Thermal Studies of Some Ionic Chelate Complexes of Bis(cyclopentadienyl)hafnium(IV)

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Bis(cyclopentadienyl)hafnium(IV) complexes of thymine (HL) of the type $[(\eta^5\text{-}C_5H_5)_2HfL]^+X^-$ (X = $CuCl_3$, $ZnCl_3$, $CdCl_3$, $HgCl_3$) have been synthesized and characterized by spectral studies (IR, UV, ^1H NMR, and ^{13}C NMR). Molar conductivity measurements reveal that the compounds are 1:1 electrolytes. From thermogravimetric curves, the order, apparent activation energy, and apparent activation entropy of the thermal decomposition reaction have been elucidated. The order in each case has been determined to be one and the degree of lability and spontaneity has been inferred from the apparent activation energy and entropy, respectively. The various thermal studies have been correlated with some structural aspects of the complexes concerned. From differential thermal analytical curves the heat of reaction has been calculated.

Thymine (5-methyl-($1H$,$3H$)-pyrimidine-2,4-dione) is a constituent of nucleic acids. The interaction of metal ions with nucleic acids and their constituents has received considerable attention over the years [1, 2]. The importance of these investigations lies in the possible biological role of the metals in nucleic acid processes, as well as the use of model nucleic acid compounds in the understanding of the complex structures of the nucleic acids themselves. This biomolecule possesses a number of bonding sites and thus forms a number of stable metal complexes [3]. The study of such complexes is interesting from a structural viewpoint. Moreover, pyrimidine analogues are also associated with diverse biofunctions such as anticonvulsant [4] and antineoplastic [5] activity. These analogues also act as immunosuppressants [3]. Recent studies on determination of kinetic parameters from thermal data [6, 7] prompted us to analyze the variation in thermal stability of some metal complexes in terms of their structural parameters. This follows from our interest to investigate the thermal behaviour of metal—biomolecule complexes [8, 9].

EXPERIMENTAL

Uracil was procured from Aldrich Sigma, U.S.A. and hafnocene dichloride, $(\eta^5\text{-}C_5H_5)_2HfCl_2)$, was purchased from Alfa products, Ventron, U.S.A. These were used without further purification. 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 ^1H NMR and ^{13}C NMR spectra. Rigaku Thermoflex, model PTC-l0A, Rigaku corporation Japan, was used for simultaneous recording of TG-DTA curves in air at a heating rate of 10 K min^{-1}. For TG, the instrument was calibrated using calcium oxalate while for DTA calibration was done using indium, both the chemicals were supplied along with the instrument. A flat-bed type A1-crucible was used with α-alumina (99 % pure) as the reference material for DTA.

Complexes $[(\eta^5\text{-}C_5H_5)_2HfL]^+X^-$
A: X = $CuCl_3$; **B:** X = $ZnCl_3$; **C:** X = $CdCl_3$;
D: X = $HgCl_3$

The solution of the metal salt (0.25 mmol: $CuCl_2$·$2H_2O$ 0.043 g, $ZnCl_2$ 0.034 g, $CdCl_2$ 0.046 g or $HgCl_2$ 0.068 g) in acetone (10 cm^3) was added to a stirred solution of 0.095 g (0.25 mmol) of bis(η^5-cyclopentadienyl)hafnium(IV) dichloride and 0.032 g (0.25 mmol) of thymine (HL) in acetone (20 cm^3). The contents were stirred for 8 h and filtered, whereupon the filtrate was reduced to one-fourth of its original volume followed by the addition of petroleum ether. The precipitated complexes were filtered, dried and crystallized from acetone by the addition of a few drops of petroleum ether.

The chemical analysis and spectral data revealed that the complexes were pure. This was also supported by TLC. They were soluble in THF, DMSO, and DMF.

Table 1. Physical Characteristics and Analytical Data of Thymine Complexes

Complex	Decomp. θ/K	Λ ($C = 1.5 \times 10^{-3}$ mol dm^{-3})/ (Ω^{-1} cm^2 mol^{-1})	w_i(found)/% w_i(calc.)/%	
			Cl	N
A	443	29.8	17.55	4.50
			17.62	4.64
B	409	26.4	17.35	4.52
			17.56	4.63
C	462	28.5	16.20	4.12
			16.30	4.29
D	473	26.4	14.50	3.95
			14.36	3.78

$[(\eta^5\text{-}C_5H_5)_2HfL]^+ \, X^-$

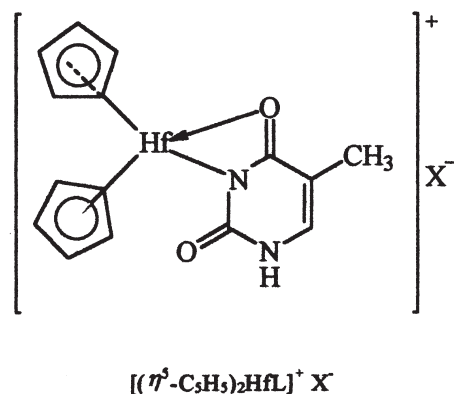$A : X = CuCl_3$; $B : X = ZnCl_3$; $C : X = CdCl_3$; $D : X = HgCl_3$

Formula 1

The complexes were light brown in colour. The molar conductivity measurements in nitrobenzene solution were of the order of *ca.* 30 Ω^{-1} cm^2 mol^{-1} indicating that the complexes were 1:1 electrolytes. The analytical data of the complexes are presented in Table 1.

The IR spectra of thymine showed a doublet peaked at $\tilde{\nu} = 1760$ cm^{-1} and 1678 cm^{-1}, which may be attributed to $\nu(C\text{-}2{=}O)$, in-plane $\nu(C\text{-}4{=}O) + \nu(C{=}C)$ and out-of-plane $\nu(C\text{-}4{=}O)$ [10]. In metal complexes, the former band shifted to *ca.* 1670 cm^{-1}, whereas the latter absorbed at *ca.* 1600 cm^{-1}. The $\nu(C\text{—}N)$ stretching frequency was also perturbed from 1390 cm^{-1} in the ligand to *ca.* 1350 cm^{-1} in the complexes since the hafnium(IV) ion displaced the proton at N-3 [11, 12]. Thus, the thymine moiety acted as a bidentate group, being chelated to the hafnium(IV) ion through carbonyl at C-4 and deprotonated N-3.

In the UV spectrum, the thymine ligand showed two absorption bands at $\lambda = 266$ nm (log$\{\varepsilon\} = 3.9$) and 225 nm sh (log$\{\varepsilon\} = 1.3$) due to the π—π^* transition of the carbonyl group and due to the corresponding transition of the N═C═O chromophore, respectively [13]. On complexation, the absorption due to the carbonyl group shifted to *ca.* 278 nm (log$\{\varepsilon\} \approx$ 5.5), indicating the involvement of carbonyl oxygen in complexation. The N═C═O chromophore in the metal complexes absorbed at *ca.* 230 nm sh (log$\{\varepsilon\} \approx$ 5.3)

The ^{1}H NMR signal of thymine [14] appeared as a broad singlet at $\delta = 7.81$ (s, br, 1H, H-6). This signal remained unaffected on complexation. Thymine and its metal complexes showed another band at $\delta = 2.00$ (s, br, 3H) due to —CH$_3$ group at C-5. A multiplet appeared in the region $\delta = 6.9$—7.0 (m, 10H) due to the cyclopentadienyl group in the metal complexes.

The ^{13}C NMR spectra of the organohafnium(IV)—thymine complexes showed signals at $\delta \approx 111.6$ C-2, ≈ 131.0 C-4, ≈ 66.9 C-5, ≈ 97.0 C-6 while the signals in pure thymine [15] appeared at $\delta = 110.7$ C-2 and 124.1 C-4. This downfield shift, on complexation, was attributed to the involvement of C-4 carbonyl in

complexation. The resonance signal due to the methyl group at C-5 appeared at $\delta \approx 26.8$. In the metal complexes, a resonance signal appeared at $\delta \approx 122.2$ due to carbons of the cyclopentadienyl rings.

RESULTS AND DISCUSSION

The TG and DTA curves of the complexes (Formula 1) are shown in Figs. 1 and 2, respectively.

The TG curve of the complex $[(\eta^5\text{-}C_5H_5)_2HfL]^+$-$[CuCl_3]^-$ revealed a mass loss in the temperature range 444—806 K. The observed mass loss of 50 % corresponded to the formation of a mixture of HfO$_2$ and CuO for which the theoretical relative mass loss was 51.9 %.

An exothermic peak with $T_{max} = 694$ K was observed in the DTA curve of this complex and corresponded to its decomposition to a mixture of HfO$_2$ and CuO.

The TG curve of the complex $[(\eta^5\text{-}C_5H_5)_2HfL]^+$-$[ZnCl_3]^-$ indicated that the mass loss initiated at 409 K and continued up to a temperature of 795 K. The observed relative mass loss of 48 % corresponded to the formation of a mixture of HfO$_2$ and ZnO for which the theoretically calculated relative mass loss was 51.8 %.

The DTA profile showed an exothermic peak with $T_{max} = 725$ K, corresponding to the decomposition of the complex to a mixture of HfO$_2$ and ZnO.

From the TG curve of the complex $[(\eta^5\text{-}C_5H_5)_2$-$HfL]^+[CdCl_3]^-$ it was observed that the mass loss extended over the temperature range 462—800 K. The observed relative mass loss of 49 % corresponded to the formation of a mixture of HfO$_2$ and CdO for which the theoretically calculated relative mass loss was 48 %.

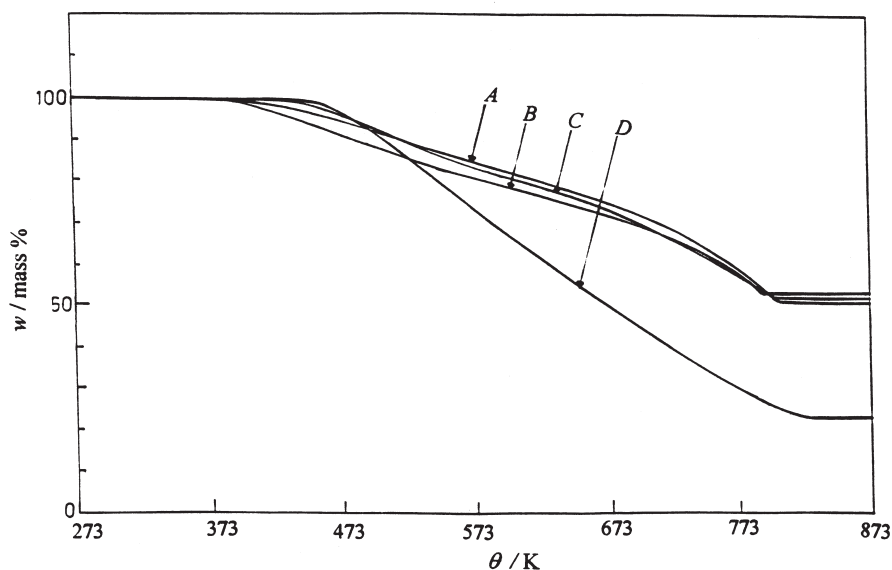The exothermic thermal effect with $T_{max} = 756$ K, observed in the DTA curve of the complex, was due

Fig. 1. TG curves of complexes.

Table 2. Thermal Data of Thymine Complexes

| Complex	Thermogravimetry				Differential thermal analysis		
	Temp. range	Order of reaction	Activation energy (E_a)	Activation entropy ($S^{\#}$)	Thermal effect (Temp. range/K)	T_{max}	Δh
	K	n	kJ mol^{-1}	J K^{-1} mol^{-1}		K	J g^{-1}
A	444—806	1	11.53	0.944	Exothermic (630—770)	694	68.05
B	409—795	1	17.74	3.718	Exothermic (650—813)	725	110.92
C	462—800	1	28.70	8.499	Exothermic (655—813)	756	150.47
D	473—828	1	40.91	13.848	Exothermic (635—815)	767	315.27
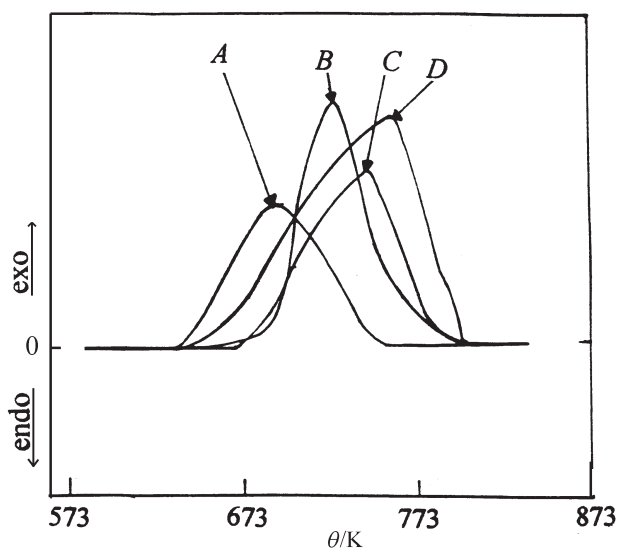
Fig. 2. DTA curves of complexes.

to its decomposition to a mixture of HfO_2 and CdO.

The TG curve of the complex $[(\eta^5\text{-}C_5H_5)_2HfL]^+\text{-}[HgCl_3]^-$ revealed that the mass change took place in the temperature range 473—828 K. The observed relative mass loss of 75 % corresponded to the formation of HfO_2, as HgO volatilized at such high temperatures. The theoretical relative mass loss was 71.6 %.

The DTA profile showed an exothermic peak with $T_{max} = 767$ K due to the decomposition of the complex to HfO_2.

The results of the TG and DTA evaluations are presented in Table 2. The mass loss data of the complexes are given in Table 3. 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* [16]. 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 the $[(\eta^5\text{-}C_5H_5)_2HfL]^+X^-$ complexes re-
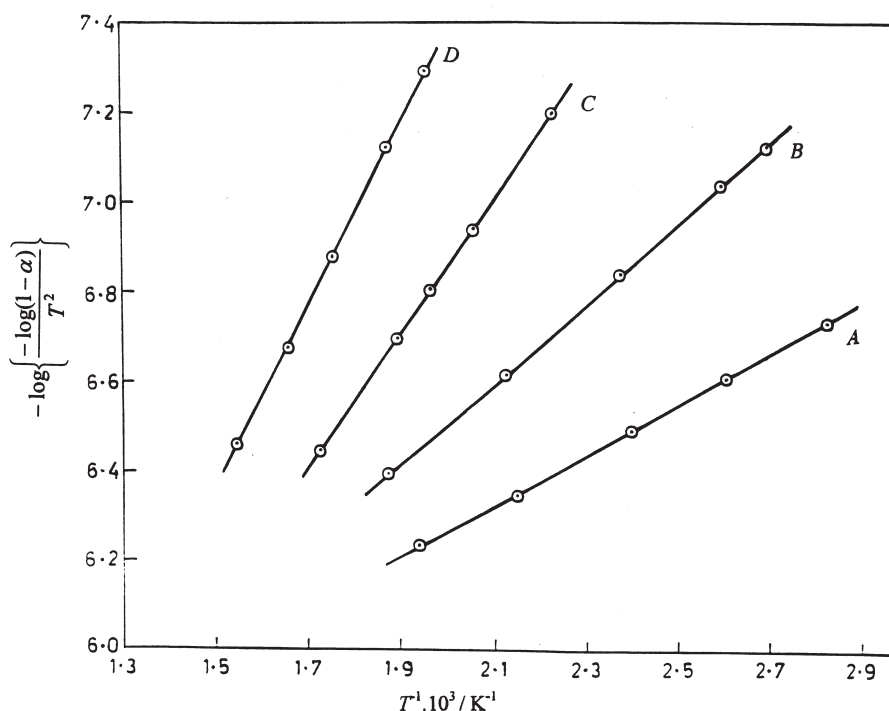
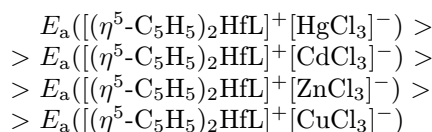**Fig. 3.** Kinetic parameters of complexes from TG.

Table 3. Mass Loss Data of Thymine Complexes

Complex	Relative mass loss/%		Nature of product
	Found	Calc.	
A	50	51.9	HfO_2 and CuO
B	48	51.8	HfO_2 and ZnO
C	49	48	HfO_2 and CdO
D	75	71.6	HfO_2

vealed that the E_a values follow the order

$$E_a([(\eta^5\text{-}C_5H_5)_2HfL]^+[HgCl_3]^-) >$$
$$> E_a([(\eta^5\text{-}C_5H_5)_2HfL]^+[CdCl_3]^-) >$$
$$> E_a([(\eta^5\text{-}C_5H_5)_2HfL]^+[ZnCl_3]^-) >$$
$$> E_a([(\eta^5\text{-}C_5H_5)_2HfL]^+[CuCl_3]^-)$$

This may be explained on the basis of the fact that larger cations are stabilized by larger anions. The complex cation $[(\eta^5\text{-}C_5H_5)_2HfL]^+$ is very large in size and the size of the M(II) ions increases in the order Cu(II), Zn(II), Cd(II), Hg(II). In the $[(\eta^5\text{-}C_5H_5)_2HfL]^+[HgCl_3]^-$ complex, the large size of the Hg(II) ion in the anionic moiety helps in enhanced stabilization of the complex due to lower solubility which arises due to lower solvation. This makes thermal degradation of the complex relatively difficult and thus, the reaction involves a higher E_a value. For the complex $[(\eta^5\text{-}C_5H_5)_2HfL]^+[CuCl_3]^-$, the small size of the Cu(II) ion leads to a relatively poor stabilization

of the complex and thus, the thermal decomposition reaction involves a lower E_a value.

The apparent activation entropy $(S^{\#})$ has been calculated by the method of *Zsakó* [17]. The apparent activation entropy has a positive value for all the complexes. Hence, thermal degradation of these complexes is a spontaneous process. The $[(\eta^5\text{-}C_5H_5)_2HfL]^+[HgCl_3]^-$ complex has the highest $S^{\#}$ value while the $[(\eta^5\text{-}C_5H_5)_2HfL]^+[CuCl_3]^-$ analogue has the lowest one. Hence, the former decomposes with the greatest degree of randomness and the latter with the least.

The heat of reaction (Δh) has been calculated for the thermal effects [18]. The temperature-dependent calibration coefficient was obtained from the Curell equation [19].

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