

THERMAL ANALYSIS OF Fe (II), Ni (II) AND Cu (II) CHELATES OF SOME TRIAZINE DERIVATIVES

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The thermal analysis of Fe(II), Ni(II) and Cu(II) complexes with 1, 3, 5- trimethyl hexahydro-triazine (TMAZ) and 1, 4, 7- triazacyclononane (TACN) were studied by microanalysis, TG and DTA techniques. Metal - TMAZ complexes show somewhat similar TG and DTA profiles when heated in N₂ atmosphere. An endothermic peak appears in the range 60-130°C which attributed to liberation of the organic ligand. TACN complexes show exothermic peak in the range 200-245°C proceeded to endothermic peak for dehydration of metal chelates in the range 125-155°C. The exothermic peak, corresponding to rapid mass-loss in TG curves, which may be due to oxidation reduction reaction. A relative thermal stability of metal complexes is reported.

Keywords: Thermal analysis, Fe(II), Ni(II), Cu(II), Triazine derivatives.

Introduction

TACN is too small to form equatorial complexes with transition metal ions but must instead coordinate facially giving "sandwich" complexes in a 1 : 2 ratio such as [Ni (TACN)₂]²⁺ [1]. TMAZ do form straight forwarded complexes with Fe(III), Fe(II), Co(II) and Cu(II) chlorides in a 1 : 1 ratio [2]. A literature survey showed that no much work has been done on the thermal analysis of TMAZ and TACN complexes. On the other hand few systems are reported showing the relationship between thermal stability of metal chelates and structure of chelating agents [3-10]. The purpose of this work is the study of thermal behaviour of freshly prepared Fe(II), Ni(II) and Cu(II) chelates of cyclic triazine (TMAZ) and macrocyclic triazine compounds (TACN) with these metal ions. The techniques employed are microanalysis, thermogravimetry (TG) and differential thermal analysis (DTA). Microanalysis are utilized for knowing the solid complex formulae. TG curves are utilized for calculation of the activation energies of the processes involved, whereas DTA curves are used to evaluate the enthalpy changes accompanying the reactions.

Experimental

The chemicals used were all of Anal- R or chemically pure grade.

Preparation of the ligands and their complexes: (a) TACN. 3HCl compound was prepared according to recommended method [11] and (b) The TMAZ compound was prepared by the reaction of equimolar quantities of formaldehyde and methylamine in presence of NaOH as catalyst [12].

bp.74°C (11.5 mm)¹ (CDCl₃); 3.2 (S, 2H; NCH₂N), 2.3 (S, 3H; NCH₃)

M/E 43 (CH₃NCH₂), 42 (CH₂NH₂).

The stoichiometry of metal-TACN and TMAZ complexes are confirmed by spectrophotometric molar ratio and

continuous variation methods [13]. Metal -TACN complexes were prepared as mentioned before [14]. A solution of TACN in ethanol was prepared by dissolving TACN. 3HCl (4.2g) and KOH (0.72g) in water, adding ethanol (20ml) and refrigerating overnight. The solution was filtered to remove KCl and the filtrate was added to aqueous solutions of metal chlorides in molar ratio of 2:1 (ligand : metal). The mixtures were left over a week at room temperature. The yellowish iron (II), blue nickel (II) and copper (II) solid complexes were isolated and dried over anhydrous calcium chloride.

The metal-TMAZ complexes were synthesized according to published procedures [15] by the addition of hot ethanolic solutions of NiBr₄[(C₂H₅)₄N]₂, FeCl₂ and CuCl₂ (0.5 gm) containing a drop of ethylformate to warm ethanolic solution of TMAZ (0.48 gm), on a steam bath for about 15 mins. The precipitate of the complexes which separated on cooling as dark blue in the case of Ni (II), yellowish in the case of Fe (II) and in the case of Cu (II) as green and the crystals were deposited after few minutes. The microanalysis of Fe (II)-, Ni(II)- and Cu(II) -TACN and TMAZ chelates are listed in Table I.

Thermo-analytical techniques. Thermogravimetry (TG) was done using a Du Pont 440 thermal analyser equipped with a thermobalance. The samples (w 5mg) were heated in N₂ atmosphere at rate of 10°C min⁻¹. The sample was contained in a boat-shaped platinum pan suspended in the centre of furnace.

The balance operates on a null-balancing principle employing a taut-bond electric meter movement. The balance position is maintained in a reference (horizontal) position by an optically accurate zero loop. This loop uses a light source focused on twin photovoltaic cells through a signal flag having a slit aperture which is suspended from the balance beam.

Differential thermal analysis (DTA) was carried out using a Du Pot 900 thermal analyser fitted with a standard cell which allowed a maximum temperature of 500°C. Samples ($\approx 5\text{mg}$) were heated in N_2 atmosphere ($50\text{ cm}^3\text{ min}^{-1}$) at rate of $10^\circ\text{C min}^{-1}$, glass beads were chosen as reference material.

Results and Discussion

The mass-loss curves of Fe(II)-, Ni(II)- and Cu(II)-TACN are shown in Fig. 1. The Cu(II)-TACN chelate curve shows that this chelate does not contain water of hydration, where it can be seen that the weight remains constant upto 200°C . On the other hand the mass-loss curves of Ni(II) and Fe(II) chelates show dehydration processes takes place between $40\text{--}90^\circ\text{C}$ and $40\text{--}183^\circ\text{C}$, respectively. A corresponding weight losses in these ranges suggest the association of four water molecules with TACN in the case of Ni(II) chelate and two water molecules in case of Fe(II).

In general the dehydrated water may be considered either as crystal or as co-ordinated water. According to Nikolav *et al.* [14] water eliminating below 150°C can be considered as the crystal water and that above 150°C may be due to that coordinated to the metal ion. In the present studies it is observed that water of hydration has been eliminated between $40\text{--}90^\circ\text{C}$ in the case of Ni(II) chelate which suggests the presence of water of hydration as crystal water. On the other hand in the case of Fe(II) chelate there is coordinated water as well as crystal one, where the dehydration takes place between $40\text{--}183^\circ\text{C}$.

The dehydration and decomposition can be clearly distinguished on the basis of the DTG curves (Fig. 1). Table 2 shows the data of the rates of the two processes. According to the

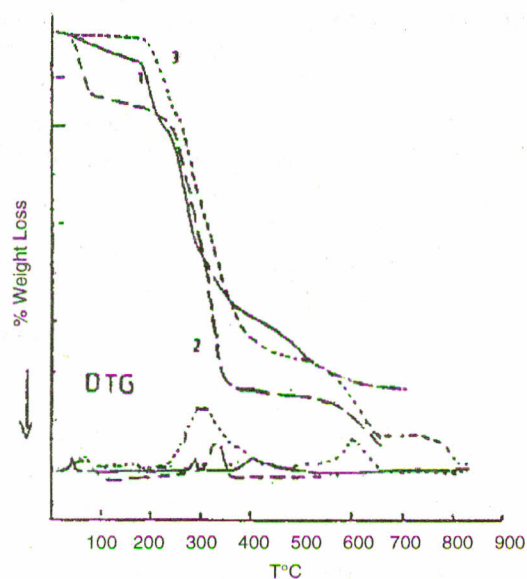


Fig. 1. TG curves of Fe(II)-, Ni(II)- and Cu(II)-TMAZ chelates; 1-Fe $(\text{TMAZ})_2\text{Cl}_2$, 2-NiBr $_4$ $[(\text{C}_2\text{H}_4)_4\text{N}]_2$ TMAZ and 3-Cu $(\text{TMAZ})_2\text{Cl}_2$.

DTG curves, Fe $(\text{TACN})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ chelate evolved 2 moles of water (8.2% found, 8.55% calc.) as one step and Ni $(\text{TACN})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ evolved 4 moles of water of dehydration per mole (14% found, 14.01% calc.) as two steps (2 moles of water in each step).

After dehydration the chelates show stability upto 180 , 200 and 205°C in the case of Fe(II), Ni(II) and Cu(II) chelates respectively. Then the TG curves show rapid mass-loss, which may be caused by oxidation-reduction reactions.

All the anhydrous complexes exhibit considerable thermal stability, decompositions occurring within temperature range $250\text{--}400^\circ\text{C}$ and $60\text{--}70^\circ\text{C}$ in the case of TACN and TMAZ chelates, respectively.

The mass-loss curves of Fe(II)-, Ni(II)- and Cu(II)-TMAZ chelates are shown in Fig. 2. Examination of TG curves indicates that all chelates do not contain water of hydration. It can be seen that the weight remains constant upto 50°C in the case of Fe(II), 95°C in the case of Ni(II) and 100°C in case of Cu(II) chelate.

Fe(II) chelate is the least stable one, where it exhibits decomposition occurring within the range $50\text{--}140^\circ\text{C}$ where Ni(II) and Cu(II) chelates are observed to be stable upto 95°C and 100°C respectively. Then TG curves show rapid mass-loss between $95\text{--}170^\circ\text{C}$ and $100\text{--}135^\circ\text{C}$, respectively.

The decomposition can be clearly distinguished on the basis of the DTG curves (Fig. 2). Table 2 shows the data of the rate of this process.

All the anhydrous complexes exhibit considerable thermal stability, decompositions occurring within temperature range $250\text{--}400^\circ\text{C}$ and $60\text{--}70^\circ\text{C}$ in the case of TACN and TMAZ chelates, respectively.

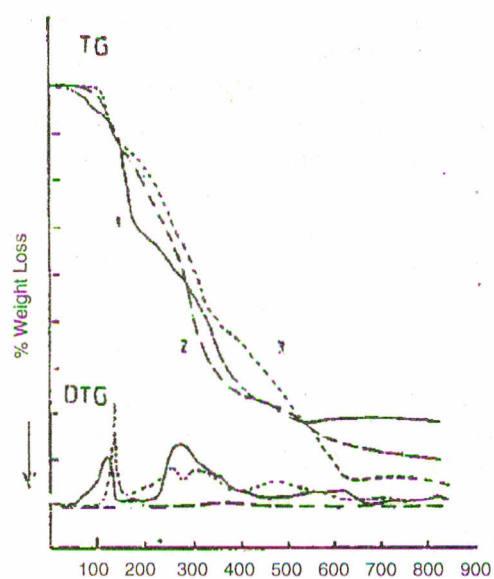


Fig. 2. TG curves of Fe(II)-, Ni(II)- and Cu(II)-TACN chelates; 1-Fe $(\text{TACN})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, 2-Ni $(\text{TACN})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and 3-Cu $(\text{TACN})_2\text{Cl}_2$.

DTA curves (Fig. 3). The curves of TACN chelates show endothermic peak of the dehydration processes occurring with in the range between 125-155°C and exothermic peak for decomposition processes which may be due to oxidation reduction reactions occurring within the range 200-243°C. On the other hand the DTA curves show that the decompositions of all TMAZ chelates are endothermic processes which may be due to liberation of TMAZ compound occurring within the range 60-130°C. In the present studies initial decomposition temperature (T_a) and inflection temperature (T_b) have been used to determine thermal stability of metal chelates. The (T_a) is frequently used to define the relative thermal stability of metal chelates [10]. (T_a), (T_b), initial (T_i), peak (T_p) and completion (T_c) temperatures of the dehydration and decomposition of each chelates, as obtained from the relevant TG and DTG curves, alongwith corresponding weight losses are given in Table 2.

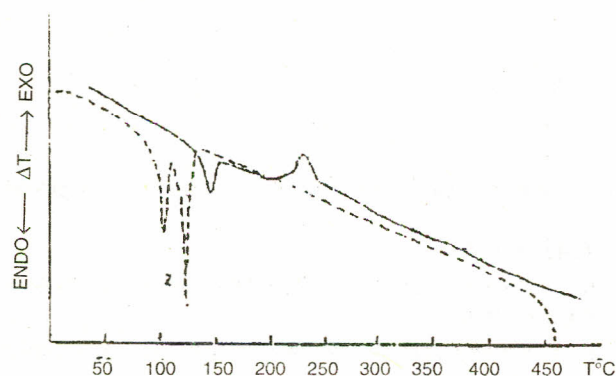


Fig. 3. DTA curves of (1)- $\text{Fe}(\text{TACN})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ chelate and 2- $\text{NiBr}_4[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{TMAZ}$ chelate.

Activation energies (E^*) of each dehydration and decomposition processes which computed from analysis of the corresponding TG curves using the method of Horowitz and Metzger [10] {A plot of $\ln [W^0 - W_t^f / W - W_t^f]$ versus θ straight line whose slope is E^*/RT_s . Where W_0 and W_t^f are the initial and the final total weights, respectively. W is the weight at a defined temperature, T_s is the reference temperature at which $(W - W_t^f) / (W_0 - W_t^f) = 1/e$ and $\theta = T + T_s$ } are also used for determination of thermal stability of metal chelates. Where the metal chelate with high activation energy is more thermal stable and the vice versa.

Enthalpy changes (ΔH) accompanying dehydration and decomposition of each chelates were determined by standard methods [16] from corresponding DTA curves, which use the following equation:

$$\Delta H = \frac{K \times \text{Peak area (in)}^2 \times \text{Range setting } (\mu\text{V})}{\text{Weight (g)}}$$

where

$$K = \frac{[\Delta H \text{ of standard (cal/g)}][\text{Sample weight (g)}]}{[\text{transition area (in)}^2][\text{range setting } (\mu\text{V})]}$$

(where in order to determine the calibration constant (K) as function of temperature, calibration runs three times with different weights of standard substance. All areas were averaged. Once the area had been determined, K was calculated from the know H value of $(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})$. The ΔH values are given in Table 3.

On the basis of experimental findings (T_a , E^* and ΔH values) in these studies the relative thermal stability of TACN complexes can be given as:

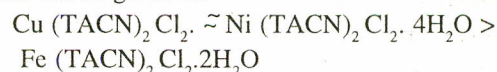


TABLE I. COLOUR AND MICROANALYSIS OF Fe (II)-, Ni (II)- AND Cu (II)- CHELATES OF TMAZ AND TACN.

Complex	Colour	Calculated (found %)			
		M	C	H	N
<i>METAL (II)-TACN CHELATES</i>					
$\text{Fe}(\text{TACN})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	Yellowish	13.26 (13.19)	34.22 (34.20)	8.07 (8.11)	19.95 (19.90)
$\text{Ni}(\text{TACN})_2\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	Blue		31.90 (31.60)	8.19 (8.19)	18.61 (18.54)
$\text{Cu}(\text{TACN})_2\text{Cl}_2$	Blue		36.57 (36.45)	7.67 (7.87)	21.33 (21.30)
<i>METAL (II)-TMAZ CHELATES</i>					
$\text{Fe}(\text{TMAZ})\text{Cl}_2$	Yellowish	21.82 (21.78)	28.15 (28.06)	5.91 (6.0)	16.42 (16.50)
$\{\text{Ni} \text{Br}_4 [(\text{C}_2\text{H}_5)_4\text{N}]_2\text{TMAZ}\}$	Dark blue	7.65 (7.6)	34.4 (34.4)	7.22 (3.3)	9.12 (8.98)
$\text{Cu}(\text{TMAZ})\text{Cl}_2$	Green	24.55 (24.40)	27.3 (27.13)	5.70 (5.80)	15.90 (16.07)

TABLE 2. TG AND DTG DATA OF Fe (II)-, Ni (II)- AND Cu (II)- TACN AND TMAZ CHELATES.

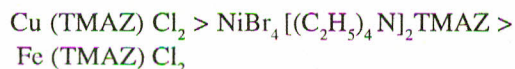
Compound	Ta°C	Tb°C	Ti°C	Tp°C	Tc°C	E'
Fe (TACN) ₂ Cl ₂ · 2H ₂ O			40	45	50	0.412
Fe (TACN) ₂ Cl ₂	170	368	280	302	310	18.669
Ni (TACN) ₂ Cl ₂ · 4H ₂ O			40	65	70	5.092
Ni (TACN) ₂ Cl ₂ · 2H ₂ O			71	78	85	4.976
Ni (TACN) ₂ Cl ₂	198	360	300	350	370	27.730
Cu (TACN) ₂ Cl ₂	205	400	220	300	400	30.534
Fe TMAZ Cl ₂	50	140	80	100	110	2.377
Ni Br ₄ [(C ₂ H ₅) ₄ N] ₂ TMAZ	95	160	40	140	150	6.475
Cu (TMAZ) Cl ₂	100	135	110	140	150	15.372

TABLE 3. DTA DATA OF Fe (II)-, Ni (II)- AND Cu (II)- TACN AND TMAZ CHELATES.

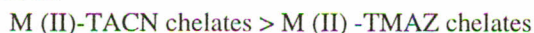
Compound	Endothermic (°C)			ΔH KJ/mol	Exothermic (°C)			ΔH Kj/mol
	Tb	Tm	Te		To	Tma	Td	
[Fe (TACN) ₂ Cl ₂ · 2H ₂ O]	110	126	114	19.04	190	225	240	24.2
[Ni (TACN) ₂ Cl ₂ · 4H ₂ O]	125	144	165	22.2	200	230	245	27.3
Cu (TACN) ₂ Cl ₂					204	235	245	27.8
Fe (TMAZ) Cl ₂	60	104	110	25.0				
	110	123	130	50.1				
Ni Br ₄ [(C ₂ H ₅) ₄ N] ₂ TMAZ	65	110	115	30.4				
	116	126	140	55.9				
Cu (TMAZ) Cl ₂	65	112	115	30.2				
	112	125	140	60.5				

Tb, Tm and Te are the temp. at onset, maximum and end of endothermic process. To, Tma and Td are the temp. at onset, maximum and end of exothermic process.

and the relative thermal stability of TMAZ chelates can also be given as:



Finally the relative thermal stability of transition metal macrocyclic triazine (TACN) and cyclic triazine (TMAZ) complexes is:



The high thermal stability of TACN complexes is attributed to two factors, the first factor is the stability of TACN ring at high temperatures and the second one is the nature of TACN complexes which are almost found as sandwich structure [13]. On the other hand the low thermal stability of TMAZ complexes is attributed to ring inversion and the ring is opened at high temperature as well as the nature of complexes which is almost in a 1 : 1 ratio [15].

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