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

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Abstract

TG, DTA and other analytical methods were applied to investigate the thermal behaviour and structures of the compounds $Mg(ClAc)_2(Py)_2{\cdot}2H_2O$ (I), $Mg(Cl_2Ac)_2(Py){\cdot}H_2O$ (II), $Mg(Cl_3Ac)_2(Py){\cdot}6H_2O$ (III) and $Mg(SCN)_2(Py)_3{\cdot}2H_2O$ (IV), where $ClAc=ClCH_2COO^-$, $Cl_2Ac=Cl_2CHCOO^-$, $Cl_3Ac=Cl_3CCOO^-$ and Py=Pyridine. The compositions of the complexes and the solid-state intermediates and products of thermolysis were identified by means of elemental analysis. Possible schemes of destruction of the complexes are suggested. The final products of the thermal decompositions were MgO (I–III) and MgS (IV). The IR data suggest unidentate coordination of the carboxylate ions to Mg(II) in complexes I–III. Py is coordinated to the Mg(II) through the nitrogen atom of its heterocyclic ring.

Keywords: acetate, DTA and IR, halogenoacetates, Mg(II), pyridine, SCN, TG

Introduction

The relationship between the structures and thermolyses of metal carboxylate complexes, and the influence of the natures of the metal and ligand on the process of thermal decomposition are of interest. Heterocyclic compounds play a significant role in many biological systems [1, 2]. It is not surprising, therefore, that many authors have investigated heterocyclic compounds and also examined them as ligands in coordination compounds of a number of central atoms [3–10]. In order to improve our understanding of drug – metal ion interactions, we have been studying the thermal properties of Mg(II) complexes with pyridine. This work is a continuation of previously reported studies [11–15] on the thermal and spectral properties of Mg(II) complexes with substituted pyridines. This paper describes the preparation of complexes formed by Mg(II) acetate, mono-, di- and trichloroacetates and SCN with Py, together with thermal analyses and IR spectral investigations of these complexes.

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Experimental

Preparation of the complexes

Compounds I–IV were prepared by the gradual addition of 0.01 mole Py to a methanolic solution of the appropriate acetato, halogenoacetato or thiocyanato Mg(II) complex in a molar ratio of 4:1. The solutions were reduced in volume at room temperature and left to crystallize. The fine microcrystals that precipitated were filtered off, washed with diethyl ether and dried at room temperature.

Measurements

The IR spectra were obtained on a Philips analytical PU9800 FTIA 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, reveal good agreement with the calculated data.

Table 1 Analytical data on compounds

Complex	Experimental/%				Theoretical/%			
	C	H	N	Mg	C	H	N	Mg
$Mg(ClAc)_2(Py)_2{\cdot}2H_2O$	41.55	4.47	6.85	5.99	41.45	4.44	6.91	5.93
$Mg(Cl_2Ac)_2(Py)\ H_2O$	28.16	2.37	3.74	6.45	28.63	2.38	3.71	6.44
$Mg(Cl_3Ac)_2(Py){\cdot}6H_2O$	18.76	2.45	2.52	4.52	20.13	3.17	2.61	4.53
$Mg(SCN)_2(Py)_3{\cdot}2H_2O$	49.82	4.49	16.96	5.80	49.39	4.59	16.94	5.82

Thermal behaviour of the compounds

The thermal decomposition data on compounds I–IV are collected in Table 2. The complexes are thermally relatively stable. The thermal decompositions of the compounds are multistage processes. Subsequent detachment of the ligands was observed. The results on the thermal decompositions of the complexes were compared with literature results on the metal complexes with the carboxylates and halogenocarboxylates [16–18].

The TG and DTA curves of $Mg(ClAc)_2(Py)_2{\cdot}2H_2O$ are given in Fig. 1. The TG curve indicates that it is thermally stable up to 140°C, where the dehydration process

Table 2 Thermal decomposition data

Complex	DTA results		TG results		
	T_{peak}/°C	T_{range}/°C	Mass loss/% found (calc.)	Moiety lost	Residue
$Mg(ClAc)_2(Py)_2\cdot 2H_2O$	175 endo	150 240	8.90(8.88)	$2H_2O$	
	260 endo	240–320	39.00(39.98)	2Py	MgO
	640 exo	590–780	decomposition		
$Mg(Cl_2Ac)_2(Py)\cdot H_2O$	120 endo	105–190	4.75(4.77)	H_2O	
	240 endo	190–340	20.90(20.94)	Py	MgO
	570 exo	340–700	decomposition		
$Mg(Cl_3Ac)_2(Py)\cdot 6H_2O$	180 endo	130–270	20.10(20.15)	$6H_2O$	
	315 endo	270–500	14.75(14.73)	Py	MgO
	550 exo	500–700	decomposition		
$Mg(SCN)_2(Py)_3\cdot 2H_2O$	140 endo	100–195	8.70(8.71)	$2H_2O$	
	290 endo	195–500	57.40(57.34)	3Py	MgS
	680 exo	500–700	decomposition		

commences. This is followed by two mass loss steps, in the intervals 140–240°C and 240–600°C. On the basis of the mass losses (Table 2), these two steps were attributed to the formation of the intermediates $Mg(ClAc)_2(Py)_2$ and $Mg(ClAc)_2$, while the final solid product was MgO. The most probable thermal decomposition scheme is

$$Mg(ClAc)_2(Py)_2\cdot 2H_2O \xrightarrow{140-240^{\circ}C} Mg(ClAc)_2(Py)_2 \xrightarrow{240-600^{\circ}C} Mg(ClAc)_2 \xrightarrow{600-690^{\circ}C} MgO$$

The DTA curve of complex I (Fig. 1) displays two endothermic peaks, with maxima at 175 and 260°C, corresponding to the loss of $2H_2O$ and 2Py, respectively, and an exothermic peak with maximum at 640°C, corresponding to the loss of 2ClAc, with the simultaneous formation of MgO.

$Mg(Cl_2Ac)_2(Py)\cdot H_2O$ is stable up to 105°C (Fig. 2). Above this temperature, the elimination of neutral ligand begins. In the temperature range 105–190°C, the compound lost H_2O, which gave an endothermic peak at 120°C in the DTA curve. In the range 190–530°C, Py was eliminated in one step, this being observed as an endothermic peak at 240°C in the DTA curve. At temperatures higher than 530°C, the decomposition of $2Cl_2Ac$ took place in one step, which gave an exothermic peak at 570°C in the DTA curve. The final product was MgO. The most probable thermal decomposition scheme here is

$$Mg(Cl_2Ac)_2(Py)\cdot H_2O \xrightarrow{105-190^{\circ}C} Mg(Cl_2Ac)_2(Py) \xrightarrow{190-530^{\circ}C} Mg(Cl_2Ac)_2 \xrightarrow{530-690^{\circ}C} MgO$$

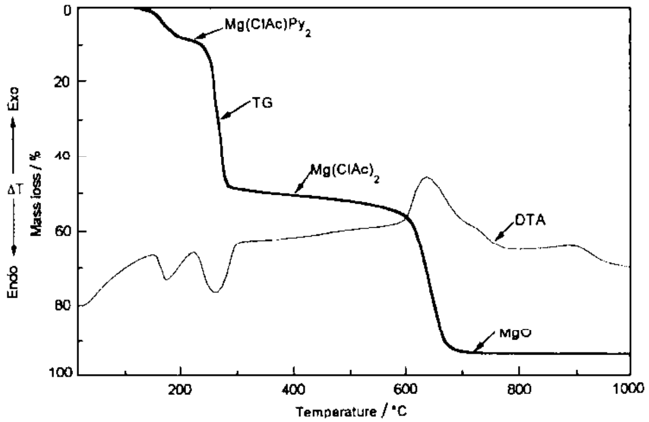

Fig. 1 TG and DTA curves of $Mg(ClAc)_2(Py)_2 \cdot 2H_2O$

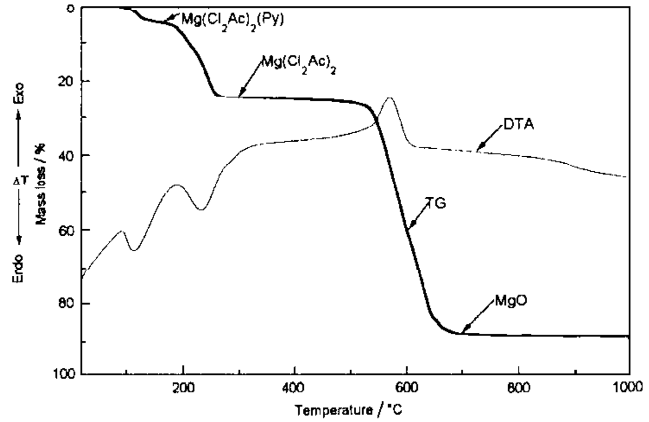

Fig. 2 TG and DTA curves of $Mg(Cl_2Ac)_2(Py) \cdot H_2O$

The TG and DTA curves for $Mg(Cl_3Ac)_2(Py) \cdot 6H_2O$ are depicted in Fig. 3. The TG curve indicates that it is stable at temperatures up to 110°C, when decomposition begins. MgO is formed as final product at 640°C. The TG curve shows two bendings, at 280 and 510°C. They correspond to the presence of two intermediate decomposition products: $Mg(Cl_3Ac)_2(Py)$ and $Mg(Cl_3Ac)_2$. The most probable thermal decomposition scheme here is

$$Mg(Cl_3Ac)_2(Py) \cdot 6H_2O \xrightarrow{110-280^\circ C} Mg(Cl_3Ac)_2(Py) \xrightarrow{280-510^\circ C} Mg(Cl_3Ac)_2$$

$$\xrightarrow{510-640^\circ C} MgO$$

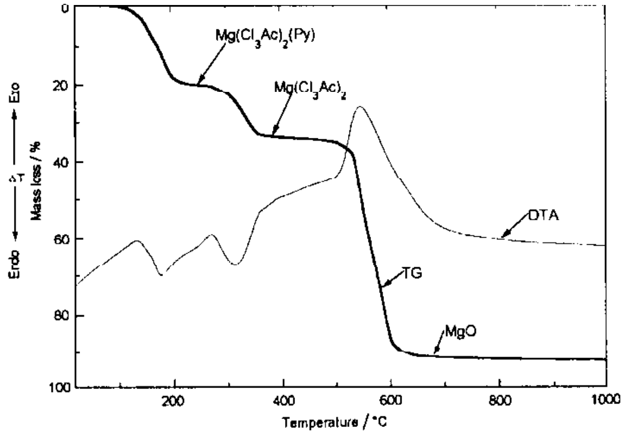

Fig. 3 TG and DTA curves of $Mg(Cl_3Ac)_2(Py)\cdot 6H_2O$

The DTA curve of complex III (Fig. 3) displays two endothermic peaks, with maxima at 180 and 315°C, corresponding to the loss of $6H_2O$ and Py, respectively, and an exothermic peak with maximum at 550°C, corresponding to the loss of $2Cl_3Ac$, with the simultaneous formation of MgO.

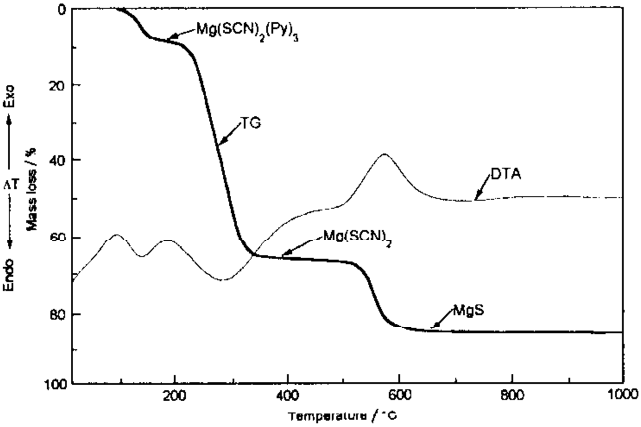

Fig. 4 TG and DTA curves of $Mg(SCN)_2(Py)_3\cdot 2H_2O$

The TG and DTA curves of $Mg(SCN)_2(Py)_3\cdot 2H_2O$ (IV) are given in Fig. 4. The TG curve indicates that this complex is stable up to 110°C (Fig. 4), where a slow decomposition to MgS starts; this is the final product at 625°C. The TG curve exhibits two bendings, at 210 and 520°C. They correspond to two intermediate decomposition products: $Mg(SCN)_2(Py)_3$ and $Mg(SCN)_2$. The most probable thermal decomposition scheme here is

$$Mg(SCN)_2(Py)_3\cdot 2H_2O \xrightarrow{110-210^{\circ}C} Mg(SCN)_2(Py)_3 \xrightarrow{210-520^{\circ}C} Mg(SCN)_2 \xrightarrow{520-625^{\circ}C} MgS$$

The DTA curve for the complex (Fig. 4) exhibits two endothermic peaks, at 140 and 290°C, corresponding to the loss of $2H_2O$ and 3Py, respectively, and an exothermic maxima with centre at about 790°C, corresponding to the loss of (SCN+CN), with the simultaneous formation of MgS.

IR spectra

The absorption bands in the ranges 3372–3125 cm^{-1} ν(OH) and 1620–1604 cm^{-1} δ(HOH) confirm the presence of water of crystallization, while those in the range 650–1000 cm^{-1} indicate the presence of water coordinated in the complexes [19]. The magnitude Δ_{COO} has been used by Nakamoto [20] as a criterion of the mode of carboxylate binding with metal ions. Calculations on the examined spectra resulted in values of Δ_{COO} in the range 272–232 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} [21] for complexes I–III are in good accord with the literature data for unidentate-bonded acetate structures. The absorption bands in the range 256–214 cm^{-1} ν(Mg–N) confirm the coordination of Py to Mg(II) through the nitrogen atom of its heterocyclic ring [22].

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