

Thermoanalytical behaviour of carbaryl and its copper(II) and zinc(II) complexes

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Abstract Non-isothermal techniques, i.e. thermogravimetry (TG) and differential scanning calorimetry (DSC), have been applied to investigate the thermal behaviour of carbaryl (1-naphthyl-*N*-methylcarbamate = 1-Naph-*N*-Mecbm) and its complexes, $M(1\text{-Naph-}N\text{-Mecbm})_4X_2$, where $M = \text{Cu}$, $X = \text{Cl}$, NO_3 and CH_3COO and $M = \text{Zn}$, $X = \text{Cl}$. Carbaryl and $\text{Zn}(1\text{-Naph-}N\text{-Mecbm})_4\text{Cl}_2$ complex exhibit two-stage thermal decomposition while the copper(II) complexes exhibit three and four-stage decomposition in their TG curves. The nature of the metal ion has been found to play highly influential role on the nature of thermal decomposition products as well as energy of activation ' E^* '. The presence of different anions does not seem to alter the thermal decomposition patterns. The complexes display weak to medium intensity exothermic and endothermic DSC curves, while the free ligand exhibits two endothermic peaks. The kinetic and thermodynamic parameters namely, the energy of activation ' E^* ', the frequency factor ' A ' and the entropy of activation ' S^* ' etc. have been rationalized in relation to the bonding aspect of the carbaryl ligand. The nature and chemical composition of the residues of the decomposition steps have been studied by elemental analysis and FTIR data.

Keywords 1-Naphthyl-*N*-methylcarbamate · Copper(II) · Zinc(II) · TG · DSC · Coats Redfern Method, Residues

Introduction

Carbamates are of particular interest due to their applications in polymer industry [1–4], as agrochemicals [1–3, 5, 6] and pharmaceuticals, [1–3, 7] etc. The decomposition of carbamates is a fairly slow process, and catalysts have been proposed to speed up the reaction [8]. Thermal decomposition of carbamates has been reported in the literature to give varied products such as amine, alkene, carbon dioxide, alcohol and isocyanate depending upon the type of carbamate [8–10]. However, thermal investigations on metal carbamates are scanty. In view of this, the present investigation attempts to determine the thermal stability and decomposition patterns of some metal carbamate complexes, viz. $M(1\text{-Naph-}N\text{-Mecbm})_4X_2$ ($M = \text{Cu}$, $X = \text{Cl}$, NO_3 and CH_3COO ; $M = \text{Zn}$, $X = \text{Cl}$) by thermogravimetric (TG) measurements under non-isothermal conditions in air atmosphere. It becomes important to mention that 1-Naph-*N*-Mecbm is a commercial insecticide. Kinetic parameters of thermal reactions have been computed and correlated to provide a deep insight into the thermoanalytical decomposition patterns of the above-said compounds.

Experimental

The high purity standard of carbaryl (insecticide) was supplied by the courtesy of the Environmental Protection Agency (EPA), NC, USA. Its copper(II) and zinc(II) complexes, viz. $M(1\text{-Naph-}N\text{-Mecbm})_4X_2$ ($M = \text{Cu}$, $X = \text{Cl}$, NO_3 and CH_3COO and $M = \text{Zn}$, $X = \text{Cl}$) were obtained by the method as reported in the reference [11]. Anal. (%) $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4\text{Cl}_2$ Found: C, 60.90; H, 4.25; N, 5.86; Cu, 6.41; Cl, 7.25; Calculated: C, 61.37; H, 4.69; N, 5.97; Cu, 6.77; Cl, 7.56: Decomposition

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temperature: 210 °C, yield: 40%; IR (KBr) cm^{-1} : 1625 (C=O); 1424 (CN); 342 (MO); Anal. (%) $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4(\text{NO}_3)_2$ Found: C, 58.25; H, 4.65; N, 8.30; Cu, 6.782; Calculated: C, 58.09; H, 4.44; N, 8.47; Cu, 6.41; Cl, 7.56; Decomposition temperature: 262 °C, yield: 40%; IR (KBr) cm^{-1} : 1639 (C=O); 1427 (CN); 342 (MO); Anal. (%) $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4(\text{CH}_3\text{COO})_2$ Found: C, 63.50; H, 5.27; N, 5.85; Cu, 6.95; Calculated: C, 63.31; H, 5.07; N, 5.68; Cu, 6.45; Decomposition temperature: above 360 °C, yield: 50%; IR (KBr) cm^{-1} : 1632 (C=O); 1422 (CN); 344 (MO) and Anal. (%) $\text{Zn}(1\text{-Naph-}N\text{-Mecbm})_4\text{Cl}_2$ Found: C, 61.10; H, 6.32; N, 6.16; Cu, 6.27; Cl, 7.47; Calculated: C, 61.25; H, 6.32; N, 6.16; Cu, 6.27; Cl, 7.47; Decomposition temperature: 310 °C, yield: 50%; IR (KBr) cm^{-1} : 1712 (C=O); 1389 (CN); 342 (MO). Thermal analyses of the complexes were carried out on Thermogravimetric Analyzer (TGA)—Model 2950, Make—TA Instruments, USA and Differential Scanning Calorimeter (DSC)—Model 2920, Make—TA Instruments, USA. The thermocouple used was Pt/Pt—Rh (10%) with a temperature range of 20–1,200 °C. Thermal investigations were carried out by heating the sample (3 mg) in a Pt crucible in a static air atmosphere, and Al_2O_3 was taken as reference. A heating rate of 10 °C min^{-1} was employed. The TG data was analysed by using Coats and Redfern equation for calculating kinetic and thermodynamic parameters. The instrument calibration was checked periodically with a sample of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Results and discussion

Carbaryl, i.e. 1-Naph-*N*-Mecbm (Fig. 1) and its copper(II) and zinc(II) compounds, the thermal studies of which have been conducted in the air, exhibit their melting/decomposition temperatures ranging from 143 to >360 °C (obtained in open glass capillaries). Owing to the paucity of the literature reports on the thermal decomposition patterns of metal carbamates, it was considered worthwhile to investigate their thermal stability using TG and differential scanning calorimetric (DSC) analytical techniques. The TG curves of free ligand, 1-Naph-*N*-Mecbm and its complexes, viz. dichlorotetrakis(1-naphthyl-*N*-methylcarbamate)zinc(II) and $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4\text{X}_2$, X = Cl, NO_3 and CH_3COO are illustrated in Figs. 2, 3, 4, 5, 6, and thermal data (Table 1) has been inferred from these curves. The possible schemes of decomposition for 1-Naph-*N*-Mecbm (carbaryl) ligand and its copper(II) and zinc(II) complexes, viz. $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4\text{X}_2$, X = Cl, CH_3COO and NO_3 and $\text{Zn}(1\text{-Naph-}N\text{-Mecbm})_4\text{Cl}_2$ have been suggested from TG curves (Figs. 2, 3, 4, 5, 6) using TG and DSC analytical techniques.

The TG curve (Fig. 2) of free ligand (1-Naph-*N*-Mecbm) exhibits a plateau and depicted it to be fairly stable up

Fig. 1 1-Naphthyl-*N*-methylcarbamate

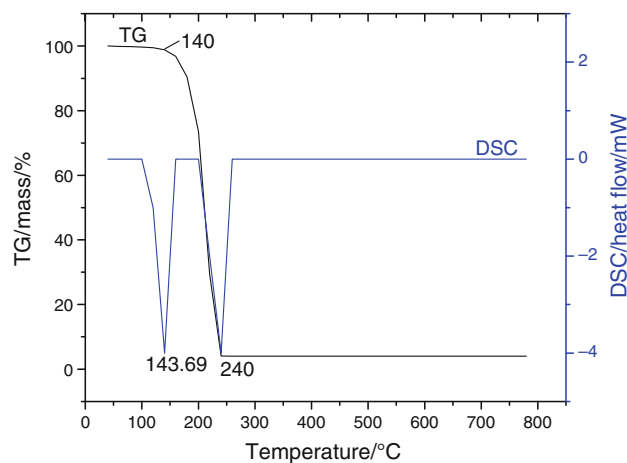
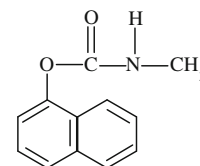


Fig. 2 TG/DSC curves of 1-Naph-*N*-Mecbm

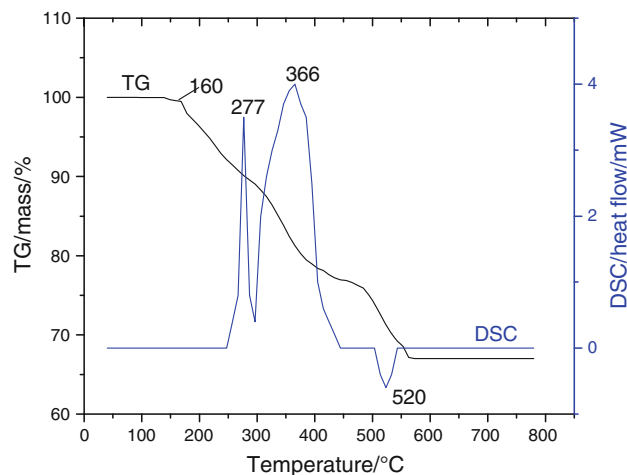
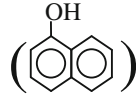


Fig. 3 TG/DSC curves of $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4\text{Cl}_2$

to 140 °C. The free ligand shows two step thermal decompositions though its TG curve shows a continuous mass loss corresponding to two different volatile species between 140–200 and 200–240 °C. The TG curve of the ligand for the first step has shown a mass loss of 28% between 140 and 200 °C which can be ascribed to the loss of methyl isocyanate (CH_3NCO) moiety. A mass loss of 71.5% against the theoretical loss of 71.64% in the second decomposition step in the temperature range 200–240 °C has been accounted

for the loss of naphthol () moiety. The two step decomposition amounting to 28 and 71.5% loss of methyl

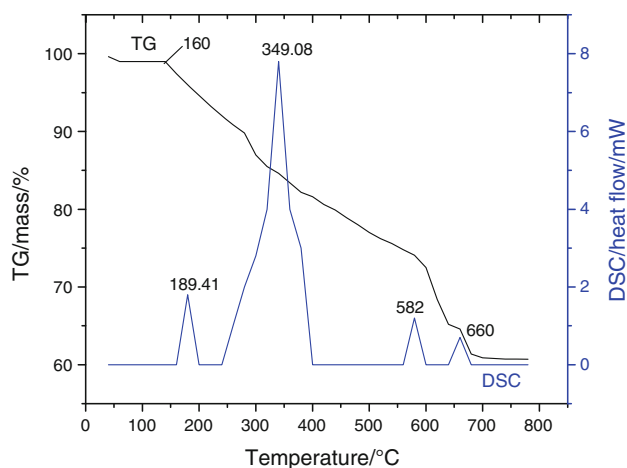


Fig. 4 TG/DSC curves of $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4(\text{NO}_3)_2$

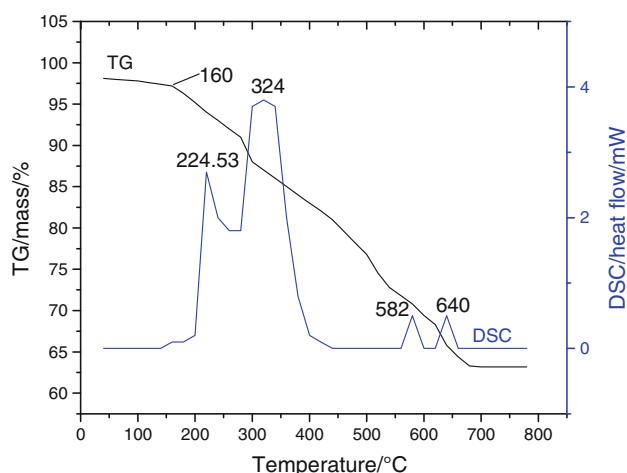


Fig. 5 TG/DSC curves of $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4(\text{CH}_3\text{COO})_2$

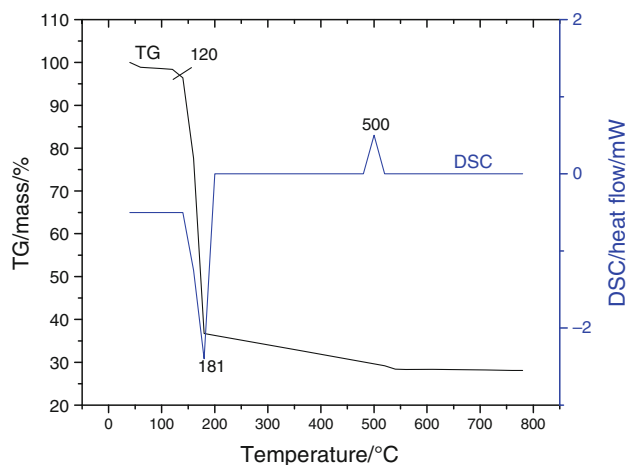


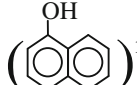
Fig. 6 TG/DSC curves of $\text{Zn}(1\text{-Naph-}N\text{-Mecbm})_4\text{Cl}_2$

isocyanate and naphthol moieties, respectively, equal to a sum of 99.5% is in consonance with approximately 100% mass loss of carbaryl (1-Naph-*N*-Mecbm) leaving no

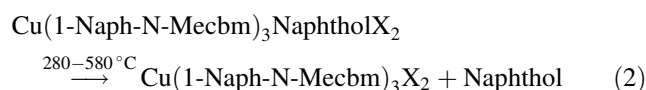
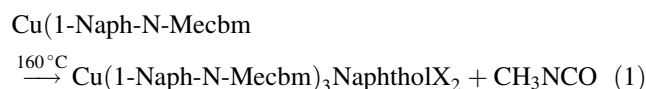
residue in the crucible up to 240 °C. The DSC curve (Fig. 2) of the ligand shows an endothermic peak at 143.69 °C in conformity with its melting point; the decomposition in TG curve is accompanied by an endothermic peak at 240 °C lying between 200 and 260 °C.

The TG curves (Figs. 3, 4, 5) of $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4\text{X}_2$, $\text{X} = \text{Cl}, \text{NO}_3$ and CH_3COO reveal them to be stable up to 160 °C. This suggests that coordination of 1-Naph-*N*-Mecbm (Fig. 1) to the metal ion enhances the overall stability of the complexes.

Interestingly, the initial temperature of decomposition (IDT) has not been found to be dependent on the nature of the anions. The complexes dichlorotetrakis(1-naphthyl-*N*-methylcarbamate)copper(II) and $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4\text{X}_2$ ($\text{X} = \text{NO}_3$ and CH_3COO) have been observed to display three and four step decomposition patterns, respectively. The striking feature of the first step decomposition for the three copper(II) complexes is that they exhibit a mass loss of 6% for all the three complexes in the temperature range 160–280 °C. This has been attributed to the liberation of 1 mole of volatile moiety, methyl isocyanate (CH_3NCO) with the formation of $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_3\text{NaphtholX}_2$ ($\text{X} = \text{Cl}, \text{NO}_3$ and CH_3COO) as the possible intermediate in each case. The second stage of decomposition showing a mass loss of about 15% in the temperature range 280–580 °C (Table 1) has been observed to be associated

with the loss of 1 mole of naphthol () moiety, in







good agreement to the theoretical values. The following reactions (Eqs. 1 and 2) are proposed for two-stage thermal decompositions yielding the similar type of



where $\text{X} = \text{Cl}, \text{NO}_3$ and CH_3COO intermediate, i.e. $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_3\text{X}_2$, where $\text{X} = \text{Cl}, \text{NO}_3$ and CH_3COO . Thereafter, the third step decomposition depicts the thermal decomposition behaviour depending upon the nature of the anion.

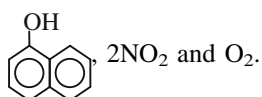
For the complex dichlorotetrakis(1-naphthyl-*N*-methylcarbamate)copper(II), a further mass loss of 8% against the theoretical mass loss of 7.6% in the temperature range 480–560 °C has been accounted for the liberation of chlorine (Cl_2) molecule with the formation of $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_3$ as the highly stable final product of decomposition. The decomposition in TG curve (Fig. 3) for the complex has been supplemented by two exothermic DSC

Table 1 Thermal decomposition data of 1-Naph-N-Mecbm and its complexes with copper(II) and zinc(II)

Sr. no.	Compound mol. mass	Sample mass/mg	Initial dec. temp/°C	Stages of dec.	TG temperature/°C	Mass loss/% (mol. mass)		Theor. mass left/ % mol mass	Species lost	Species formed	DTA peak/ °C	Nature
						Exp.	Theo.					
1	1-Naph-N-Mecbm 201	5	140	1st	140–200	28 (56.28)	28.35 (57)	71.64 (144)	CH ₃ NCO		143.69	Endo
				2nd	200–240	71.5 (143.7)	71.5 (144)	0		–	240	Endo
2	Cu(1-Naph-N-Mecbm) ₄ Cl ₂ 938.5	5	160	1st	160–280	6 (56.31)	6 (57)	93.93 (881.5)	CH ₃ NCO	Cu(1-Naph-N-Mecbm) ₃ NaphtholCl ₂	277	Exo
				2nd	280–480	15.13 (142)	15.34 (144)	78.95 (737.5)		Cu(1-Naph-N-Mecbm) ₃ Cl ₂	366	Exo
				3rd	480–560	8 (75.08)	7.60 (71)	71.37 (666.5)	Cl ₂	Cu(1-Naph-N-Mecbm) ₃	520	Endo
3	Cu(1-Naph-N-Mecbm) ₄ (NO ₃) ₂ 991.54	5	160	1st	160–280	6 (59.49)	5.75 (57)	94.23 (934.54)	CH ₃ NCO	Cu(1-Naph-N-Mecbm) ₃ Naphthol(NO ₃) ₂	189.41	Exo
				2nd	280–580	14.72 (145)	14.52 (144)	79.73 (790.54)		Cu(1-Naph-N-Mecbm) ₃ (NO ₃) ₂	349.08	Exo
				3rd	580–640	9.5 (94)	9.28 (92)	70.46 (698.54)	2NO ₂	Cu(1-Naph-N-Mecbm) ₃ O ₂	582	Exo
				4th	640–680	3.4 (33.71)	3.2 (32)	67.2 (666.54)	O ₂	Cu(1-Naph-N-Mecbm) ₃	660	Exo
4	Cu(1-Naph-N-Mecbm) ₄ (CH ₃ COO) ₂ 985.5	5	160	1st	160–280	6 (59.13)	5.78 (57)	94.22 (928.5)	CH ₃ NCO	Cu(1-Naph-N-Mecbm) ₃ Naphthol(CH ₃ COO) ₂	224.53	Exo
				2nd	280–500	14.71 (145)	14.61 (144)	79.61 (784.5)		Cu(1-Naph-N-Mecbm) ₃ (CH ₃ COO) ₂	324	Exo
				3rd	500–620	9 (88.69)	8.92 (88)	70.69 (696.5)	2CO ₂	Cu(1-Naph-N-Mecbm) ₃ C ₂ H ₆	582	Exo
				4th	620–680	3 (29.56)	3.04 (30)	67.65 (666.5)	C ₂ H ₆	Cu(1-Naph-N-Mecbm) ₃	640	Exo
5	Zn(1-Naph-N-Mecbm) ₄ Cl ₂ 940.4	5	120	1st	120–180	63.25 (595)	64.12 (603)	35.88 (337.4)		Zn(1-Naph-N-Mecbm)Cl ₂	181.04	Endo
				2nd	180–520	7.54 (70.90)	7.55 (71)	28.12 (266)	Cl ₂	Zn(1-Naph-N-Mecbm)	500	Exo

curves at 277 and 366 °C and one endothermic peak at 520 °C.

For the complex dinitratotetrakis(1-naphthyl-*N*-methylcarbamate)copper(II), the subsequent mass loss of 9.5% in the temperature range 580–640 °C has been proposed due to the loss of 2 moles of nitrogen dioxide (NO₂) moiety corresponding to the theoretical value of 9.28%. This is followed by a mass loss of 3.4% due to the loss of 1 mole of oxygen (O₂) within the temperature range 640–680 °C in the fourth step of decomposition, leaving a high percentage of the residue Cu(1-Naph-*N*-Mecbm)₃, 66.4% in the crucible. The four-stage decomposition in the TG curve (Fig. 4) for the complex is accompanied by four exothermic peaks at 189.41, 349.08, 582 and 660 °C, being attributed to the volatile products such as CH₃NCO,



However, for the complex diacetatotetrakis(1-naphthyl-*N*-methylcarbamate)copper(II), the third stage of decomposition shows a mass loss of 9% in the temperature range 500–620 °C, in equivalence with the theoretical value of 8.92% calculated for the loss of 2 moles of carbon dioxide (CO₂). This step is followed by the loss of another volatile product, i.e. ethane (C₂H₆) in the temperature range 620–680 °C equivalent to the experimental mass loss of 3% in consonance with the theoretical mass loss of 3.04% forming Cu(1-Naph-*N*-Mecbm)₃ as the ultimate product of thermal decomposition. This product exhibits very high stability even up to 800 °C. The third and fourth steps of thermal decomposition for the complexes having NO₃ and

CH₃COO as the anions are based on respective anionic decompositions. The DSC curve (Fig. 5) of the complex has shown four exothermic peaks at 224.53, 324, 520 and

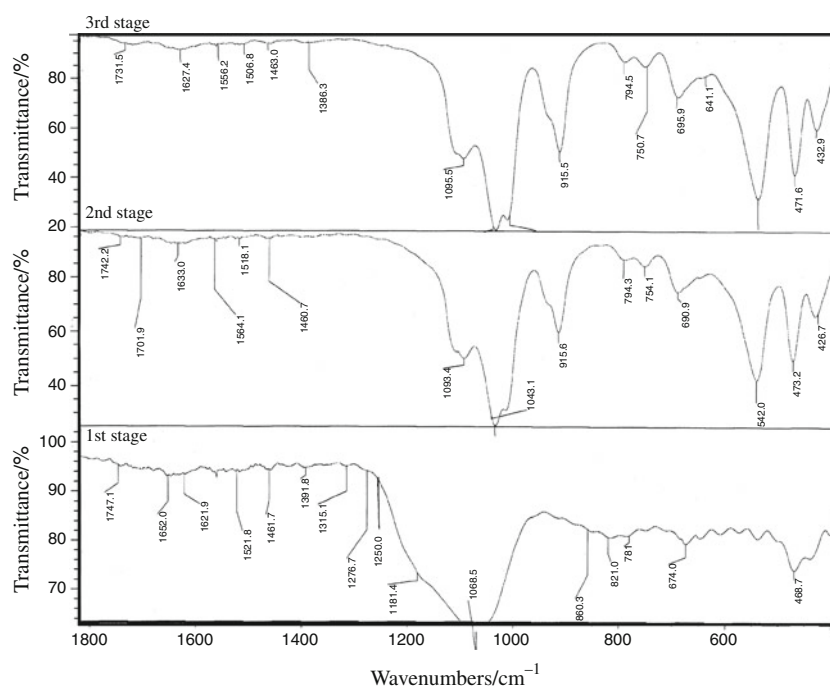
640 °C due to the volatile products CH₃NCO, CO₂ and C₂H₆.



That dichloronaphtholtris(1-naphthyl-*N*-methylcarbamate)copper(II) and dichlorotris(1-naphthyl-*N*-methylcarbamate)copper(II) are the first step and second step intermediates in the TG/DSC study of the complex Cu(1-Naph-*N*-Mecbm)₄Cl₂ has further been ensured by halting its thermal decomposition stages so as to collect the residues of the proposed intermediates. The chemical composition of these species and the nature of the organic moiety present have been confirmed by the elemental analysis (copper and chloride content) and by recording the FTIR spectrum of the species. The FTIR spectrum of the proposed species of the residue of the 1st stage, i.e. Cu(1-Naph-*N*-Mecbm)₃NaphtholCl₂ (Fig. 7) exhibits some additional bands at 1391.8, 1315 and near 1276.7 cm⁻¹ due to O–H in-plane bending vibrations, and the band at 1,250 cm⁻¹ is assigned to the coupled vibrations of O–H in-plane bending and C–O stretching vibrations of O–H group. Another weak band at 860.3 cm⁻¹ represents O–H out of plane bending vibrations [12]. All these bands corresponding to naphthol are in addition to those bands present in the parent copper(II) complex, i.e. Cu(1-Naph-*N*-Mecbm)₄Cl₂.

For second-stage intermediate tris(1-naphthyl-*N*-methylcarbamate)copper(II), FTIR bands for naphthol species

Fig. 7 FTIR spectrum of TG residues left of complex Cu(1-Naph-*N*-Mecbm)₄Cl₂



are absent while bands due to organic moiety are highly intense and characteristic of carbaryl. The IR spectral bands of second- and third-stage residues are exactly similar to each other wherein the final residue (3rd stage) is obtained by the loss of Cl_2 molecule (Fig. 7).

Anal. (%) $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_3\text{NaphtholCl}_2$: Found: Cu, 7.5; Cl, 8.25; Calculated: Cu, 7.20; Cl, 8.05; $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_3\text{Cl}_2$: Found: Cu, 8.8; Cl, 9.9; Calculated: Cu, 8.61; Cl, 9.63; $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_3$: Found: Cu, 9.8; Calculated: Cu, 9.53.

Additional evidence on the decomposition mechanism for $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4\text{X}_2$ ($\text{X} = \text{NO}_3$ and CH_3COO) was obtained from the elemental and FTIR analysis of the last-stage residue, having same chemical nature for both of the complexes, i.e. $\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_3$. Anal. (%) Found: Cu, 9.36 and 9.58%; Calculated: Cu, 9.53, respectively.

These results of final-stage residues of all the copper(II) carbamate complexes are fully consistent with each other.

The curve of the complex dichlorotetrakis(1-naphthyl-*N*-methylcarbamate)zinc(II) shows the stability up to 120 °C exhibiting a plateau in the curve up to this temperature after which the complex decomposes exothermally in two steps. A mass loss of 63.25% against the theoretical mass loss of 64.12% within the temperature range 120–180 °C corresponds to the loss of three molecules of carbaryl and has been related to the formation of dichloro(1-naphthyl-*N*-methylcarbamate)zinc(II) as the stable intermediate in the first step of decomposition. Further mass loss of 7.54% against the theoretical mass loss of 7.55% in the temperature range 180–520 °C has

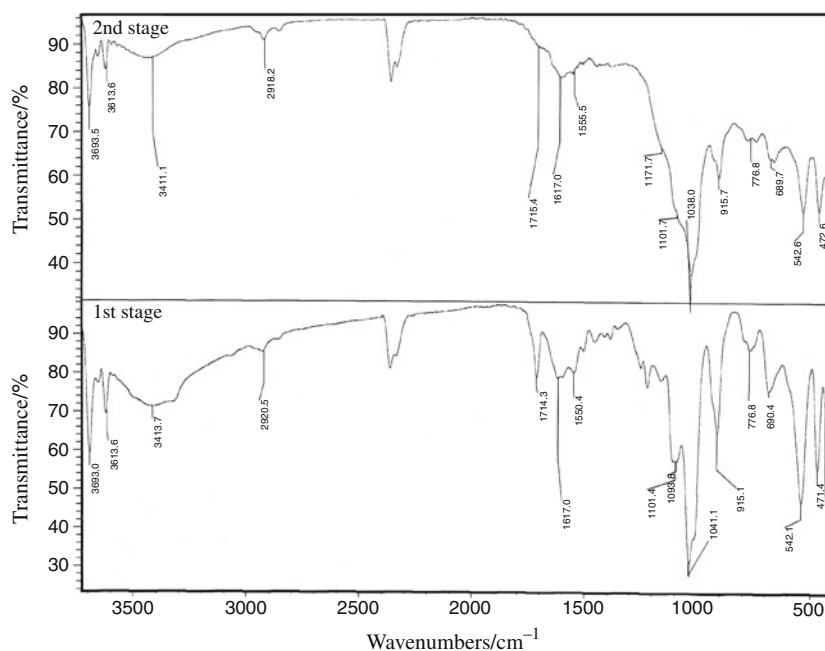
been accounted for the loss of chlorine (Cl_2) molecule leaving behind the $\text{Zn}(1\text{-Naph-}N\text{-Mecbm})$ as the ultimate product of decomposition. The DSC curve (Fig. 6) has shown an endothermic peak at 181 °C accompanied by an exothermic peak at 500 °C, which may be attributed to the sublimation followed by loss of 1 mole of chlorine (Cl_2).

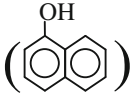
The characterization of the first and second step intermediate species, i.e. $\text{Zn}(1\text{-Naph-}N\text{-Mecbm})\text{Cl}_2$ and $\text{Zn}(1\text{-Naph-}N\text{-Mecbm})$ for the TG/DSC for $\text{Zn}(1\text{-Naph-}N\text{-Mecbm})_4\text{Cl}_2$ complex has further been explored for the FTIR and elemental analysis data. The FTIR (Fig. 8) of both the intermediates are exactly similar to each other exhibiting peculiar absorptions of the carbaryl molecule at $\sim 1,714\text{ cm}^{-1}$ ($\nu(\text{C}=\text{O})$), $\sim 3411\text{ cm}^{-1}$ ($\nu(\text{N}-\text{H})$) alongwith far IR absorptions of parent metal complex at 342 cm^{-1} because of $\nu(\text{M}-\text{O})$ vibrations.

Anal. (%) $\text{Zn}(1\text{-Naph-}N\text{-Mecbm})\text{Cl}_2$: Found: Zn, 19.1; Cl, 21; Calculated: Zn, 19.38; Cl, 21.04; $\text{Zn}(1\text{-Naph-}N\text{-Mecbm})$: Found: Zn, 25.2; Calculated: Zn, 25.5.

Carbamates are reported to decompose thermally either by liberating isocyanate and alcohol or by forming amine, an olefin and carbon dioxide [8–10]. On the basis of the observed TG data, it is of interest to note that for the three copper(II) complexes under study nature of the anions does not seem to alter the composition of the final product of thermal decomposition. However, thermal decomposition patterns have been found to be highly dependent upon the nature of the metal ion, i.e. copper and zinc. Copper exhibits strong binding effect with 1-Naph-*N*-Mecbm ligand as compared with zinc metal ion. This is evident from the fact that only one 1-Naph-*N*-Mecbm ligand has

Fig. 8 FTIR spectrum of TG residues left of complex $\text{Zn}(1\text{-Naph-}N\text{-Mecbm})_4\text{Cl}_2$



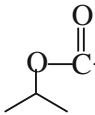
been found to get decomposed into methyl isocyanate (CH_3NCO) and naphthol () in the temperature

range 160–580 °C alongwith loss of the respective anionic moieties, while the three ligand molecules remain intact with copper(II) even up to temperature as high as 800 °C. The fact that bonding of 1-Naph-*N*-Mecbm ligand with zinc(II) is relatively weaker in comparison with its copper(II) analogue is further inferred from its thermal behaviour. Because the final product of thermal decomposition is $\text{Zn}(1\text{-Naph-}N\text{-Mecbm})$, wherein three ligand molecules (1-Naph-*N*-Mecbm) have been found to get decomposed, and only one molecule of 1-Naph-*N*-Mecbm remained intact with zinc metal ion.

Kinetic parameters

For the evaluation of kinetic parameters from TG, DTA and DSC, etc. techniques, the TG technique which involves the measurement of mass offers more accuracy over DTA and DSC techniques involving measurement of ΔT and dH/dT , respectively. Of the several methods, developed to allow kinetic analysis of TG data, the integral method developed by Coats and Redfern is widely accepted as a reliable method. Using TG data, different stages of decomposition were subjected to non-isothermal kinetic analysis and the kinetic and thermodynamic parameters have been computed from the TG data by Coats–Redfern

equation [13–15]. The parameters like entropy ' S^* ' [16], free energy ' G^* ' [17] and enthalpy of activation ' H ' were obtained from their standard relations and results are being presented in Table 2. An insight into the values of energy of activation (38.62–52.89 kJ mol^{-1}) for the first stage of decomposition of the ligand and its copper(II) complexes (Table 2) under study is indicative of comparable thermal stability of the ligand with its complexes. For the second stage of decomposition, the value of energy of activation of the free ligand is 126.75 kJ mol^{-1} , whereas for the copper(II) coordination complexes, it lies in the range 48.13–94.56 kJ mol^{-1} . Though this step deals with the loss of naphthol moiety in all the complexes under study, yet the highest value for the free ligand can be explained, if one visualizes its structure (Fig. 1).

The O–C bond of the group  of free ligand is

relatively stronger in comparison to its copper(II) complexes, wherein weakening of this bond occurs upon binding with the metal ion due to delocalization of electron density towards the dipositive metal ion centre. The kinetic data for third-stage thermal decomposition for dichlorotetrakis(1-naphthyl-*N*-methylcarbamate)copper(II) complex and for third- and fourth-stage thermal decompositions for dinitratotetrakis(1-naphthyl-*N*-methylcarbamate)copper(II) and diacetatotetrakis(1-naphthyl-*N*-methylcarbamate)copper(II) complexes depict very high values of activation energy (107.83–490.22 kJ mol^{-1} Table 2). These are

Table 2 Kinetic and thermodynamic parameters of non-isothermal decomposition of carbaryl and its copper(II) and zinc(II) complexes from TG data using Coats and Redfern equation

Sr. no.	Compound	Stages of decomp.	Activation energy $E^*/$ kJ mol^{-1}	Frequency factor ' A ' $\times 10^{-6}/\text{s}^{-1}$	Activation entropy $S^*/$ $\text{J K}^{-1} \text{mol}^{-1}$	Free energy of activation $G^*/$ kJ mol^{-1}	Enthalpy of activation $H^*/$ kJ mol^{-1}
1	1-Naph- <i>N</i> -Mecbm	1st	52.89	0.00	−419.07	292.65	52.89
		2nd	126.75	0.00	−558.21	446.11	126.75
2	$\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4\text{Cl}_2$	1st	50.98	0.00	−410.60	285.89	50.98
		2nd	64.18	0.00	−416.09	302.23	64.18
		3rd	192.65	0.21	−559.15	512.54	192.65
3	$\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4(\text{NO}_3)_2$	1st	45.43	0.01	−401.91	275.36	45.43
		2nd	94.56	0.02	−433.95	342.82	94.56
		3rd	207.73	0.00	−551.83	523.44	207.73
		4th	490.22	0.00	−844.34	973.27	490.21
4	$\text{Cu}(1\text{-Naph-}N\text{-Mecbm})_4(\text{CH}_3\text{COO})_2$	1st	38.62	0.03	−394.22	264.16	38.62
		2nd	48.13	0.04	−391.06	272	48.13
		3rd	107.83	0.00	−449.59	365.04	107.83
		4th	485.71	0.00	−852.78	973.59	485.71
5	$\text{Zn}(1\text{-Naph-}N\text{-Mecbm})_4\text{Cl}_2$	1st	49.64	0.00	−416.81	288.10	49.64
		2nd	178.80	0.00	−557.57	497.79	178.80

suggestive of higher thermal stability of the intermediates (Table 1) of second step in the former and second and third steps in the latter complexes. These steps have been correlated to the different nature of decomposition of the anions, i.e. Cl, NO₃ and CH₃COO in their TG curves. The value of ' E^* ' for the loss of nitrate (NO₃) ion is generally higher than that for chloride [18].

The kinetic data for first stage thermal decomposition of dichlorotetrakis(1-naphthyl-*N*-methylcarbamate)zinc(II) complex indicates a comparable magnitude of ' E^* ' value (49.64 kJ mol⁻¹) with those of free ligand and copper(II) complexes, while striking difference in its ' E^* ' value (178.80 kJ mol⁻¹) for its second-stage decomposition has been observed. This ' E^* ' value has been attributed to the loss of three molecules of 1-Naph-*N*-Mecbm group. Though ' E^* ' is expected to show a decrease in comparison to the free ligand, yet its higher value seems to be in consonance with the weaker Zn–O binding due to its d¹⁰ nature. The activation energy ' E^* ' data is in line with the fact that the higher the activation energy, the higher is the thermal stability of particular moiety (Table 1).

The frequency factor ' A ' generally is known to be related to ' E^* ' by the fact that larger the value of activation energy, the smaller is the frequency factor and vice versa. The observed negligible frequency factor ' A ' for all the compounds is in agreement with the computed magnitude of the ' E^* ' of the respective compounds. The abnormally negligible or very low values of frequency factor for the compounds further suggest that the decomposition reactions proceed slowly. Nevertheless, the magnitude of energy of activation may be considered to be the determining factor for whether the decomposition reaction is fast or slow rather than the frequency factor. The higher the activation energy, the slower is the decomposition process. From TG, DSC data, the complexes dinitratotetrakis(1-naphthyl-*N*-methylcarbamate)copper(II) and diacetatotetrakis(1-naphthyl-*N*-methylcarbamate)copper(II) seem to undergo slow thermal decomposition for their third stage.

The negative values of entropy of activation ' S^* ' (–391.06 to –852.78 kJ mol⁻¹) for all the compounds suggest that the decomposition reactions are slower than normal [19, 20]. It further indicates that the activated complexes have more ordered structure than the reactants. The higher positive values of free energy of activation ' G^* ' (272–973.59 kJ mol⁻¹) for all the compounds are suggestive of their stability. The magnitude of enthalpy of activation ' H^* ' (38.62–490.21 kJ mol⁻¹) has shown that ' E^* ' and ' H^* ' are equivalent. This observation is corroborated by negligible values of ' K_r ', the specific rate constant. The thermal decomposition seems to follow first order kinetics with R3 mechanism (Phase boundary reaction-spherical symmetry mechanism).

Conclusions

Based on the computed kinetic and thermodynamic parameters for the compounds under study, following conclusions can be drawn:

- (1) The metal carbamates have been found to have high thermal stability because of their high IDT values. All the complexes have been found to yield high percentage (~70%) of the residue, i.e. tris(1-naphthyl-*N*-methylcarbamate)copper(II) in copper(II) complexes and Zn(1-Naph-*N*-Mecbm) as residue 28% in case of dichlorotetrakis(1-naphthyl-*N*-methylcarbamate)zinc(II) complex even up to as high temperature as 800 °C.
- (2) The role of the nature of the anions does not significantly alter the thermal decomposition patterns because of the same composition and almost similar percentage of residue in all cases, except to bring about a variation in the temperature as far as the stability of the intermediate is concerned.
- (3) The three copper(II) complexes with different anions present outside coordination sphere exhibit the same pattern of first step decomposition in the temperature range between 120 and 280 °C with evolution of methyl isocyanate moiety. While second step decomposition leads to the evolution of naphthol moiety in all the three copper(II) 1-naphthyl-*N*-methylcarbamates irrespective of the nature of the anion, the temperature range corresponding to the loss of naphthol moiety is variable. This variation in temperature range can be attributed to hydrogen bonding interactions occurring between the anion and the hydrogen of the 1-Naph-*N*-Mecbm in conjugation with different lattice forces of the three copper complexes due to variable symmetries of the anions, i.e. chloride, nitrate and acetate.
- (4) In no case, i.e. copper(II) and zinc(II) complexes thermal decomposition leads to the formation of their metal oxide.
- (5) It is interesting but surprising to note from the TG data for the zinc(II) complex that one 1-Naphthyl-*N*-methylcarbamate (1-Naph-*N*-Mecbm) remains bound to zinc metal ion such that the most plausible product, i.e. ZnO to be obtained as a result of oxidative decomposition of the intermediate could not be obtained even up to 800 °C. Because for the transition metal complexes, thermal degradation reactions result into the formation of their metal oxides [21].

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