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STUDY OF THE THERMAL DECOMPOSITION OF BROMAZEPAN COMPLEXES WITH Co(II), Ni(II), Cu(II) AND Zn(II)

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ABSTRACT

The thermal behaviour of complexes of bromazepan with Co(II), Ni(II), Cu(II) and Zn(II) was studied by thermogravimetry (TG) and differential thermal analysis (DTA). The complexes decompose in two steps: dehydration and decomposition. A correlation between the dehydration temperatures of MB_2X_n and the coordinating ability of X is observed.

INTRODUCTION

The interaction of metallic ions with benzodiazepines has been the subject of several investigations [1–6]. More recently, complexes of bromazepan (B) with several transition metal ions have been studied [7,8], with investigation of the magnetic and spectroscopic properties as well as an approximation of their molecular geometries.

The present work is a study of the thermal behaviour of a series of similar complexes by means of TG and DTA.

EXPERIMENTAL

Methods

Thermal analyses by means of TG and DTA were carried out on a Setaram thermobalance, in a dry nitrogen dynamic atmosphere. Experiments were carried out on samples of ca. 30 mg, at a heating rate of 4°C min^{-1}, using ignited Al_2O_3 as a reference. To calculate the number of water molecules in the complexes studied, TG was carried out at a heating rate of 1.3°C min^{-1}. The kinetic analysis of the dehydration processes was performed by means of the TG data obtained at variable temperatures, following Satava's integral method [9].

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Samples

The complexes studied, whose synthesis and characterization have been described previously [7,8], are the following: $CoB_2(ClO_4)_2 \cdot 3.5H_2O$; $NiB_2(ClO_4)_2 \cdot 4H_2O$; $CuB_2(ClO_4)_2 \cdot H_2O$; $ZnB_2(ClO_4)_2 \cdot 3H_2O$; $CoB_2SO_4 \cdot 2H_2O$; $NiB_2SO_4 \cdot 4H_2O$; $CuBSO_4 \cdot 1.5H_2O$; $ZnB_2SO_4 \cdot 2.5H_2O$; $CoB_2Cl_2 \cdot H_2O$; $NiB_2Cl_2 \cdot 2H_2O$; CuB_2Cl_2; and ZnB_2Cl_2.

RESULTS AND DISCUSSION

Figures 1 and 2 show the TG and DTA curves for the chloride and sulphate complexes, respectively. The thermal behaviour of these complexes is generally described by the following differentiated processes: (i) dehydration; (ii) decomposition of the corresponding anhydrate complexes. Perchlorate complexes decompose violently once dehydrated at temperatures of 200–350 °C.

Under the conditions used in the present work, the dehydration process takes place in a single step for all complexes, except the sulphate complexes of Cu(II) and Zn(II), where the process takes place in two steps, as shown by the corresponding DTA curve.

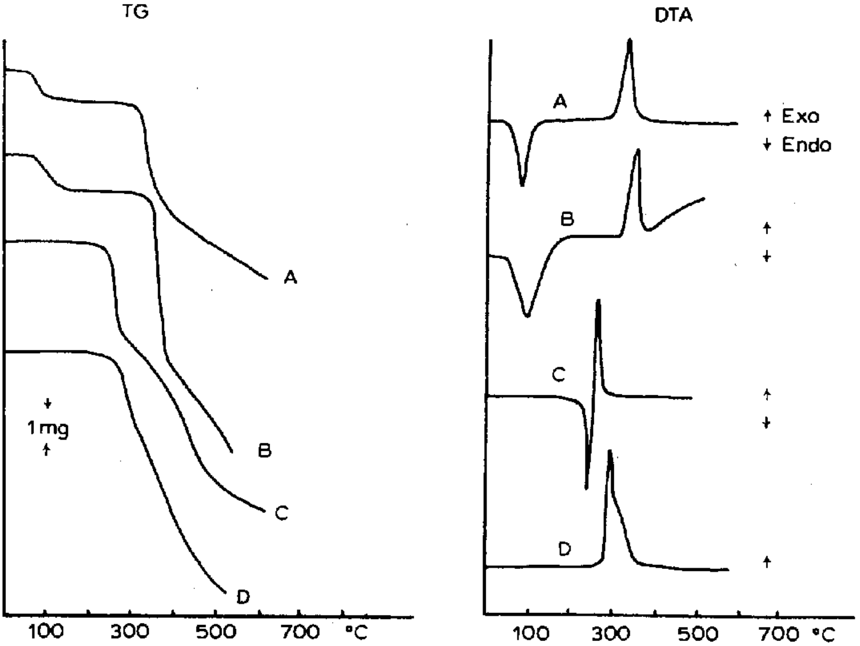

Fig. 1. TG and DTA curves of: (A) $CoB_2Cl_2 \cdot H_2O$; (B) $NiB_2Cl_2 \cdot 2H_2O$; (C) CuB_2Cl_2; (D) ZnB_2Cl_2.

TABLE 1

Dehydration temperatures and weight losses of the complexes studied

Compound	Dehydration temp. (°C)	Weight loss (%)		Temp. range first step decomposition (°C)	Weight loss (%)	
		Calcd.	Obs.		Calcd.	Obs.
$CoB_2(ClO_4)_2\cdot 3.5H_2O$	134	6.6	6.6	–	–	–
$CoB_2SO_4\cdot 2H_2O$	120	4.3	4.7	298–350	19	18
$CoB_2Cl_2\cdot H_2O$	95	2.3	2.6	300–380	20	17
$NiB_2(ClO_4)_2\cdot 4H_2O$	147	7.4	7.3	347	–	–
$NiB_2SO_4\cdot 4H_2O$	140	8.3	8.4	309–370	19.8	19
$NiB_2Cl_2\cdot 2H_2O$	80	4.1	4.5	310–370	21	14
$CuB_2(ClO_4)_2\cdot H_2O$	140	1.9	1.6	214	–	–
$CuBSO_4\cdot 1.5H_2O$	180	5.3	5.1	271	–	–
CuB_2Cl_2	–	–	–	230–340	21	14
$ZnB_2(ClO_4)_2\cdot 3H_2O$	180	5.6	5.7	–	–	–
$ZnB_2SO_4\cdot 3.5H_2O$	120	5.4	5.4	270–350	–	–
ZnB_2Cl_2	–	–	–	260–380	20.5	12.5

Table 1 gives dehydration temperatures and the percentage weight lost in this process. There is a trend towards a decrease in the temperature of dehydration for the same ion as the anion is changed. This fact probably reflects the coordinating character of the counterion. It has been shown [8]

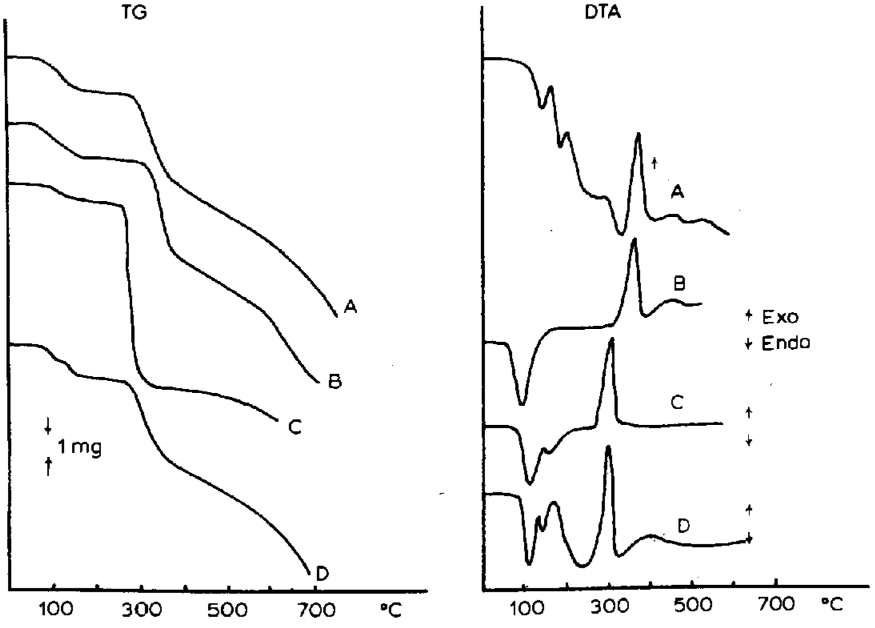

Fig. 2. TG and DTA curves of: (A) $CoB_2SO_4\cdot 2H_2O$; (B) $NiB_2SO_4\cdot 4H_2O$; (C) $CuBSO_4\cdot 1.5H_2O$; (D) $ZnB_2SO_4\cdot 3.5H_2O$.

TABLE 2

Activation energies of the complexes studied

Compound	Activation energy (kcal mol^{-1})	
$CoB_2(ClO_4)_2 \cdot 3.5H_2O$	7	
$NiB_2(ClO_4)_2 \cdot 4H_2O$	6	
$CuB_2(ClO_4)_2 \cdot H_2O$	6	
$ZnB_2(ClO_4)_2 \cdot 3H_2O$	8	
$CoB_2SO_4 \cdot 2H_2O$	8	
$NiB_2SO_4 \cdot 4H_2O$	7	
	1st step	*2nd step*
$CuBSO_4 \cdot 1.5H_2O$	17	5
$ZnB_2SO_4 \cdot 3.5H_2O$	16	–

that the coordinative capacity increases in the order $MB_2(ClO_4)_2 < MB_2SO_4 < MB_2Cl_2$. Thus, there is the possibility that a decrease in the coordinative character of the anion, in turn, induces an increase in the coordinative character of the water molecules (essentially water of crystallization) which would explain the observed trend.

A kinetic study of the present results indicates that, in all cases, the dehydration process takes place by a nucleation mechanism. The present data fit this model best, giving a set of activation energy values in better agreement with those found in the literature for the same type of complexes [10].

The activation energy values shown in Table 2 allow us to conclude that the water molecules present interact weakly with the metallic ions, since the values obtained for the activation energy are independent of the metal ion. Also, the two complexes with undergo dehydration in two steps have anomalous activation energy values for the first step, indicating that the water molecules lost in the second step are those with a structural function similar to the water molecules present in the complexes which dehydrate in a single step.

The anhydrate products are stable within a temperature range of ~ 150–300 °C. Above 300 °C decomposition begins and it is possible to detect a well-defined first decomposition step for chloride and sulphate compounds. In general, this step takes place between 290 and 370 °C with a narrow exothermic peak and a weight loss of ~ 19–12.5%. Based on these data it is possible to suggest that during such step pyridile radicals are eliminated, so that for the complexes $CoB_2SO_4 \cdot 2H_2O$, $CoB_2Cl_2 \cdot H_2O$ and $NiB_2SO_4 \cdot 4H_2O$ it corresponds essentially to the loss of two moles of pyridine per mole of compound (see Table 1).

Finally, the decomposition process continues in a progressive manner.

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