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Thermal Decomposition of Nickel(II) and Copper(II) Hexaaza Macrotricyclic Complexes

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The thermal behaviour of nickel(II) and copper(II) hexaaza macrotricyclic complexes was investigated from ambient temperature to 1200 ºC under nitrogen atmosphere. The complexes demonstrated good thermal stability and are of greatly determined by the nature of ligand molecule and the counter anion present in the macrocyclic complexes. A possible mechanism of the thermal decomposition of the various complexes is also suggested.

Keywords: Hexaaza macrocycle, Metal complexes, Thermal analysis.

INTRODUCTION

The interest in synthetic macrocycles and their metal complexes depends on the fact that they mimic naturally occurring macrocyclic molecules in their structure and functional features and on their rich chemical behaviour[1]. Among transition metal ions, nickel(II) and copper(II) have been the most widely investigated species for several reasons: (i) they are often very effective as a templating agent in many synthesis (ii) their complexes display unusually high solution stability (iii) Ni^{2+} can exist in either high-spin or low-spin form according to the ligand's structural features[2,3]. In our earlier works we reported the synthesis, spectral and structural characterization of several hexaaza macrotricyclic nickel(II) and copper(II) complexes by template condensation of amines and formaldehyde[4-6]. To achieve a greater insight into the chemical structure of these complexes, a thermo analytical study of the water soluble complexes using thermogravimetric analysis (TG) and differential thermal analysis (DTA) techniques was performed.

The thermal studies of variety of transition metal complexes have been studied by several groups[7-11]. Though a quite large number of macrocyclic complexes are available in the literature, only selected data of thermal analysis have been published earlier[12,13]. Therefore in the present study, we describe the thermal decomposition behaviour of nickel(II) and copper(II) hexaaza macrotricyclic complexes (Fig. 1).

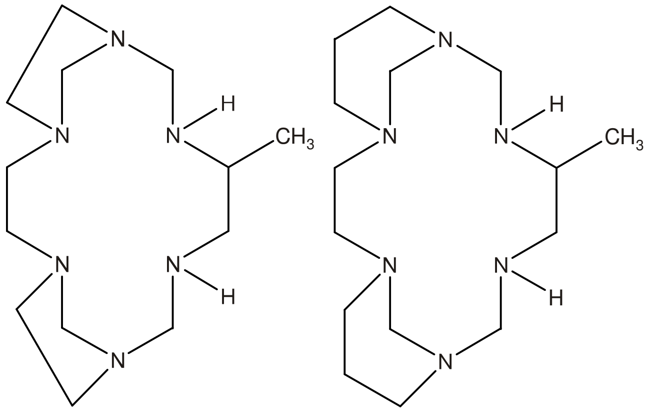

Fig. 1. Structures of hexaazamacrocycle under study

EXPERIMENTAL

All the nickel(II) and copper(II) complexes of hexaazamacrocycles *viz*., PCHA and CBA (Fig. 1) were synthesized by the metal template Mannich reaction of appropriate polyamines with formaldehyde in the presence of metal ions. The synthetic procedure is described in our previous works[4,6]. Thermogravimetric analysis was performed on a Netzsch STA thermogravimetric analyzer. A weighed sample of a compound (10 mg) was placed in a alumina crucible and heated at a rate of 10 °C min^{-1} under nitrogen atmosphere from ambient temperature to 1200 °C.

RESULTS AND DISCUSSION

The crystal structure analysis reveals that, in the case of $[Ni(PCHA)](ClO_4)_2$ and $[Ni(CBA)](ClO_4)_2$, the two perchlorate ions present outside the coordination sphere as a counter ion whereas in the case of perchlorate derivative of copper(II) complexes *viz*., $[Cu(PCHA)(ClO_4)_2]$ and $[Cu(CBA)(ClO_4)_2]$, the two perchlorate ions are coordinated to the metal centre. From the conductance measurements, it was observed that the hexafluorophosphate derivatives of both Ni(II) and Cu(II) complexes *viz.*, $[Ni(CBA)](PF_6)_2$ and $[Cu(CBA)](PF_6)_2$ behave as a 2:1 electrolyte and the thiocyanate derivatives *viz.*, $[Ni(CBA)(NCS)_2]$ and $[Cu(CBA)(NCS)_2]$ behave as a non electrolyte in aqueous medium[14].

The representative TG and DTA plots for $[Cu(PCHA)(ClO_4)_2]$ and $[Ni(CBA)](NCS)_2$ are shown in Figs. 2 and 3. All the complexes are found to be stable at room temperature. The observed percentage weight loss corresponds to various steps in all the TG curves are provided in Table-1.

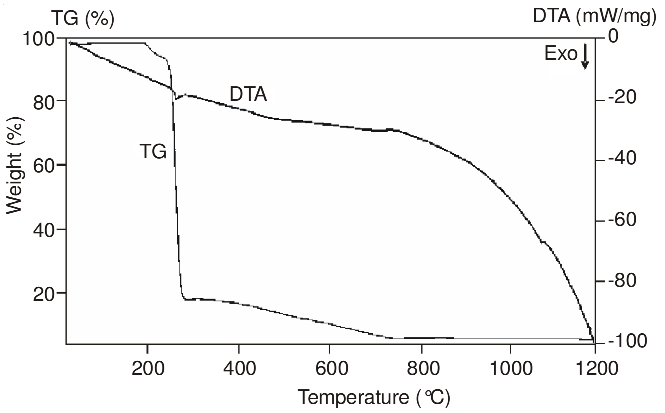

Fig. 2. Thermal curves of $[Cu(PCHA)(ClO_4)_2]$

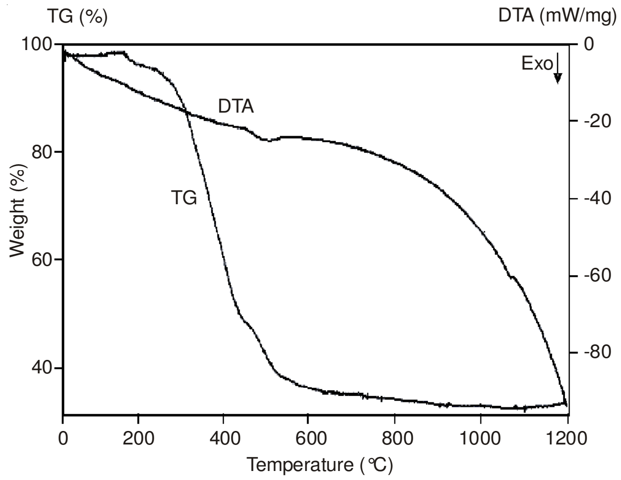

Fig. 3. Thermal curves of $[Ni(CBA)](NCS)_2$

Two patterns of thermal behaviour can generally be discerned, one in which a steep single step metal complex decomposition or two step process in which removal of anion followed by the decomposition of macrocycle. The perchlorate derivatives of macrocyclic complexes $[Ni(CBA)(ClO_4)_2]$ and $[Cu(CBA)(ClO_4)_2]$ exhibit a decomposition step which is indicated by a sudden weight loss and the decomposition temperature is 245 and 268 °C, respectively. This may be due to an explosive reaction because of the presence of perchlorate anion in the molecule. Similar explosive effect is reported in the case of thermal decomposition of amine complexes of nickel(II) nitrate and cobalt(III) halides[15,16].

The complex $[Cu(PCHA)(ClO_4)_2]$ is stable up to 196 °C and then a mass loss of 80 % is observed at this temperature. This is followed by a 12 % weight loss which may be due to the evolution of some gases and in the present case only 8 % of the metal oxide is left as residue in the crucible and the remaining may be thrown outside. Similar observation has been made for several other complexes[17] including $[M(en)_2](ClO_4)_2$ (where M = Ni, Cu, Co, Mn and Zn and en = ethylenediamine). The complexes $[Cu(PCHA)(ClO_4)_2]$, $[Ni(CBA)](NCS)_2$ and $[Cu(CBA)](NCS)_2$ are stable up to 196, 200 and 214 °C, respectively. The temperature range at which they decompose are 196-718 °C for $[Cu(PCHA)(ClO_4)_2]$; 200-535 °C for $[Ni(CBA)](NCS)_2$ and 214-1015 °C for $[Cu(CBA)](NCS)_2$.

The square planar hexafluorophosphate derivatives of Ni(II) and Cu(II) *viz.*, $[Ni(CBA)](PF_6)_2$ and $[Cu(CBA)](PF6)_2$ undergo decomposition in two stages. The initial weight loss (21-42 %) for both the complexes correspond to the removal of anion and the calculated weight loss are in good agreement with the observed one and the second stage involves the decomposition of macrocycle resulting in the formation of metal fluoride. It is interesting to note that in the case of $[Ni(PCHA)](ClO_4)_2$, $[Cu(PCHA)(ClO_4)_2]$ and $[Cu(CBA)(ClO_4)_2]$ the percentage weight of the residue is very low since some of them might have been thrown out from the crucible during its decomposition. In case of $[Ni(CBA)](PF_6)_2$ and $[Ni(CBA)(NCS)_2]$, 22-40 % residue was observed which may be due to the formation of metal fluoride and metal sulphide.

It is a known fact that counter ions play a major role in the thermal stability of complexes[8]. In case of the nickel(II) complexes of macrocyclic ligand CBA, the thermal stability varies in the following order:

$$[Ni(CBA)](ClO_4)_2 > [Ni(CBA)](NCS)_2 > [Ni(CBA)](PF_6)_2$$

The perchlorate derivative of copper(II) complexes with various macrocyclic ligands *viz.* PCHA and CBA exhibit the following order of stability:

$$\underset{196\ °C}{[Cu(PCHA)(ClO_4)_2]} < \underset{206\ °C}{[Cu(CBA)(ClO_4)_2]}$$

TABLE-1
THERMAL ANALYSIS DATA OF HEXAAZA MACROCYCLIC COMPLEXES

Complexes	Thermo gravimetric data					DTA Peak Temp. (°C)
	IDT (°C)	Temp. range (°C)	Species lost	Mass loss (%)	Residue (%)	
$[Ni(PCHA)](ClO_4)_2$	205	205-416, 416-1100	ClO_4-complex (decomp)	20, 77	2	1074 (endo)
$[Cu(PCHA)(ClO_4)_2]$	196	196-718	Complex (decomp)	90	8	264 (endo), 1072 (endo)
$[Ni(CBA)](ClO_4)_2$	245	245	Complex (decomp)	95	4	257 (endo), 571 (endo), 1040 (endo)
$[Ni(CBA)](PF_6)_2$	188	188-410, 410-600	PF_6-$(CH_2)_{11}N_6$	42, 36	22	282 (endo), 571 (endo), 1065 (endo)
$[Ni(CBA)(NCS)_2]$	200	200-535	$(CH_2)_8N4·2NCS$	60	40	507 (endo), 1065 (endo)
$[Cu(CBA)(ClO_4)_2]$	206	268	Complex (decomp)	92	7	252 (endo), 1064 (endo)
$[Cu(CBA)](PF6)_2$	232	333-555, 555-1010	PF_6-macrocycle (decomp)	21, 69	10	1074 (endo)
$[Cu(CBA)(NCS)_2]$	214	214-1015	Complex (decomp)	86	14	1074 (endo)

The variation in the stability may be attributed to the nature of ligand molecule present in the macrocyclic complex. The macrocyclic complex with 1,3-diaazacyclocpentane ring is less stable compared to the complex contaning 1,3-diazacyclo-hexane ring moiety. The thermo gravimetric data obtained was comparable with the mass spectral data of the complexes in which the precursor peak for most of the complexes are $[M\text{-}2\ anion]^{2+}$ or $[M\text{-}anion]^{+}$ which indicates the preferential disso-ciation of anion in all the complexes[4,18].

Most of the complexes show an endothermic peak in the temperature range of 1040-1074 ºC, which may be due to the decomposition of the macrocycle and the anion species. The DTA curves of perchlorate derivatives of copper(II) and nickel(II) complexes show only endothermic peak which may be due to sudden mass loss results in lack of contact between the crucible and the sensors. The formation of gases like chlorine and phosphorous(V) fluoride during the thermal degradation has also been suggested[19].

Conclusion

The thermograms of nickel(II) and copper(II) hexaaza macrotricyclic complexes show no weight loss up to 188 ºC indicating the absence of lattice or coordinated water molecule. Thermal decomposition occurs mostly in a single or two stages and all the thermal parameters consist with its higher stability. The thermal behaviour of all the complexes is largely dependent on the nature of the metal ion, macrocycle and also the type of counter ion present in the complex.

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