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THERMOANALYTICAL INVESTIGATION OF MAGNESIUM(II) COMPLEXES WITH NICOTINAMIDE AS BIO-ACTIVE LIGAND

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Abstract

The stoichiometry of thermal decomposition was studied for the following Mg(II) nicotinamide (NA) complexes: $Mg(Ac)_2(NA)_5 \cdot 2H_2O$ (I), $Mg(ClAc)_2(NA)_6 \cdot 6H_2O$ (II), $Mg(Cl_2Ac)_2(NA)_6 \cdot 5H_2O$ (III) and $Mg(Cl_3Ac)_2(NA)_6 \cdot 2H_2O$ (IV), where $Ac=CH_3COO^-$, $ClAc=ClCH_2COO^-$, $Cl_2Ac=Cl_2CHCOO^-$ and $Cl_3Ac=Cl_3CCOO^-$. Heating the compounds results first in the release of water molecules. The NA molecules are released in one step (complexes II and III) or in two steps (complexes I and IV). The compositions of the complexes, the solid-state intermediates and the products of thermolysis were identified by means of elemental analysis and complexometric titration. The results reveal that MgO is left as residue at the end of thermal degradation of compounds I–IV. NA is coordinated to Mg(II) through the nitrogen atom of the heterocyclic ring. The IR data indicate unidentate coordination of the carboxylate ions to the Mg(II) in complexes I–IV.

Keywords: acetate, DTA and IR, halogenoacetates, Mg(II), nicotinamide

Introduction

Carboxylatomagnesium(II) complexes are of interest from both chemical and biological aspect. Complexes of Mg(II) carboxylates with nitrogen donor ligands have attracted increasing interest in recent years. This interest largely stems from the discovery that the carboxylate groups possess a pronounced tendency to serve as a bridge between metal(II) atoms in complexes with a nitrogen donor ligand in terminal position [1, 2]. From our point of view, it is challenging to study the interactions between metal ions and heterocyclic nitrogen compounds that occur in living systems and are used as medicaments. Many authors have investigated heterocyclic compounds and also examined them as ligands in coordination compounds of several central atoms, in consequence of their important roles in many biological systems [3–8]. This work is a continuation of our previously reported studies [9–12]. Nicotinamide is known as an important component in biological systems [13]. However, the reported data on the thermal decompositions and IR spectral analysis of

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Mg(II) complexes with NA are rather rare. Therefore, this paper is aimed at the synthesis, thermal analysis and IR spectral analysis of four new Mg(II) complexes, I–IV.

Experimental

Preparation of the complexes

Compounds I–IV were prepared by dissolving 1.22 g NA in ethanol, followed by the gradual addition of an ethanolic solution of the appropriate acetato or halogenoacetato Mg(II) complexes in a molar ratio of 6:1. The solutions were reduced in volume at room temperature and left to crystallize. The complexes which formed were filtered off, washed with diethyl ether and dried at room temperature.

Measurements

The IR spectra were obtained on a Philips analytical PU9800 FTIR spectrometer by using Nujol mulls in the range 200–4000 cm^{-1}, while thermal decomposition studies were carried out on a Paulik-Paulik-Erdey derivatograph (type OD 102, MOM, Budapest) in air atmosphere, using a platinum crucible with a sample mass of 100 mg in the temperature range 20–1000°C. A rate of temperature increase of 10°C min^{-1} was chosen for all measurements.

Results and discussion

The contents of N, C and H were determined by elemental analysis, and that of Mg by complexometric titration. The analytical data on compounds I–IV, reported in Table 1, revealed good agreement with the calculated data.

Table 1 Analytical data on compounds

Complex	Theoretical (%)				Experimental (%)			
	C	H	N	Mg	C	H	N	Mg
$Mg(Ac)_2(NA)_5 \cdot 2H_2O$	51.77	5.08	17.77	3.05	51.93	5.13	17.72	3.03
$Mg(ClAc)_2(NA)_6 \cdot 6H_2O$	45.67	4.95	15.98	2.31	45.74	4.95	15.94	2.34
$Mg(Cl_2Ac)_2(NA)_6 \cdot 5H_2O$	43.58	4.36	15.25	2.21	43.40	4.46	15.18	2.23
$Mg(Cl_3Ac)_2(NA)_6 \cdot 2H_2O$	42.96	3.58	15.04	2.20	42.95	3.66	15.05	2.26

Thermal behaviour of the compounds

The termal decomposition data on compounds I–IV are collected in Table 2. The thermal decompositions of these compounds are multi-stage processes. The final product in each case was MgO. The results on the thermal decompositions of the complexes were compared with literature results on the metal complexes with carboxylates and halogenocarboxylates [14–16].

Table 2 Thermal decomposition data

Complex	DTA results		TG results		
	T_{peak}/°C	T_{range}/°C	Mass loss/% found (calc.)	Moiety loss	Residue
$Mg(Ac)_2(NA)_5 \cdot 2H_2O$	140 endo	110–250	4.50(4.57)	$2H_2O$	
	335 endo	250–500	61.90(61.89)	4NA	MgO
	530 endo	500–615	15.50(15.48)	NA	
	650 exo	615–660	decomposition		
$Mg(ClAc)_2(NA)_6 \cdot 6H_2O$	220 endo	150–310	10.25(10.27)	$6H_2O$	
	410 endo	310–400	69.60(69.63)	6NA	MgO
	850 exo	400–950	decomposition		
$Mg(Cl_2Ac)_2(NA)_6 \cdot 5H_2O$	220 endo	170–280	8.20(8.17)	$5H_2O$	
	370 endo	280–500	66.40(66.41)	6NA	MgO
	790 exo	500–950	decomposition		
$Mg(Cl_3Ac)_2(NA)_6 \cdot 2H_2O$	125 endo	75–170	3.20(3.22)	$2H_2O$	
	230 endo	170–340	21.80(21.84)	2NA	MgO
	425 endo	340–520	43.70(34.68)	4NA	
	710 exo	520–800	decomposition		

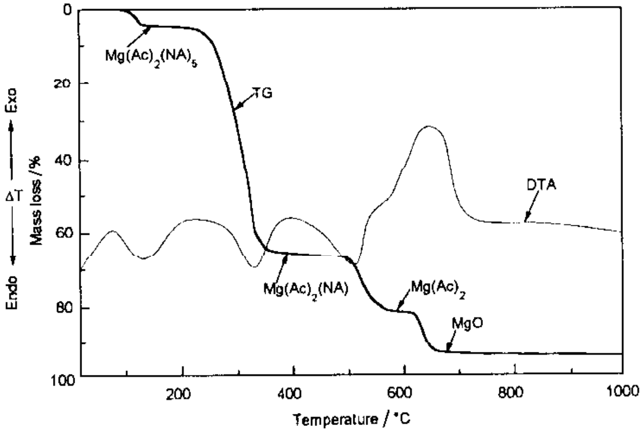

Fig. 1 TG and DTA curves of $Mg(Ac)_2(NA)_5 \cdot 2H_2O$

The TG and DTA curves for $Mg(Ac)_2(NA)_5 \cdot 2H_2O$ are depicted in Fig. 1. The TG curve for this complex indicates that it is stable at temperatures up to 110°C, when decomposition begins, leading to MgO as the final product formed at 660°C. The TG curve shows three bendings at 250, 500 and 615°C, which correspond to the presence of three intermediate decomposition products: $Mg(Ac)_2(NA)_5$, $Mg(Ac)_2(NA)$ and $Mg(Ac)_2$. The most probable thermal decomposition scheme is

$$Mg(Ac)_2(NA)_5{\cdot}2H_2O \xrightarrow{110-250^{\circ}C} Mg(Ac)_2(NA)_5 \xrightarrow{250-500^{\circ}C} Mg(Ac)_2(NA)$$

$$\xrightarrow{500-615^{\circ}C} Mg(Ac)_2 \xrightarrow{615-660^{\circ}C} MgO$$

The DTA curve for the complex (Fig. 1) presents three endothermic peaks, at 140, 335 and 530°C, corresponding to the loss of $2H_2O$, 4NA and NA, respectively, and a broad exothermic maximum centred at about 650°C, corresponding to the loss of 2Ac, with the simultaneous formation of MgO.

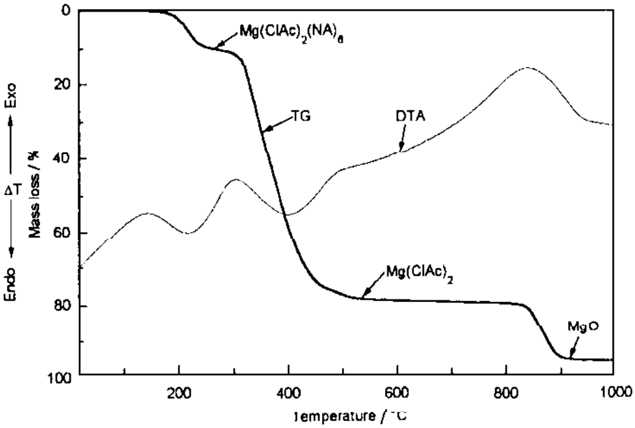

Fig. 2 TG and DTA curves of $Mg(ClAc)_2(NA)_6{\cdot}6H_2O$

The TG and DTA curves of $Mg(ClAc)_2(NA)_6{\cdot}6H_2O$ are given in Fig. 2. The TG curve indicates that it is thermally stable up to 170°C, where the dehydration process commences. This is followed by two mass loss steps in the intervals 170–300°C and 300–830°C. On the basis of the mass losses (Table 2), these two steps were attributed to the formation of the intermediates $Mg(ClAc)_2(NA)_6$ and $Mg(ClAc)_2$, while the final solid product was MgO. The most probable thermal decomposition scheme is

$$Mg(ClAc)_2(NA)_6{\cdot}6H_2O \xrightarrow{170-300^{\circ}C} Mg(ClAc)_2(NA)_6 \xrightarrow{300-830^{\circ}C} Mg(ClAc)_2$$

$$\xrightarrow{830-910^{\circ}C} MgO$$

The DTA curve of complex II (Fig. 2) displays two endothermic peaks, with maxima at 220 and 410°C, corresponding to the loss of $6H_2O$ and 6NA, respectively, and an exothermic peak with maximum at 850°C, corresponding to the decomposition of 2ClAc with simultaneous formation of MgO.

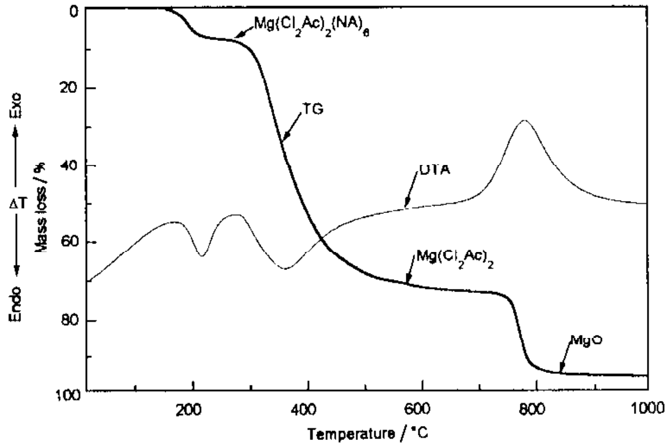

Fig. 3 TG and DTA curves of $Mg(Cl_2Ac)_2(NA)_6{\cdot}5H_2O$

$Mg(Cl_2Ac)_2(NA)_6{\cdot}5H_2O$ is stable up to 155°C (Fig. 3). Above this temperature, the elimination of neutral ligand begins. In the temperature range 155–300°C, the compound lost $5H_2O$ in one step, accompanied by an endothermic peak at 220°C in the DTA curve. Between 300 and 750°C, 6NA was eliminated in one step, observed as an endothermic peak at 370°C in the DTA curve. At a temperature higher than 750°C, decomposition of $2Cl_2Ac$ took place in one step, with an exothermic peak at 790°C in the DTA curve. The final product was MgO. The most probable thermal decomposition scheme here is

$$Mg(Cl_2Ac)_2(NA)_6{\cdot}5H_2O \xrightarrow{155-300^{\circ}C} Mg(Cl_2Ac)_2(NA)_6 \xrightarrow{300-750^{\circ}C} Mg(Cl_2Ac)_2$$

$$\xrightarrow{750-820^{\circ}C} MgO$$

The TG and DTA curves for $Mg(Cl_3Ac)_2(NA)_6{\cdot}2H_2O$ are shown in Fig. 4. The TG curve indicates that it is stable up to 110°C, when slow decomposition to MgO commences, the final product being formed at 530°C. The TG curve exhibits three bendings, at 200, 360 and 590°C, corresponding to the presence of three intermediate decomposition products: $Mg(Cl_3Ac)_2(NA)_6$, $Mg(Cl_3Ac)_2(NA)_4$ and $Mg(Cl_3Ac)_2$. The most probable thermal decomposition scheme is

$$Mg(Cl_3Ac)_2(NA)_6{\cdot}2H_2O \xrightarrow{110-200^{\circ}C} Mg(Cl_3Ac)_2(NA)_6 \xrightarrow{200-360^{\circ}C}$$

$$Mg(Cl_3Ac)_2(NA)_4 \xrightarrow{360-590^{\circ}C} Mg(Cl_3Ac)_2 \xrightarrow{590-710^{\circ}C} MgO$$

The DTA curve of complex IV (Fig. 4) displays three endothermic peaks, with maxima at 125, 230 and 425°C, corresponding to the loss of $2H_2O$, 2NA and 4NA,

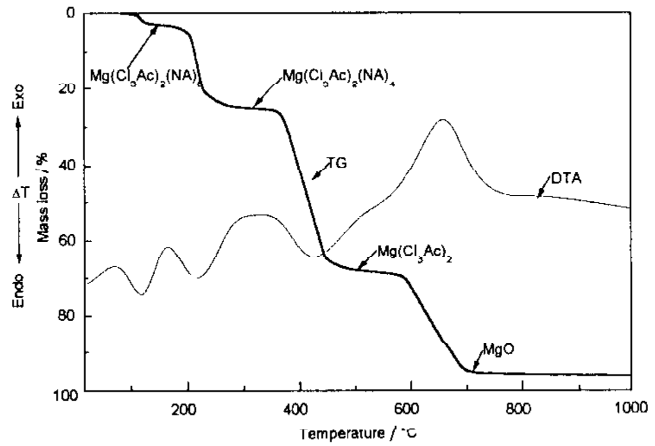

Fig. 4 TG and DTA curves of $Mg(Cl_3Ac)_2(NA)_6{\cdot}2H_2O$

respectively, and an exothermic peak with maximum at 660°C, corresponding to the decomposition of $2Cl_3Ac$ with the simultaneous formation of MgO.

IR spectra

The absorptiom bands in the ranges 3551–3245 cm^{-1} ν(OH) and 1627–1612 cm^{-1} δ(HOH) confirm the presence of water of crystallization, and those in the range 650–1000 cm^{-1} demonstrate the presence of water coordinated in the complexes [17]. The magnitude of Δ_{COO} has been used by Nakamoto [18] as a criterion of the mode of carboxylate binding with metal ions. Calculations on the examined spectra gave values of Δ_{COO} in the range 340–263 cm^{-1}. These values, the three bands (COO deformation) at 920–720 cm^{-1} and a strong band [$\pi(CO)_2$] near 540 cm^{-1} [19] for complexes I–IV are in good accord with the literature data for unidentate-bonded acetate structures. The absorption bands in the range 239–206 cm^{-1} ν(Mg–N) confirm the coordination of NA to Mg^{2+} through the nitrogen atom of its heterocyclic ring [20].

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