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THERMAL DECOMPOSITION OF METAL COMPLEXES OF CIMETIDINE

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ABSTRACT

A study of the thermal decomposition of $[M(cimetidine)_2]X_2 \cdot nH_2O$ complexes ** where M = Co(II), Ni(II) and Cu(II), X = $\frac{1}{2}SO_4$, NO_3 and BF_4 is reported. The sulphate complexes decompose by two processes: dehydration and pyrolytic decomposition. The nitrate and tetrafluoroborate cimetidine complexes undergo only the pyrolytic decomposition process.

INTRODUCTION

Recently we have reported the thermal study of chloride and perchlorate cimetidine complexes of formulae $[M(CM)_2]X_2 \cdot nH_2O$ (M = Co(II), Ni(II) or Cu(II); X = ClO_4 and Cl) and $[Cu(CM)SO_4]2H_2O$ [1].

In this paper we report the thermal study of the nitrate, tetrafluoroborate and sulphate cimetidine complexes.

EXPERIMENTAL

The thermal analyses were carried out on a Mettler TG-50 thermobalance using samples of ca. 15 mg and a heating rate of 10 °C min^{-1} under a dynamic oxygen atmosphere. Calcined α-Al_2O_3 was used as reference. The DTA curves were recorded in a RAX 1200 thermobalance.

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** Cimetidine (CM) is *N*-cyano-*N'*-methyl-*N''*(2-[(5-methyl-1H-imidazol-4-yl)methylthio]-ethyl)guanidine.

Infrared spectra were obtained using KBr pellets on a Perkin-Elmer 843 infrared spectrophotometer. X-ray powder diffraction patterns were obtained by means of a Kristalloflex 810 Siemens diffractometer using Cu *Kα* radiation.

Samples

The complexes $[M(CM)_2]X_2 \cdot nH_2O$ (M = Co(II), Ni(II) and Cu(II); X = $\frac{1}{2}SO_4$, NO_3 and BF_4) were prepared as previously described [2,3].

RESULTS AND DISCUSSION

The thermal decomposition curves of $[M(CM)_2]SO_4 \cdot nH_2O$, $[M(CM)_2](NO_3)_2$ and $[M(CM)_2](BF_4)_2$ are shown in Fig. 1: weight losses, the temperature range and dehydration enthalpies of those processes are shown in Table 1.

Sulphate complexes

The thermal behaviour of the sulphate cimetidine complexes are described by two differential processes: (1) dehydration; and (2) pyrolytic decomposition.

Dehydration

Under the experimental conditions used, the dehydration process occurs in a single step for $[Co(CM)_2]SO_4 \cdot 3H_2O$ and $[Ni(CM)_2]SO_4 \cdot 3H_2O$, this

TABLE 1

Temperatures and weight losses of the complexes studied

Compound	Dehydration				Decomposition		
	Temperature range (°C)	Peak temp. DTA	Weight loss (%)		Temperature range (°C)	Weight loss (%)	
			Calcd.	Obs.		Calcd.	Obs.
$[Co(CM)_2]SO_4 \cdot 3H_2O$	50–132	70	7.6	7.7	232–550	10.5	11.1
$[Ni(CM)_2]SO_4 \cdot 3H_2O$	50–145	100	7.6	7.5	255–550	10.5	10.3
$[Cu(CM)_2]SO_4 \cdot 4H_2O$	50–140	80	9.5	9.4	213–650	10.8	6.1
$[Co(CM)_2](NO_3)_2$					240–575	10.9	10.8
$[Ni(CM)_2](NO_3)_2$					240–575	10.9	11.1
$[Cu(CM)_2](NO_3)_2$					210–625	11.5	10.8
$[Co(CM)_2](BF_4)_2$					270–750		14.3
$[Ni(CM)_2](BF_4)_2$					280–750		17.4
$[Cu(CM)_2](BF_4)_2$					255–750		20.3

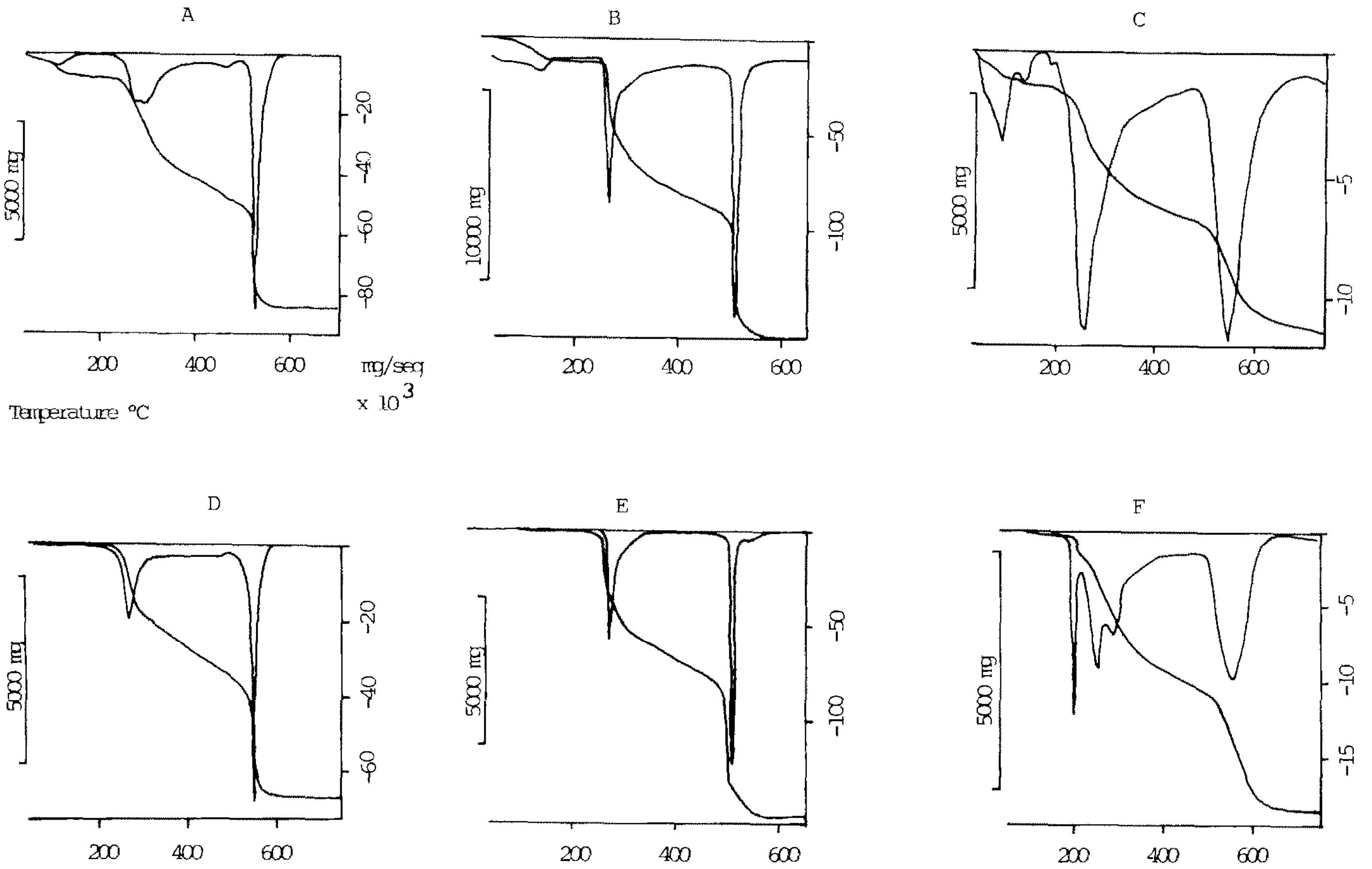

Fig. 1. TG and DTG curves of (A) $Co(CM)_2SO_4 \cdot 3H_2O$; (B) $Ni(CM)_2SO_4 \cdot 3H_2O$; (C) $Cu(CM)_2SO_4 \cdot 4H_2O$; (D) $Co(CM)_2(NO_3)_2$; (E) $Ni(CM)_2(NO_3)_2$; (F) $Cu(CM)_2(NO_3)_2$; (G) $Co(CM)_2(BF_4)_2$; (H) $Ni(CM)_2(BF_4)_2$; (I) $Cu(CM)_2(BF_4)_2$. (Parts G, H, I appear on page 216.)

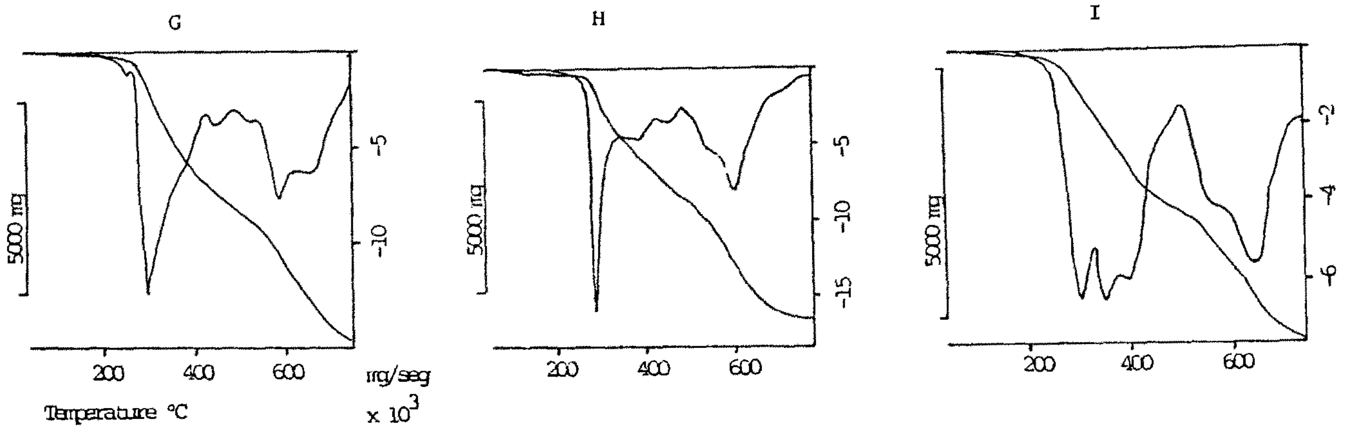

Fig. 1 (continued).

TABLE 2

Activation energies of the complexes

Compound	Dehydration temperature (° C)	Activation energy (kJ mol^{-1})	
		Coats and Redfern method	Dharwadkar method
$[Co(CM)_2]SO_4 \cdot 3H_2O$	70	25	21
$[Ni(CM)_2]SO_4 \cdot 3H_2O$	100	30	32
$[Cu(CM)_2SO_4] \cdot 4H_2O$	80	23	22

behaviour is according to the thermal dehydration of the other cimetidine complexes [1]; however, in the $[Cu(CM)_2]SO_4 \cdot 4H_2O$ complex the process occurs in two steps. In the first one three water molecules are involved; in the second only one. This seems to suggest that the latter has stronger bonding through hydrogen bonds. It is important to point out that the temperature at which the water molecules are lost in the sulphate complexes is higher than in the chloride complexes [1], which indicates that in the first ones the water molecules are linked more firmly.

Non-isothermal kinetic analyses of the dehydration processes were carried out using the Coats and Redfern [4,5] and Dharwadkar and Karkhanavala [6] methods. The activation energy values shown in Table 2 allow us to conclude that the water molecules present in the sulphate complexes interact weakly with the metallic ions, as occurs in the other binary cimetidine complexes [1] and the ternary complexes of cimetidine and L-alanine [7].

For the dehydration processes, an endothermic peak was observed from DTA curves (Fig. 2) at 70, 100 and 80 °C for Co(II), Ni(II) and Cu(II) complexes, respectively.

Pyrolytic decomposition

The anhydrous sulphate complexes are stable below 220 ° C. The pyrolytic decomposition of these complexes takes place in two steps: (1) in the range 220–480 ° C with a 44% weight loss. This may be due to pyrolysis of the sulphate ion and partial elimination of the ligand [8]; (2) 480–550 ° C for cobalt and nickel complexes and 480–650 ° C for $Cu(CM)_2SO_4 \cdot 4H_2O$ with a corresponding 37% weight loss due to elimination of the remaining ligand. The DTG curves show that the first step is a complex process for the Co(II) compound while the other two metal complexes show a simple process. The second step takes place as a simple thermal process.

The final residues obtained correspond to the metal divalent oxide. This observation has been confirmed by X-ray powder patterns of the decomposition products.

The DTA curves of these compounds show two exothermic peaks (Fig. 2)

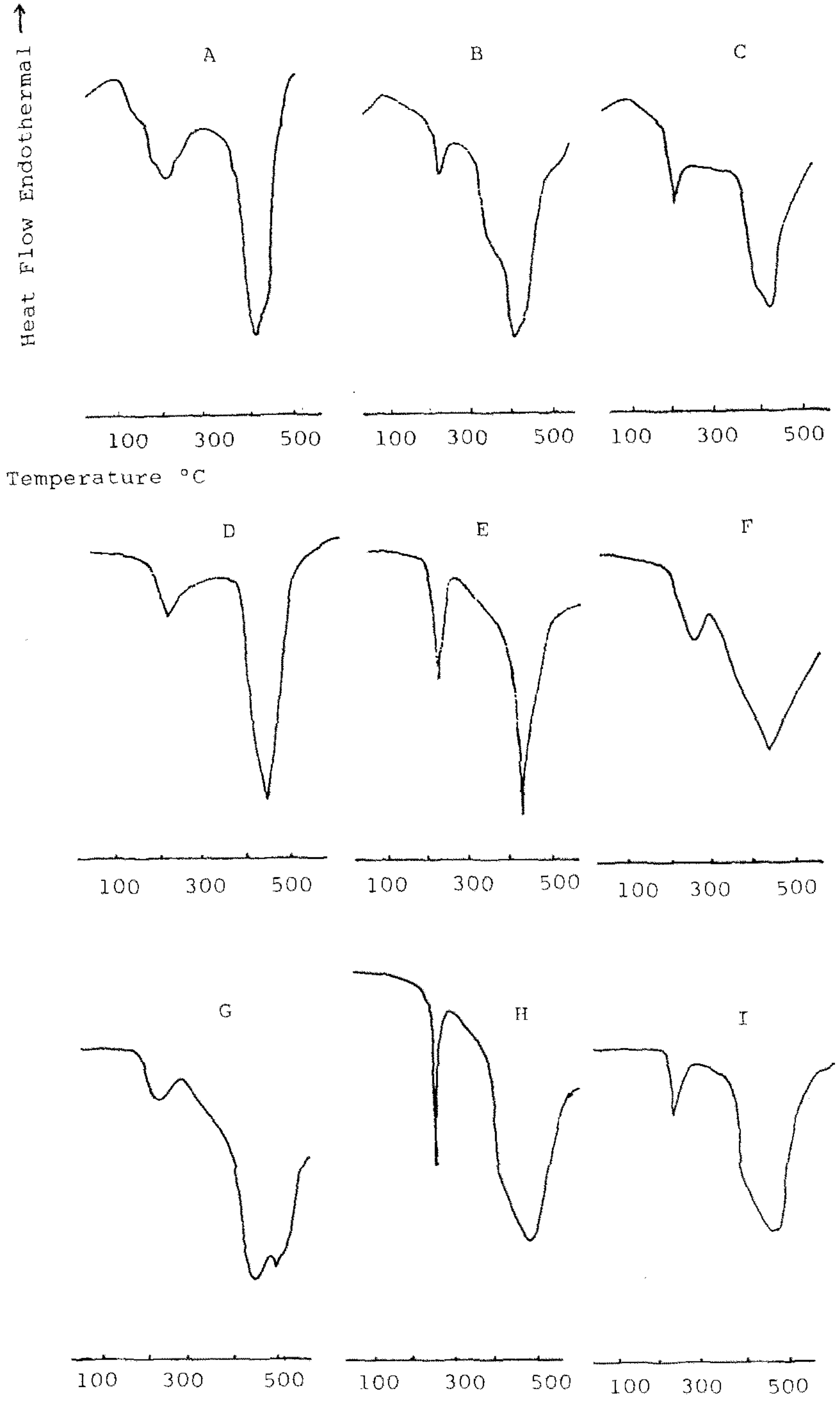

Fig. 2. DTA curves of (A) $Co(CM)_2SO_4 \cdot 3H_2O$; (B) $Ni(CM)_2SO_4 \cdot 3H_2O$; (C) $Cu(CM)_2SO_4 \cdot 4H_2O$; (D) $Co(CM)_2(NO_3)_2$; (E) $Ni(CM)_2(NO_3)_2$; (F) $Cu(CM)_2(NO_3)_2$; (G) $Co(CM)_2(BF_4)_2$; (H) $Ni(CM)_2(BF_4)_2$; (I) $Cu(CM)_2(BF_4)_2$.

at 240–260 and 420 ° C, corresponding to the decomposition of the ligand and the sulphate ion.

Nitrate complexes

The pyrolytic decomposition of the complexes is similar to the sulphate compounds. The complexes are stable below 210–250 ° C. The pyrolytic decomposition of the $[Co(CM)_2](NO_3)_2$ takes place in two steps: (1) 240–515 ° C range with a corresponding weight loss of 49%; and (2) 515–570 ° C with a corresponding weight loss of 40%. The final product is the CoO (residues: obs., 11%; calcd., 10.9%).

The $[Ni(CM)_2](NO_3)_2$ shows the pyrolytic decomposition in three steps: (1) 250–475 ° C range corresponding to a weight loss of 47%; (2) 475–500 ° C with a weight loss of 32%; and (3) up to 550 ° C with a weight loss of 10%. The final residue is NiO (residues: obs., 11%; calcd., 10.9%).

The TG curve of $Cu(CM)_2(NO_3)$ shows a loss of weight in three steps: (1) 200–210 ° C (8% weight loss); (2) 210–510 ° C (45% weight loss); and (3) 510–625 ° C (35% weight loss). The remaining product is CuO.

The final residues, MO, have been characterized by X-ray powder patterns and IR spectra.

The DTA curves of nitrate complexes are shown in Fig. 2. Two exothermic peaks appear at 250–260, and 450 ° C for $[Co(CM)_2](NO_3)_2$ and $[Ni(CM)_2](NO_3)_2$. The $[Cu(CM)_2](NO_3)_2$ shows three exothermic peaks at 215, 225 and 475 ° C, which correspond to pyrolytic decomposition. The first peak is due to pyrolysis of the nitrate ion [9].

Tetrafluoroborate complexes

The complexes are stable above 250 ° C. The DTG curves suggest that the pyrolytic decomposition takes place in two steps which overlap. At 750 ° C the decomposition process has not finished, remaining a $MO–M(BO_2)_2$ mixture, which was characterized by X-ray diffraction and IR spectroscopy.

The DTA curves of tetrafluoroborate complexes are shown in Fig. 2. All the complexes show an exothermic peak at 240–270 ° C and a wide exothermic peak at 430–510 ° C which corresponds to a pyrolytic decomposition.

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