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THERMAL STUDY OF NEW COMPLEXES OF MAGNESIUM NITRATE WITH SOME AMIDES OF CARBOXYLIC ACIDS

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ABSTRACT

The thermal decompositions of $2CO(NH_2)_2 \cdot Mg(NO_3)_2 \cdot 4H_2O$, $4CO(NH_2)_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$, $6CO(NH_2)_2 \cdot Mg(NO_3)_2$, $4CH_3CONH_2 \cdot Mg(NO_3)_2$ $2H_2O$, $6CH_3CONH_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$ were studied. The results showed that changes of thermal stability of complex compounds depend on the organic ligand character.

INTRODUCTION

The study of interaction of magnesium nitrate with carbamide and acetamide in aqueous medium is important for theoretical foundation of the conditions of preparing new amide compounds of magnesium nitrate which are interested in agrochemistry. Synthesis of amide complex compounds, vis. $2CO(NH_2)_2 \cdot Mg(NO_3)_2 \cdot 4H_2O$, $4CO(NH_2)_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$, $6CO(NH_2)_2 \cdot Mg(NO_3)_2$, $4CH_3CONH_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$, $6CH_3CONH_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$, was performed with the use of the results of studying the equilibria of the corresponding systems. Thermogravimetric study of the obtained compounds made it possible to elucidate how thermal stability of complex compounds changes depending on the organic ligand character.

EXPERIMENTAL RESULTS AND DISCUSSION

Thermal analysis was carried out on a derivatograph of the Paulic-Paulic-Erdei system at a rate of sample heating 10 deg/min. To identify amide complexes and the products of their thermolysis was use of chemical, X-ray diffraction, crystallographic and IR spectroscopic methods.

Figures 1 to 5 present thermogravitograms of synthesized complexes. It is seen that all the compounds melt congruently; the meling point of both carbamide and acetamide complexes enhances with growing number of the organic ligand molecules

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replacing a water molecule in the coordination sphere of the complexforming ion. This points to the formation of a stronger chemical bond between the ligand and central atom. A complex character of the heating curves of the amide complexes of magnesium nitrate indicates that the complexes decompose by following the stepwise mechanism. Dehydration with a partial decomposition of aqua - amide complexes takes place within the temperature region from 180°C (for carbamide compounds) to 230°C (for acetamide ones). The IR spectroscopic investigations showed that organic ligand in amide complexes is coordinated through a carbonyl group and that donor activities of acetamide and carbamide are different. Since acetamide is a stronger base than carbamide, the Mg-acetamide bond is stronger than Mg-carbamide, i.e. thermal stability of acetamide complexes should be higher than that of carbamide complexes. We confirmed this conclusion by the thermogravimetric data obtained by us for these compouds.

The endothermal effects on the DTA curves of the investigated complexes (Figures 1 to 5) after their dehydration correspond to the spliting and subsequent removal of the amide molecules. Within the 380 - 420°C temperature range a sharply pronounced exothermal effect is observed for the amide complexes of magnesium nitrates; the effect is due to the formation of intermediate nitrosyl compounds.

A total mass loss is for: $2CO(NH_2)_2 \cdot Mg(NO_3)_2 \cdot 4H_2O$ - 88,25; $4CO(NH_2)_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$ - 90,28; $6CO(NH_2)_2 \cdot Mg(NO_3)_2$ - 92,18; $4CH_3CONH_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$ - 90,20; $6CH_3CONH_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$ - 92,31 mass.% (theory: 88,15; 90,50; 92,07; 90,37; 92,51%, respectively) Magnesium oxide is the final product of thermolysis of the amide complexes.

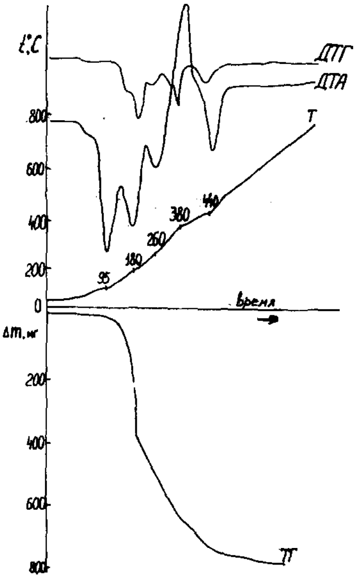

Fig. 1. T, TG, DTG and DTA curves of $2CO(NH_2)_2 \cdot Mg(NO_3)_2 \cdot 4H_2O$

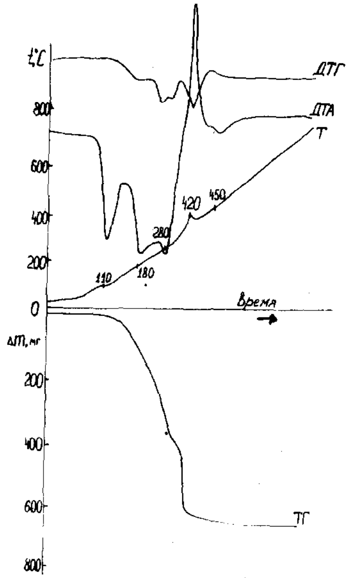

Fig. 2. T, TG, DTG and DTA curves of $4CO(NH_2)_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$

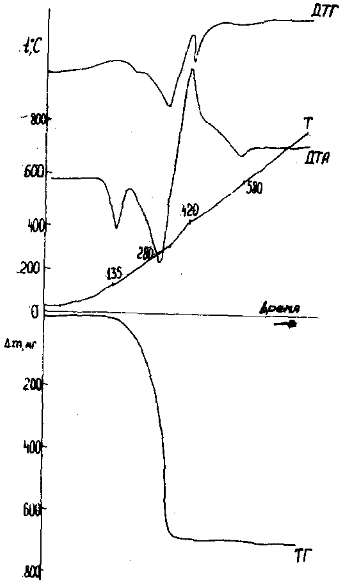

Fig. 3. T, TG, DTG and DTA curves of $6CO(NH_2)_2 \cdot Mg(NO_3)_2$

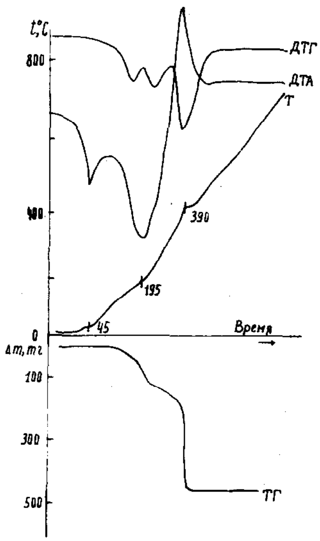

Fig.4. T,TG,DTG and DTA curves of $4CH_3CONH_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$

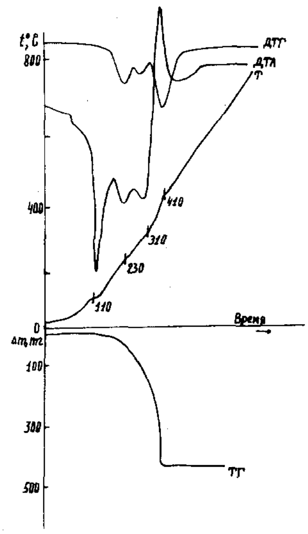

Fig.5. T,TG,DTG and DTA curves of $6CH_3CONH_2 \cdot Mg(NO_3)_2 \cdot 2H_2O$