

THE THERMAL DECOMPOSITION OF MAGNESIUM(II) COMPLEXES WITH ACETIC AND HALOGENACETIC ACIDS

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Abstract

Thermogravimetry (TG), differential thermal analysis (DTA) and other analytical methods have been applied to the investigation of the thermal behaviour and structure of the compounds $\text{Mg}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (**I**), $\text{Mg}(\text{ClAc})_2 \cdot 2\text{H}_2\text{O}$ (**II**) and $\text{Mg}(\text{Cl}_2\text{Ac})_2 \cdot \text{H}_2\text{O}$ (**III**) ($\text{Ac} = \text{CH}_3\text{COO}^-$, $\text{ClAc} = \text{ClCH}_2\text{COO}^-$, $\text{Cl}_2\text{Ac} = \text{Cl}_2\text{CHCOO}^-$). The solid phased intermediate and resultant products of thermolysis had been identified. The possible scheme of destruction of the complexes is suggested. The halogenacetato magnesium complexes (**II–III**) are thermally more stable than the acetatomagnesium complex **I**. The final products of the decomposition of compounds were MgO. Infrared (IR) data suggest to a unidentate coordination of carboxylate ions to magnesium ions in complexes **I–III**.

Keywords: acetic and halogenacetic acids, DTA, IR, Mg, TG

Introduction

Systematic studies of the stereochemistry of both coordination and organometallic magnesium compounds have expanded rapidly over the last three decades [1]. The stereoselective behaviour in such derivatives can often be related to well known stereochemical specificity of biological systems, catalyst and related phenomena. Such systems are also of considerable commercial value for stereoselective industrial processes. It is well documented that heterocyclic compounds play a significant role in many biological systems. Especially N-donor ligand systems are components of several vitamins and drugs [2, 3]. It is not surprising, therefore, that many authors have investigated heterocyclic compounds and also examined them as ligands in coordination compounds of several central atoms [4–15].

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The reveal of the relationship between the structure and thermolysis of metal carboxylate complexes, the study of the influence of metal and ligand nature on the process of thermal decomposition are of a certain interest. The thermal decomposition of Mg(II), Mn(II), Co(II), Ni(II), Zn(II), Cd(II) complexes with *p*-hydroxybenzoates and some copper and alkali metals complexes with benzoic acid derivatives were studied [16]. Acetato and halogenacetato complexes of Ni(II), Fe(III) and Cu(II) have been reviewed earlier [17]. But the reported data on thermal decomposition and IR-spectral analysis of acetato and halogenacetato Mg(II) complexes are too rare. The present paper deals with the results of synthesis, thermal analysis and infrared spectral analysis of the above mentioned new magnesium complexes **I–III**.

Experimental

Preparation of compounds

Compounds **I**, **II** and **III** were prepared by dissolving 1.16 g Mg(OH)₂ in stoichiometric quantities of solution of appropriate acetic acid:water=1:2 by gradually stirring. The solutions were reduced in volume at room temperature and left to crystallized. The products were filtered, washed with ether and dried at room temperature.

Measurements

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

Results and discussion

Analysis of compounds

The content of C and H was determined by elemental analysis and the content of Mg was determined by complexometric titration of the compounds. The analytical data of the compounds **I–III** reported in Table 1 show a good agreement between the experimental and calculated data.

Thermal behaviour of the compounds

Thermal decomposition study of the complex Mg(Ac)₂·2H₂O (Fig. 1) shows two endothermic peaks at 80 and 171°C with loss of each of the water molecules followed by further endothermic peak at 327°C, closely connected to an exothermic peak at 347°C corresponding to the mass loss of 2Ac and the formation of MgO. (Residue: found 22.50%; theory 22.59%).

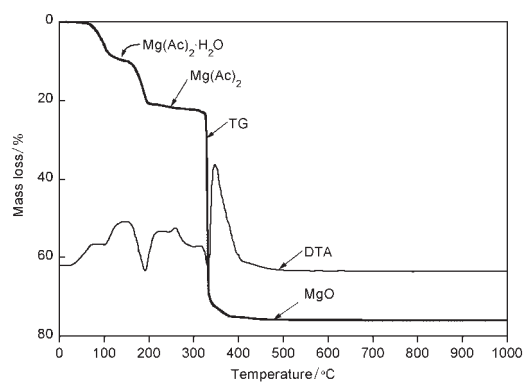


Fig. 1 TG and DTA curves of $\text{Mg}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (I). Sample mass 100 mg, heating rate: $10^{\circ}\text{C min}^{-1}$, atmosphere: air

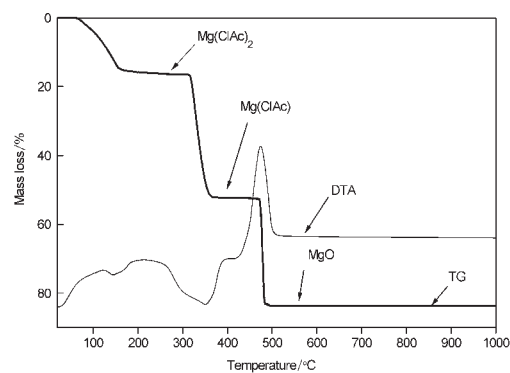


Fig. 2 TG and DTA curves of $\text{Mg}(\text{ClAc})_2 \cdot 2\text{H}_2\text{O}$ (II). Sample mass 100 mg, heating rate: $10^{\circ}\text{C min}^{-1}$, atmosphere: air

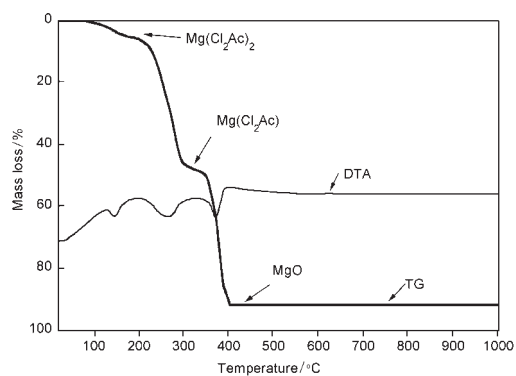


Fig. 3 TG and DTA curves of $\text{Mg}(\text{Cl}_2\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (III). Sample mass 100 mg, heating rate: $10^{\circ}\text{C min}^{-1}$, atmosphere: air

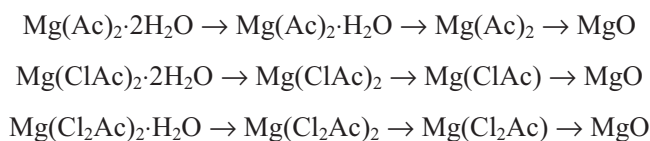
Thermal decomposition of the compound $\text{Mg}(\text{ClAc})_2 \cdot 2\text{H}_2\text{O}$ (Fig. 2) shows an endothermic reaction at 135°C with loss of the two water molecules in one step followed by further endothermic reaction at 350°C and an exothermic reaction 475°C corresponding to the mass loss of each of the ClAc and the formation of MgO. (Residue: found 9.90%; theory 9.82%).

Table 1 Analytical data of compounds

Complex	Experimental(%)			Theory(%)		
	C	H	Mg	C	H	Mg
I - $\text{Mg}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$	26.92	4.58	13.61	26.96	5.61	13.66
II - $\text{Mg}(\text{ClAc})_2 \cdot 2\text{H}_2\text{O}$	19.17	3.10	9.84	19.41	3.23	9.83
III - $\text{Mg}(\text{Cl}_2\text{Ac})_2 \cdot \text{H}_2\text{O}$	16.53	1.63	8.14	16.10	1.34	8.15

The compound $\text{Mg}(\text{Cl}_2\text{Ac})_2 \cdot \text{H}_2\text{O}$ undergoes (Fig. 3) an endothermic reaction at 140°C with the loss of the water molecule followed by further endothermic reactions at 250 and 350°C corresponding to the mass loss of each of the Cl_2Ac and the formation of MgO. (Residue: found 8.00%; theory 8.16%).

The sequence of decomposition reactions as deduced from the TG studies are summarized below:



IR-spectra

The modes of the coordinated ligands in the complexes have been investigated by means of infrared absorption spectra. The most important infrared frequencies attributed to the vibrations of the complexes **I–III** are reported in Table 2.

Table 2 Important infrared bands ($4000\text{--}200\text{ cm}^{-1}$) of complexes I–III

Assignment	I	II	III
νCOO^- (as)	1649	1644	1678
νCOO^- (s)	1458	1408	1414
$\nu(\text{C}-\text{C})$	918	949	924
$\nu(\text{CH})$	2849	2924	2924
$\nu(\text{OH})$	3351	3374	3414
$\delta(\text{HOH})$	1595	1578	1643
$\rho(\text{H}_2\text{O})$	625, 658, 689, 947	696, 779, 945, 901	677, 781, 822,
$\nu(\text{Mg}-\text{O})$	289, 324, 327, 422	255, 309, 405	303, 334, 424

as – asymmetric, s – symmetric

The absorption bands $\nu(\text{OH})$ and $\delta(\text{HOH})$ which occur in the range 3414–3351 and 1643–1595 cm^{-1} respectively, confirm the presence of water of crystallization. The absorption bands which occur in the range 1000–600 cm^{-1} (Rocking and Wagging stretching) and 424–255 cm^{-1} $\nu(\text{Mg-O})$ confirm the presence of water as coordinated in the complexes [18]. The presence of water as water of crystallization and as coordinated water in the compounds is further borne out by the thermal decomposition data. Carboxylate ions can coordinate to metal ions in a number of ways such as unidentate, bidentate (chelating) or bridging and there is an evidence of that fact in the IR spectrum. The analysis of COO^- group bands frequencies allowed on determination of parameter $\Delta_{\text{COO}} = \nu\text{COO}^-_{(\text{as})} - \nu\text{COO}^-_{(\text{s})}$. The magnitude of Δ_{COO} has been used by Nakamoto [19] as a criteria of the way of carboxylate binding with metal ions. Calculated from the examined spectra values of Δ_{COO} are in the range 264–191 cm^{-1} . These values and three bands (COO deformation) at 920–720 cm^{-1} and a strong band [$\pi(\text{CO}_2)$] near at 540 cm^{-1} [20] of complexes **I–III** is in good agreement with the literature data for unidentately bonded acetates structures.

Conclusions

The composition of complexes **I–III** is determined by elemental analysis. All complexes **I–III** are hydrated, stable in air and soluble in water, ethanol, methanol and dimethylsulfoxide. The decomposition of the compounds was initiated by elimination of water. Halogenacetatomagnesium complexes (**II–III**) are thermally more stable than the acetatomagnesium complex (**I**). Mass corresponding to 2Ac, 2ClAc and 2Cl₂Ac was eliminated in one step in complex **I** but in two steps in complexes **II** and **III** respectively. The results reveal that MgO is left as residue at the end of the thermal degradation experiments of the compounds (**I–III**). The stoichiometry of thermal decomposition can also be influenced by the changes of experimental conditions [21, 22]. Infrared data is in good accordance with the literature data for unidentately bonded acetates structures. Without X-ray analysis, no definite structure can be described for the different components. However, spectroscopic and analytical data available enable us to predict structures and we can also use thermal decomposition studies to help us.

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