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Evaluation of the kinetic and thermodynamic parameters for the thermal decomposition of bis(η^5-cyclopentadienyl)titanium(IV) *N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)alkenediamines

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Abstract

The course of the thermal degradation of $(\eta^5\text{-}C_5H_5)_2Ti(SB)$ complexes (SB, Schiff base) has been investigated using thermogravimetric (TG) and differential thermal analysis (DTA) techniques. The order of reaction and activation energy were calculated from the TG curves and the enthalpy change was calculated from the DTA curve. From the evaluated kinetic parameters, a mechanism was suggested for the thermal degradation. Spectral studies (IR, ^{1}H-NMR and UV–visible) indicate that these complexes are tetradentate and octahedral.

INTRODUCTION

In recent years, metal complexes with nitrogen and oxygen donor ligands have been extensively studied as one of the most interesting topics in the field of coordination chemistry and many reports have been documented on the properties and reactivities of such complexes [1–3].

In earlier works [4–6], TG and DTA studies of various nitrogen, oxygen and sulphur donor ligands were carried out under dynamic temperature conditions in order to confirm the purity of the complexes and the correct temperature ranges in which the resulting intermediate decomposition steps attain constant weight, thereby affording gravimetric evaluations of the metal ions.

This paper reports extensive thermoanalytical investigations of tetradentate complexes of bis(η^5-cyclopentadienyl)titanium(IV) with the O and N donor ligands as Schiff bases derived from 2-hydroxynaphthalene-1-

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

carbaldehyde and diamines (ethylenediamine, propylenediamine and hexamethylenediamine).

The present work includes the kinetics of thermal decomposition of these complexes measured under dynamic temperature conditions by both (thermogravimetric) (TG) and differential thermal analysis (DTA) techniques. Evaluation of the kinetic parameters has been performed by means of the Coats–Redfern [7], Piloyan–Novikova [8] and Horowitz–Metzger [9] methods assuming a rate law of the type $\mathrm{d}x/\mathrm{d}t = K(1-\alpha)^n$ and an Arrhenius equation of the type $K = Z\ \mathrm{e}^{-E/RT}$ to be valid, where α represents the fraction transformed, n the order of reaction, K the rate constant and E the activation energy; the graphs for $\log(-\log(1-\alpha)/T^2)$ versus $1/T \times 10^3$, $\log(\alpha/T^2)$ versus $1/T \times 10^3$ and $\log(-\ln(1-\alpha))$ versus $1/T \times 10^3$ gave straight lines with slopes $E/2.303RT$, $E/2.303RT$ and $E\theta/2.303T_{\mathrm{m}}^2$ for the Coats–Redfern, Piloyan–Novikova and Horowitz–Metzger methods respectively, where θ is a reference temperature, $T - T_{\mathrm{m}}$, T_{m} is the peak temperature and R the gas constant.

This paper reports the elucidation of the reaction mechanism on the basis of the evidence provided by the thermoanalytical methods.

EXPERIMENTAL

The TG and DTA curves were recorded simultaneously for powdered samples on a Rigaku 8150 thermoanalyser at the heating rate of 15°C min^{-1}; the chart speed was maintained at 2.5 mm min^{-1}. A platinum crucible was used with alumina as the reference material. IR spectra were recorded on a Shimadzu IR spectrophotometer (IR-435) for measurement of IR spectra in the range 4000–400 cm^{-1} and on a Shimadzu (UV-Vis) model (431) for spectra in the 109–900 nm range; the ^{1}H-NMR studies were carried out on a Hitachi-R-600 F-7 NMR spectrophotometer at a sweep width of 900 Hz and sweep time of 300 s. Schiff bases were derived from the diamines and hydroxyaldehydes in 1:2 molar ratio by refluxing for an hour in ethanol and cooling the mixture in ice bath. The yellowish-brown precipitated mass was separated and recrystallised in ether. The complexes were synthesised in non-aqueous medium in refluxing tetrahydrofuran (THF) in the 1:1 stoichiometric ratio of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and Schiff base in the presence of triethylamine.

The precipitate of $Et_3N \cdot HCl$ was removed from the mixture and the filtrate was evaporated to half volume in a vacuum at room temperature and crystallised in normal hexane. Finally the product was recrystallised from ether and stored in a vacuum desiccator.

RESULTS AND DISCUSSION

The thermal decomposition of $(\eta^5\text{-}C_5H_5)_2Ti(SB)$ complexes follows three steps as shown by the representative scheme below for the thermal decom-

TABLE 1

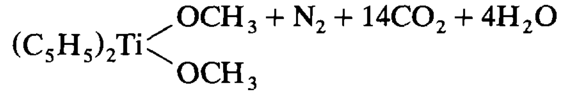
Thermal data

Sample No.	Complex	Step	TG	DTA		Weight loss (%)	ΔH (kJ mol^{-1})
			Range of volatilisation (K)	Thermal effect	T_{max} (K)		
1.	(η^5-C_5H_5)$_2$Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)ethylenediamine)	1	379.0–390.0	Endothermic	386.7	2.023	0.031
		2	430.0–476.0	Exothermic	470.2	18.875	0.121
		3	657.0–870.0	Exothermic	805.3	29.678	2.78
2.	(η^5-C_5H_5)$_2$Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)propylenediamine)	1	405.0–416.5	Endothermic	415.0	2.692	0.038
		2	574.0–610.5	Exothermic	580.8	21.942	0.146
		3	806.0–845.0	Exothermic	826.8	30.614	3.391
3.	(η^5-C_5H_5)$_2$Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)hexamethylenediamine)	1	433.0–442.0	Endothermic	438.3	1.872	0.028
		2	524.0–660.0	Exothermic	623.4	15.342	0.108
		3	670.0–865.0	Exothermic	724.3	27.736	2.034

position of the complex, $(\eta^5\text{-}C_5H_5)_2Ti(N,N'\text{-bis(2-hydroxynaphthalene-1-carbaldene)propylenediamine}$:

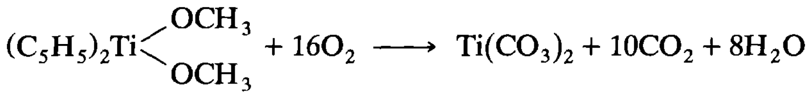
Step I

$(C_5H_5)_2TiC_{16}H_{14}O_2N_2 + 16O_2 \longrightarrow$



$$(C_5H_5)_2Ti(OCH_3)_2 + N_2 + 14CO_2 + 4H_2O$$

Step II



$$(C_5H_5)_2Ti(OCH_3)_2 + 16O_2 \longrightarrow Ti(CO_3)_2 + 10CO_2 + 8H_2O$$

Step III

$Ti(CO_3)_2 \longrightarrow TiO_2 + CO_2$

The degradation pattern of all the complexes is similar. Volatilisation of the complexes ceases, leaving titanium oxide in the crucible of the thermobalance. The percentage weight loss for every step, determined from the TG curves, and the corresponding temperature range for the complexes are

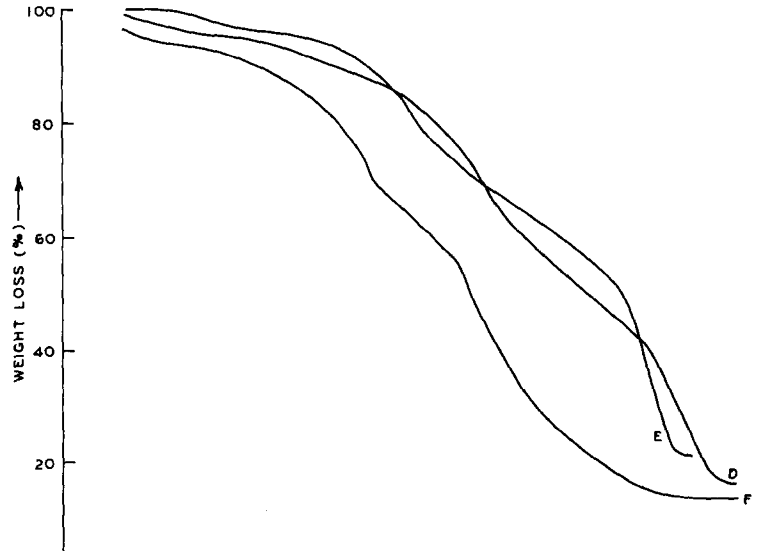


Fig. 1. TG curves: Curve D, $\eta^5\text{-}Cp_2Ti(N,N'\text{-bis(2-hydroxynaphthalene-1-carbaldene)ethylenediamine})$; curve E, $\eta^5\text{-}Cp_2Ti(N,N'\text{-bis(2-hydroxynaphthalene-1-carbaldene)propylenediamine})$; curve F, $\eta^5\text{-}Cp_2Ti(N,N'\text{-bis(2-hydroxynaphthalene-1-carbaldene)hexamethylenediamine})$.

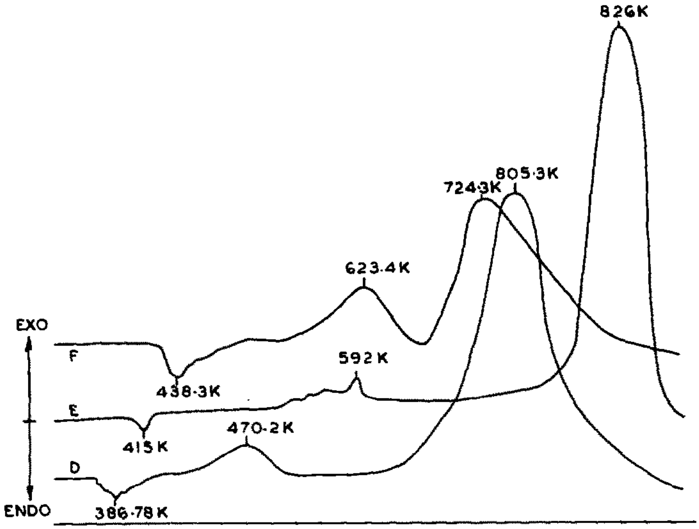


Fig. 2. DTA curves: curve D, η^5-Cp_2Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)ethylenediamine); curve E, η^5-Cp_2Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)propylenediamine); curve F, η^5-Cp_2Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)hexamethylenediamine).

presented in Table 1. From the plots of the thermal effects of the DTA curves, it is shown that Step I of the decomposition is endothermic while Steps II and III are exothermic in nature. The TG and DTA curves are shown in Figs. 1 and 2 respectively.

The following IR absorption bands were assigned: approx. 3100 cm^{-1}, ν(C–H); 1450 cm^{-1}, ν(C–C); 1015 cm^{-1}, δ(in plane)(C–H); 810 cm^{-1}, δ(out of plane)(C–H); 440 cm^{-1}, ν(Ti–C_5H_5) vibrations; approx. 1625 cm^{-1}, (–HC=N–) azomethine group; and 1320–1310 cm^{-1}, C–O stretching.

Bands appearing in the UV–visible spectra at 250, 320 and 385 nm are due to $\pi \rightarrow \pi^*$ (benzoid), $\pi \rightarrow \pi^*$ (azomethine) and $\eta \rightarrow \pi^*$ (azomethine) electronic transitions. The presence of a single band in the 402–412 nm range corresponds to the $(n-1)\ d^0$, nS^0 electronic configuration of titanium [10]. The ^1H-NMR studies of these complexes reveal a sharp singlet at approx. δ 8.4 ppm for the resonance of C_5H_5 about the metal axis. The downfield shift relative to the free ligand indicates coordination of nitrogen through the metal atom [11]. The disappearance of phenolic signals from the complexes indicate that the oxygen participates in bond formation with the metal atom [12]. The above information suggests a tetradentate nature for the ligands and an octahedral geometry for the complexes.

The TG and DTA curves indicate that the first step of decomposition is endothermic which may be caused by the adiabatic expansion of liberated N_2, CO_2 and water vapour, while the second and third steps are exother-

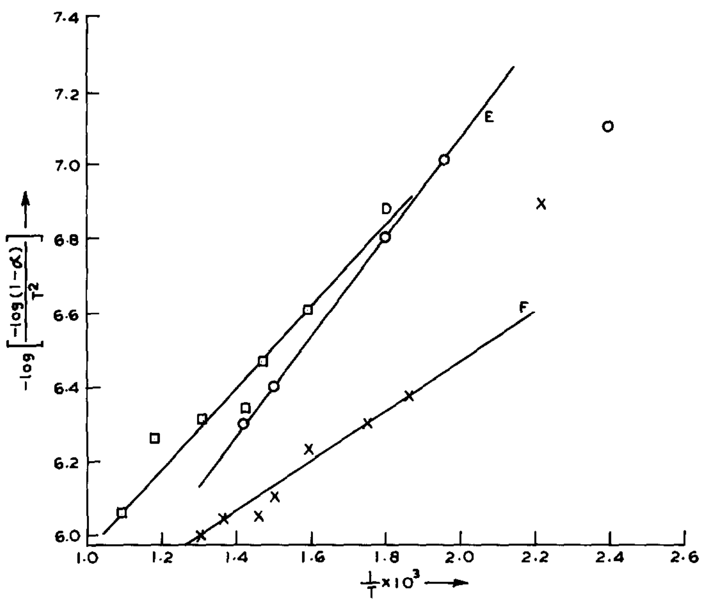


Fig. 3. TG curves plotted by the Coats–Redfern method [7]: curve D, η^5-Cp_2Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)ethylenediamine); curve E, η^5-Cp_2Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)propylenediamine); curve F, η^5-Cp_2Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)hexamethylenediamine).

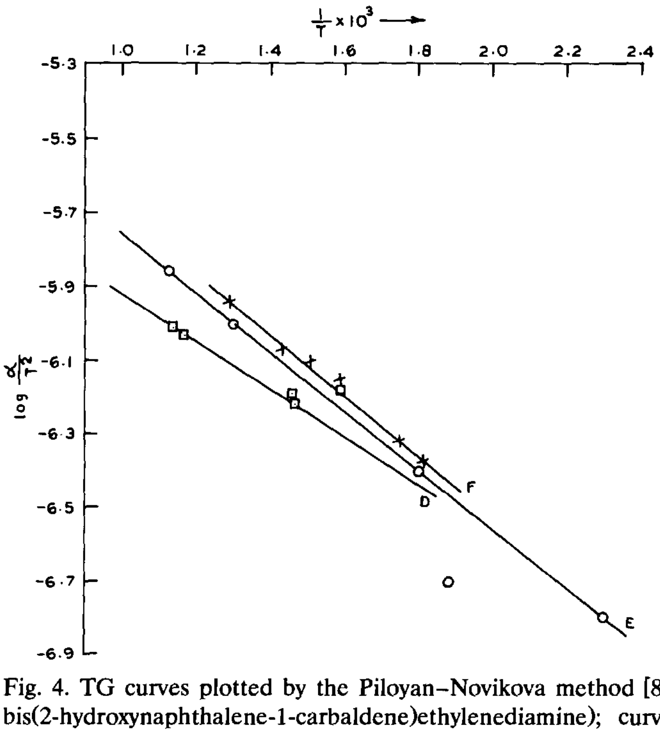


Fig. 4. TG curves plotted by the Piloyan–Novikova method [8]: curve D, η^5-Cp_2Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)ethylenediamine); curve E, η^5-Cp_2Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)propylenediamine); curve F, η^5-Cp_2Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)hexamethylenediamine).

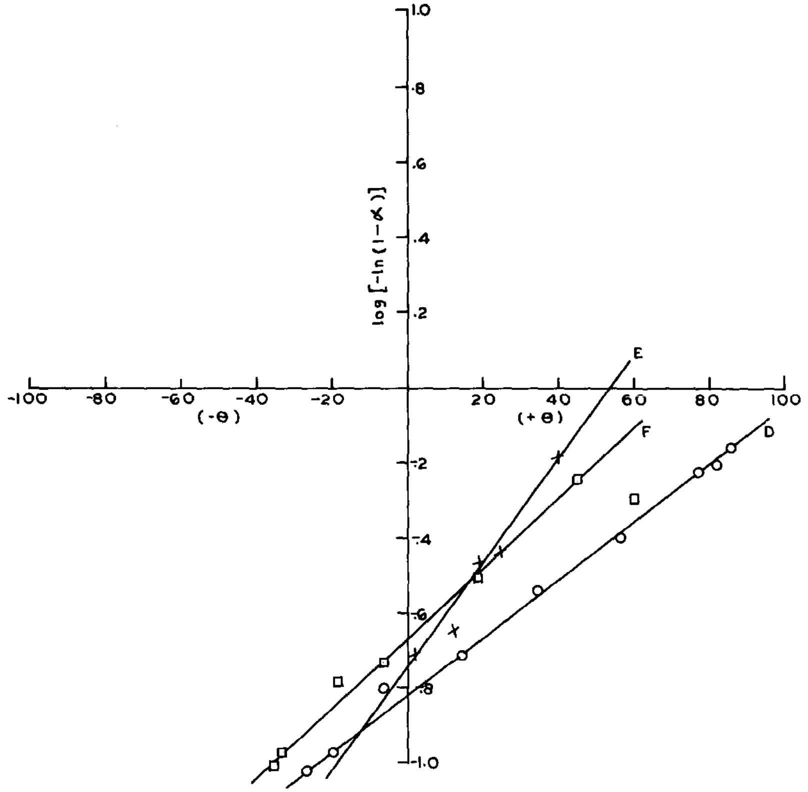


Fig. 5. TG curves plotted by the Horowitz–Metzger method [9]: curve D, η^5-Cp_2Ti(N,N'-bis(2-hydroxynaphthalene-1-carbaldene)ethylenediamine); curve E, η^5-Cp_2Ti(N,N'-bis(2-hydroxynaphthalene-1-carbaldene)propylenediamine); curve F, η^5-Cp_2Ti(N,N'-bis(2-hydroxynaphthalene-1-carbaldene)hexamethylenediamine).

mic, probably due to cleavage of $-OCH_3$ and CO_3^{2-} into CO_3^{2-} and O^{2-} and metal oxide in the second and third steps respectively.

From the TG curves, the order of reaction n, the fractional weight loss α and the activation energy E for the final step of the thermal reaction have been determined from plots of the Coats–Redfern (Fig. 3), Piloyan–Novikova (Fig. 4) and Horowitz–Metzger (Fig. 5) methods, while the value of the entropy of activation ΔS^* was computed from the equation

$$Z = \frac{KT}{h} \exp \frac{\Delta S^*}{R}$$

where K is the Boltzmann constant and h the Planck constant. Z was calculated after calculating the energy of activation E from the slope of the respective plots and Z was determined from the equation

$$Z = \frac{E}{RT^2} \beta \exp \frac{E}{RT}$$

TABLE 2

Kinetic parameters of the complexes for the final step

Sample No.	Compound	Calibration constant K (kJ cm^{-2})	Equations	Order of reaction n	E (kJ mol^{-1})	Z [a] (s^{-1})	ΔS^* (kJ mol^{-1})
1.	$(\eta^5\text{-}C_5H_5)_2Ti(N,N'$-bis(2-hydroxynaphthalene-1-carbaldene)ethylenediamine)	0.11535	Coats–Redfern	1	15.465	0.147×10^{-11}	−478.591
			Piloyan–Novikova	1	8.627	0.507×10^{-12}	−278.067
			Horowitz–Metzger	1	11.720	0.468×10^{-12}	−453.313
2.	$(\eta^5\text{-}C_5H_5)_2Ti(N,N'$-bis(2-hydroxynaphthalene-1-carbaldene)propylenediamine)	0.11262	Coats–Redfern	1	14.386	0.137×10^{-11}	−479.161
			Piloyan–Novikova	1	7.689	0.922×10^{-12}	−270.102
			Horowitz–Metzger	1	12.987	0.672×10^{-12}	−460.412
3.	$(\eta^5\text{-}C_5H_5)_2Ti(N,N'$-bis(2-hydroxynaphthalene-1-carbaldene)hexamethylenediamine)	0.12585	Coats–Redfern	1	9.754	0.113×10^{-11}	−568.390
			Piloyan–Novikova	1	6.503	0.439×10^{-12}	−290.346
			Horowitz–Metzger	1	7.456	0.534×10^{-12}	−489.230

[a] Boltzmann constant = 1.3805×10^{-23} J K^{-1}; Planck's constant = 6.62×10^{-34} J s.

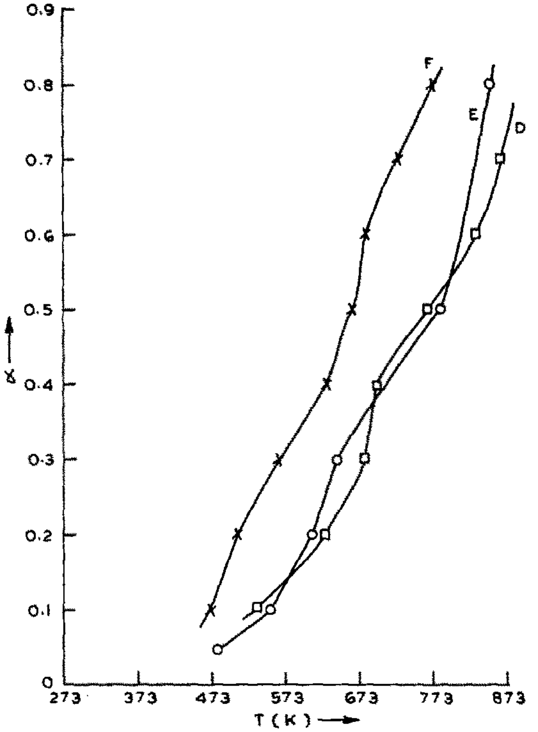


Fig. 6. Plots of the fractional weight loss versus temperature: curve D, η^5-Cp_2Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)ethylenediamine); curve E, η^5-Cp_2Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)propylenediamine); curve F, η^5-Cp_2Ti(*N*,*N*′-bis(2-hydroxynaphthalene-1-carbaldene)hexamethylenediamine).

where β is the rate of heating. Finally ΔS^* was determined from each plot for the final step. The comparative kinetic parameters are listed in Table 2. The values of the heat of reaction ΔH, in microvolts, were obtained directly from the computer fitted to the thermoanalyser; it was converted to kJ mol^{-1} using the relationship

$$\Delta H\ (\text{kJ mol}^{-1}) = \Delta H\ (\mu\text{V}) \times 60 \times \text{molecular wt.} \times 10^{-6}/1000$$

The temperature-dependent calibration constant was obtained from the Currell equation [13]. The plots for fractional weight loss of the complexes versus temperature, Fig. 6, represent the comparative temperature-enduring capacity of the complexes for the final step of the decomposition reaction.

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REFERENCES

1 K. Dey, D. Konar, A.K. Biswas and S. Ray, J. Chem. Soc., Trans., 13 (1983) 491.
2 K. Dey, S. Ray and D. Bandyopadhyay, Proc. Natl. Acad. Sci. India Sect. A, 59(II) (1989) 179.
3 G. Pokhriyal, Proc. Natl. Acad. Sci. India Sect. A, 58(III) (1988) 369.
4 N.K. Kaushik, B. Bhushan and A.K. Sharma, Thermochim. Acta, 76 (1984) 345.
5 S.S. Gupta and N.K. Kaushik, Thermochim. Acta, 106 (1986) 233.
6 S. Bhatia, N.K. Kaushik and G.S. Sodhi, Main Group Metal Chemistry, (Israel), 12(3,4) (1989) 225.
7 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
8 G.O. Piloyan and I.S. Novikova, Russ. J. Inorg. Chem., 12 (1967) 313.
9 H. Horowitz and G. Metzger, Anal. Chem., 35 (1964) 1464.
10 N.K. Kaushik, B. Bhusan and G.R. Chhatwal, J. Inorg. Nucl. Chem., 42 (1980) 457.
11 B. Khera and N.K. Kaushik, Synth. React. Inorg. Met.-Org. Chem., 14(1) (1984) 57.
12 A.K. Sharma, B. Khera and N.K. Kaushik, Monatsh. Chem., 114 (1983) 907.
13 B.R. Currell, in R.F. Schwenter and P.D. Garn (Eds.), Thermal Analysis, Vol. 2, Academic Press, New York, 1969, p. 1185.