO}$ , for which the theoretically calculated loss was 51.9%.

In the DTA profile an exothermic peak was observed with  $T_{\text{max}}$  620 K.

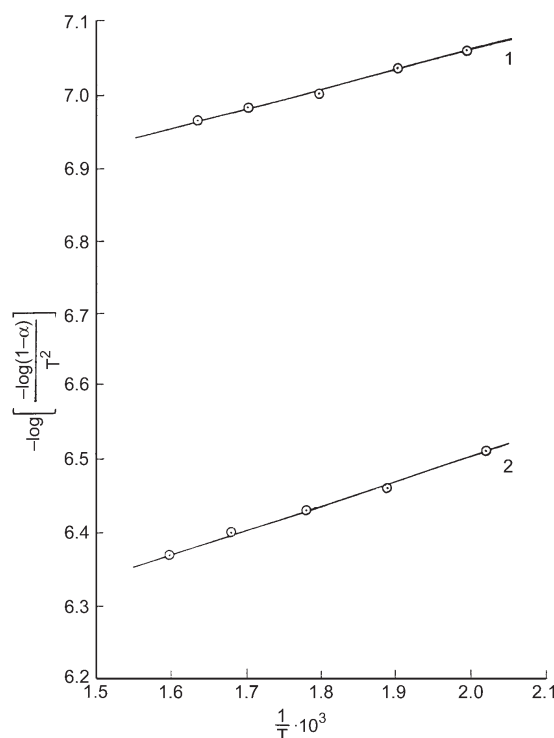
## Discussion

The results of TG and DTA evaluations are presented in Table 2. From the TG curves, the order ( $n$ ) and activation energy ( $E_a$ ) of the thermal decomposition reaction have been elucidated by the method of Coats and Redfern [15]. The linearization curves are shown in Fig. 3.

The order of reaction in each case was one. A comparison of the activation energy data for the thermal degradation of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{MCl}_3]^-$  complexes revealed that the  $E_a$  values follow the order,



This may be explained on the basis of the fact that larger cations are stabilized by larger anions. The complex cation  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+$  is very large in size and the size of the M(II) ions increases in the order  $\text{Cu(II)} < \text{Zn(II)} < \text{Cd(II)} < \text{Hg(II)}$ . In the case of the



**Fig. 3** Kinetic parameters from TG: 1 –  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{ZnCl}_3]^-$ ; 2 –  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CdCl}_3]^-$

$[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{HgCl}_3]^-$  complex, the larger size of Hg(II) ion helps in effective stabilization of the complex cation and therefore gives rise to a higher lattice energy. This makes thermal degradation relatively difficult and the reaction involves a higher value of  $E_a$ . For the complex  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CuCl}_3]^-$ , the smaller size of the Cu(II) ion leads to a relatively poor stabilization of the complex cation and to a comparatively lower lattice energy. Thus the thermal reaction involves a lower value of  $E_a$ .

The apparent activation entropy ( $S^\ddagger$ ) has been calculated by the method of Zsakó [16]. The apparent activation entropy has a positive value for all the complexes. Hence, thermal degradation of these complexes is a spontaneous process. The  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CuCl}_3]^-$  complex has the highest  $S^\ddagger$  value while the  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{HfL}]^+[\text{CdCl}_3]^-$  analogue has the lowest. Hence, the former decomposes with the greatest degree of randomness and the latter with the least.

The heat of reaction ( $\Delta H$ ) has been calculated for the thermal effects [17]. The temperature dependent calibration coefficient was obtained from the Curell equation [18].

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