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THERMAL STUDY OF MEPIRIZOL COMPLEXES WITH Co(II), Ni(II), Cu(II) AND Zn(II)

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ABSTRACT

A study of the thermal behaviour of mepirizol complexes, M(mepirizol)$_n$(ClO$_4$)$_2 \cdot x$H$_2$O and M(mepirizol)SO$_4 \cdot y$H$_2$O, is reported. All the compounds decompose in two general processes: dehydration and pyrolytic decomposition. A non-isothermal kinetic study of the dehydration process was carried out. Possible mechanisms of decomposition for the sulphate complexes are discussed.

INTRODUCTION

4-Methoxy-2-(5-methoxy-3-methyl-pyrazol-1-yl)-6-methyl-pyrimidine, (mepirizol, hereafter L), is a pyrimidyl-pyrazole derivative (its structure is shown in Fig. 1), used as an anti-inflammatory agent [1]. We have previously reported the synthesis and characterization of several mepirizol complexes with M(II) ions (M = Co, Ni, Cu, Zn) [2,3]. Resolution of the crystal and molecular structures of CuL$_2$(ClO$_4$)$_2$ [4] and CuLCl$_2$ [5] reveals that the mepirizol acts as a bidentate ligand through nitrogen atoms 2 and 1′. Interpretation of the electronic properties of the remaining compounds is in good agreement with this fact.

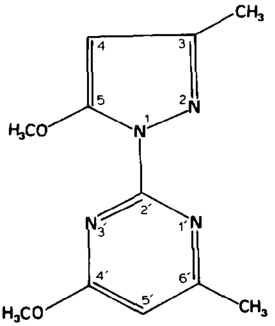

Fig. 1. 4-Methoxy-2-(5-methoxy-3-methyl-pyrazol-1-yl)-6-methyl-pyrimidine (mepirizol).

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For a more complete characterization of the compounds, we think that the study of their thermal behaviour is interesting. In the present work, we report the results of a study carried out on the features of thermal evolution of $ML_n(ClO_4)_2 \cdot xH_2O$ and $MLSO_4 \cdot yH_2O$ compounds.

EXPERIMENTAL

Methods

The thermal analyses were carried out under a static air atmosphere. TG and DTG curves were obtained with a Mettler TA 3000, and DTA curves were made using a RAX 1200 simultaneous TG–DTA thermobalance. The heating rate was 5°C min^{-1}. Calcined Al_2O_3 was used as a reference. For the non-isothermal kinetic study of the dehydration processes a 1.3°C min^{-1} heating rate was maintained.

Samples

The syntheses and characterization of the compounds studied have been previously described [2,3].

RESULTS AND DISCUSSION

Figures 2a–d show the TG and DTG curves for $MLSO_4 \cdot yH_2O$ and $CuL_2(ClO_4)_2 \cdot H_2O$ *. The DTA curves for these compounds and $ZnL_2(ClO_4)_2 \cdot 1.5H_2O$ are given in Fig. 3. Analytical data from the TG curves are listed in Table 1.

Two general processes are observed in the thermal evolution of the studied compounds: dehydration and pyrolytic decomposition with metal oxide formation.

The initial weight loss, of endothermic character, observed for all five hydrates corresponds to the complete dehydration stage. At the end of this process, stable anhydrous materials were obtained. For $ZnL_2(ClO_4)_2 \cdot 1.5H_2O$ and $CoLSO_4 \cdot 3H_2O$, the DTG and DTA curves reveal that dehydration takes place in two steps with a first elimination of 1/2 and 2 water molecules, respectively, according to the following reaction schemes:

$$ZnL_2(ClO_4)_2 \cdot 1.5\ H_2O \rightarrow ZnL_2(ClO_4)_2 \cdot H_2O \rightarrow ZnL_2(ClO_4)_2$$

$$CoLSO_4 \cdot 3H_2O \rightarrow CoLSO_4 \cdot H_2O \rightarrow CoLSO_4$$

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* The thermal behaviour of this compound can be considered as representative of all the perchlorate complexes.

The DTA curve of $CuL_2(ClO_4)_2 \cdot H_2O$ shows an endothermic peak after dehydration at 144°C, which does not correspond to a weight loss. The brown solid obtained after heating $CuL_2(ClO_4)_2 \cdot H_2O$ to 160°C has an X-ray powder diffractogram similar to that of $CuL_2(ClO_4)_2$ [2]. Thus, the endothermic process can be attributed to the rearrangement of the starting material to give crystalline $CuL_2(ClO_4)_2$.

Non-isothermal kinetic analysis of the dehydration process was carried out with application of two different procedures: the Coats and Redfern

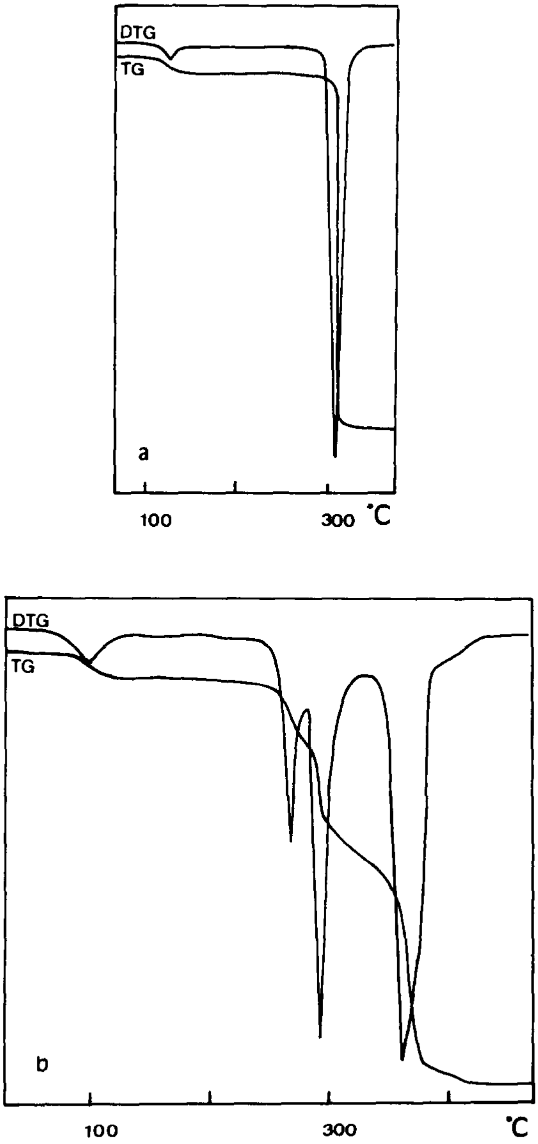

Fig. 2. TG and DTG curves for: (a) $CuL_2\ (ClO_4)_2 \cdot H_2O$; (b) $CuLSO_4 \cdot H_2O$.

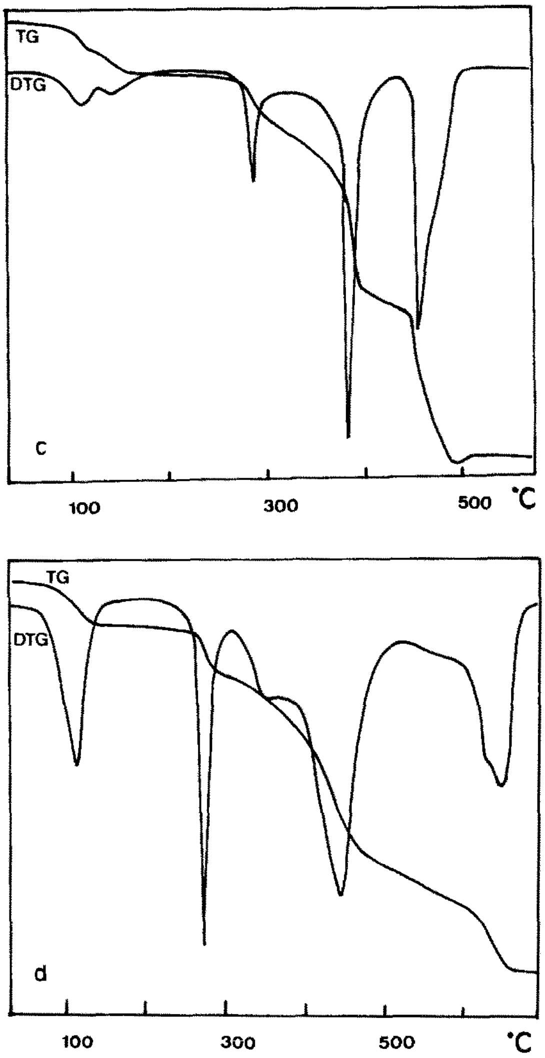

Fig. 2 (continued). (c) $CoLSO_4 \cdot 3H_2O$; (d) $ZnLSO_4 \cdot 2H_2O$.

method [6] and the mathematical approach of Abou-Shaaban and Simonelli [7]. The activation energy (E_a) values obtained are listed in Table 2.

Application of the former method to the experimental data shows that the best fit is obtained for the formal reaction order $n = 1$. On the other hand, the E_a values calculated by application of the latter procedure support these results. Comparison of the two sets of kinetic parameters shows that the deviation between them was not great, considering the approximations involved in both methods. Consequently, it seems reasonable to conclude that a random nucleation mechanism (which corresponds to the F_1 model in the Sharp notation [8]) can be assumed for all dehydration processes.

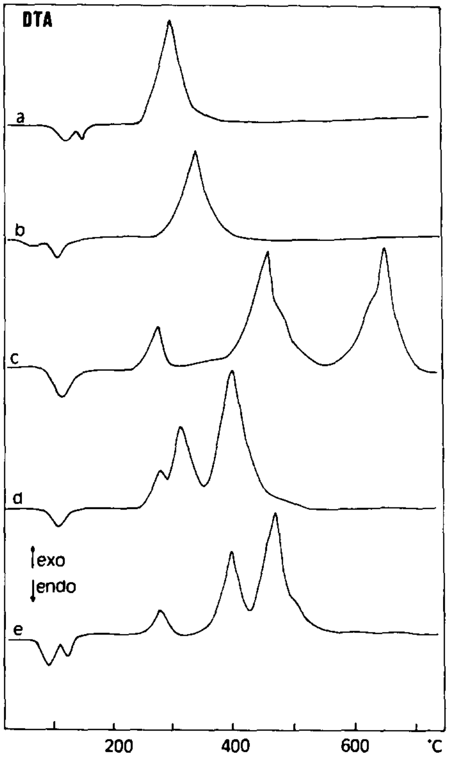

Fig. 3. DTA curves for: (a) CuL_2 $(ClO_4)_2 \cdot H_2O$; (b) ZnL_2 $(ClO_4)_2 \cdot 1.5H_2O$; (c) $ZnLSO_4 \cdot 2H_2O$; (d) $CuLSO_4 \cdot H_2O$; (e) $CoLSO_4 \cdot 3H_2O$.

The results obtained from the kinetic study can be applied, with caution, to the characterization of the role played by the water molecules in the compounds.

In a previous work we reported that the water molecules in the two copper(II) hydrates are coordinated to Cu(II) ions [2,9]; in both compounds, pentacoordinated Cu(II) is present (with nearly trigonal bipyramidal stereochemistry). However, the relatively low values of E_a suggest that the $Cu-OH_2$ interaction (particularly in the perchlorate compound) is not very strong. The formation of relatively stable anhydrous materials with tetracoordinated Cu(II) ions (CuN_4 and CuN_2O_2 chromophores) would explain this fact.

In $CoLSO_4 \cdot 3H_2O$, an octahedral environment has been proposed for the Co(II) ion (CoN_2O_4 chromophore), with no rejection for coordination of all three water molecules [3]. The existence of two steps in the dehydration process and the obtained E_a values indicate the non-equivalence between them. Although the three water molecules are probably coordinated, one of them would be more strongly linked to the Co(II) ion.

For the two zinc compounds , no previous information about the role of water is available. On the basis of the results obtained in the present study,

TABLE 1

Weight losses and temperatures from TGA/DTG curves

Compound	Temp. range (°C)	t_p [a] (°C)	Δm (%)
$CuL_2(ClO_4)_2$	295–310	305	88.4
$CuL_2(ClO_4)_2 \cdot H_2O$	75–143	127	2.5
	300–315	310	87.2
$ZnL_2(ClO_4)_2 \cdot 1.5H_2O$	40–90	60	1.2
	91–111	100	2.8
	265–280	275	87.6
$CoL_3(ClO_4)_2$	247–258	252	90.7
$NiL_3(ClO_4)_2$	265–275	272	92.6
$ZnLSO_4 \cdot 2H_2O$	86–130	120	9.2
	251–299	267	9.3
	307–450	426	42.0
	580–659	643	19.6
$CuLSO_4 \cdot H_2O$	80–120	114	5.4
	264–282	270	9.7
	285–312	294	19.0
	322–420	364	41.6
$CoLSO_4 \cdot 3H_2O$	53–108	98	8.0
	110–142	127	4.3
	281–309	290	9.6
	315–438	382	31.1
	443–501	460	29.9

[a] Temperature from DTG peak.

TABLE 2

Activation energies (E_a, kcal mol^{-1}) of the dehydration process

Compound	E_a from Coats and Redfern	E_a from Abou-Shaaban and Simonelli
$ZnL_2(ClO_4)_2 \cdot 1.5H_2O$	11	10
	40	36
$CuL_2(ClO_4)_2 \cdot H_2O$	17	14
$ZnLSO_4 \cdot 2H_2O$	22	22
$CuLSO_4 \cdot H_2O$	24	22
$CoLSO_4 \cdot 3H_2O$	19	20
	27	28

it is reasonable to assume that in the first dehydration step of the perchlorate compound, water of crystallization is removed, whereas the high E_a value associated with the elimination of the remaining molecule would be indicative of a strong $Zn-OH_2$ interaction. For the sulphate compound, the E_a of dehydration is similar to that obtained for copper(II) and cobalt(II) sulphates, and the two water molecules are probably coordinated to the cation.

The thermal evolution of perchlorate and sulphate compounds on heating the anhydrous materials obtained after dehydration is clearly different. All perchlorate complexes decompose rapidly in a single step in the range 250–300°C. The experimental weight losses in all cases are in good agreement with the theoretical value required for oxide formation. The initial decomposition temperature increases in the order $Co < Ni \approx Zn < Cu$. This behaviour is similar to that previously reported for another $MX_2(ClO_4)_2$ compound (where X is a bidentate ligand with aromatic rings, such as bipyridine or phenanthroline [10]). However, in these compounds decomposition takes place in two or three overlapping steps, whereas for the mepirizol perchlorate complexes only one step was observed.

The TG, DTG and DTA curves for $MLSO_4 \cdot xH_2O$ compounds show that their pyrolytic decomposition is complex, and at least three exothermic steps are detected. The decomposition begins above 250°C, in the order $Zn < Cu < Co$.

For $CuLSO_4 \cdot H_2O$ the weight loss associated with the first two steps of decomposition is in good agreement with the removal of the pyrimidinic ring from the ligand * (theoretical value required: 29.8%).

The elimination of "half a molecule of ligand" with the breakdown of the C2′–N1 bond could be conducive to the formation of a pyrazole moiety acting as a bidentate ligand through N1 and N2 atoms. A similar behaviour has been observed in the decomposition of copper(II) complexes with ligands having acceptor π-bonding systems, where π-bonding formation is considered responsible for the kind of decomposition mechanism found [11].

Unfortunately, the isolation of unstable intermediates is not possible, and the above interpretation must be considered as tentative.

The exothermic process observed after the partial elimination of ligand corresponds to total pyrolytic decomposition and metal oxide formation.

The thermal evolution of $CoLSO_4 \cdot 3H_2O$ is, in general, similar to that described for copper sulphate, but some differences can be established. Firstly, the weight loss for the second step of decomposition is higher (40.7 and 28.7%, respectively). A possible explanation could be that in this compound removal of the pyrimidinic group also entails elimination of

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* The weight loss of the first step is consistent with the previous elimination of methoxy and methyl groups from the pyrimidine ring.

methyl and methoxy groups linked to the pyrazole ring (the theoretical value required for the entire process is 39.0%, in good agreement with experiment). However, a possible interpretation of this proposed mechanism is not available at present. On the other hand, after the entire pyrolytic decomposition, a small mass increase (2%) is observed, probably due to oxidation of cobalt protoxide to Co_3O_4.

A more unusual behaviour is exhibited by the zinc compound. After the first step of decomposition (attributed to elimination of methoxy and methyl groups), the weight loss of the second step is consistent with complete removal of the ligand, and $ZnSO_4$ formation. This process was shown to be complex. The last exothermic step corresponds to zinc sulphate decomposition and ZnO formation. The unlikely stabilization of the intermediate and the higher decomposition temperature of zinc sulphate with respect to $CoSO_4$ and $CuSO_4$ can be used as arguments to explain this fact.

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