Thermochimica Acta, 104 (1986) 31–37
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL STUDY OF COBALT(II), COPPER(II) AND NICKEL(II) COMPLEXES OF CIMETIDINE

A. SANCHO, J. BORRÁS * and L. SOTO

Departamento de Quimica, Facultad de Farmacia, Universidad de Valencia, Valencia (Spain)

(Received 17 December 1985)

ABSTRACT

The thermal behaviour of cobalt(II), nickel(II) and copper(II) complexes of cimetidine has been studied using thermogravimetry (TG) and differential scanning calorimetry (DSC). The complexes decompose in two steps: dehydration and decomposition. The decomposition products have been characterised by X-ray powder diffraction patterns.

INTRODUCTION

Studies on metal complexes of *N*-cyano-*N'*-methyl-*N''*(2-[(5-methyl-1H-imidazol-4-yl)methylthio]ethyl)guanidine, cimetidine(CM) are currently being carried out in our laboratory. Although we have described the crystal structures of $Cu(CM)_2(ClO_4)_2$ [1] and $Cu(CM)_2(NO_3)_2$ [2] compounds previously, together with some others of the same general formula: $M(CM)_2X_2 \cdot nH_2O$ (M = Co(II), Ni(II) or Cu(II); $X = ClO_4^-$, Cl^-) and $Cu(CM)SO_4 \cdot 2H_2O$ [3], studied by spectroscopic techniques, their thermal behaviour has not been described in the literature. This is the reason why we report a TG and DSC thermal study of these compounds in this paper.

EXPERIMENTAL

Methods

The TG studies were carried out on a Mettler TG-50 thermobalance, using samples of ca. 15 mg and at a heating rate of 10°C min^{-1}, using ignited α-Al_2O_3 as a reference. The kinetic analysis of the dehydration processes was performed by means of the TG data, which were recorded on a RAX 1200 thermobalance, using samples of ca. 50 mg and at a heating rate

---

* Author for correspondence.

0040-6031/86/$03.50

of 5°C min^{-1}. The DSC curves were recorded in a Mettler differential scanning calorimeter (model DSC-20), using samples of ca. 5 mg and at a heating rate of 5°C min^{-1}. The TG and DSC studies were carried out in a dynamic atmosphere of pure air (100 ml min^{-1}).

X-ray powder diffraction patterns were obtained by means of a Kristalloflex 80 Siemens diffractometer using Cu K_α radiation.

Samples

The compounds studied, whose synthesis and characterization have been previously described [3], are the following: $Co(CM)_2Cl_2 \cdot H_2O$, $Co(CM)_2(ClO_4)_2$, $Ni(CM)_2Cl_2 \cdot 2H_2O$, $Ni(CM)_2(ClO_4)_2$, $Cu(CM)SO_4 \cdot 2H_2O$, $Cu(CM)_2Cl_2 \cdot 2H_2O$ and $Cu(CM)_2(ClO_4)_2$.

RESULTS AND DISCUSSION

Figure 1 shows the TG and DTG, and Fig. 2 shows the DSC curves for CM and M–CM complexes.

From Fig. 1 we observe that the CM is anhydrous and thermally stable below 190°C. Then, the pyrolytic decomposition takes place between a temperature range of 200 and 620°C. At this point all the product is volatilized. The pyrolytic decomposition is composed of two steps: (200–400°C and 500–620°C). The thermogram shows that weight loss of the first step is 62%, which corresponds to a thioether and cyanoguanidine moiety, (calculated 61.8%). The DTG curve shows that the first step takes place in two processes which overlap. The DSC curves show an endothermic peak at 141°C which corresponds to a melting point ($\Delta H = 48$ kJ mol^{-1}) and an exothermic peak at the 200–350°C temperature range which corresponds to a first step of pyrolytic decomposition.

The perchlorate complexes are anhydrous and decompose violently above 180°C.

The thermal behaviour of the other complexes are generally described by two differentiated processes: (1) dehydration of the hydrated compounds and (2) pyrolytic decompositon of the anhydrous complexes.

Dehydration

Under the experimental conditions used, the dehydration process occurs in a single step for all complexes.

Weight losses, the temperature ranges and dehydration enthalpies of those processes are shown in Table 1.

The expected endothermic behaviour for the dehydration processes has been observed from DSC in the same temperature range (Fig. 2).

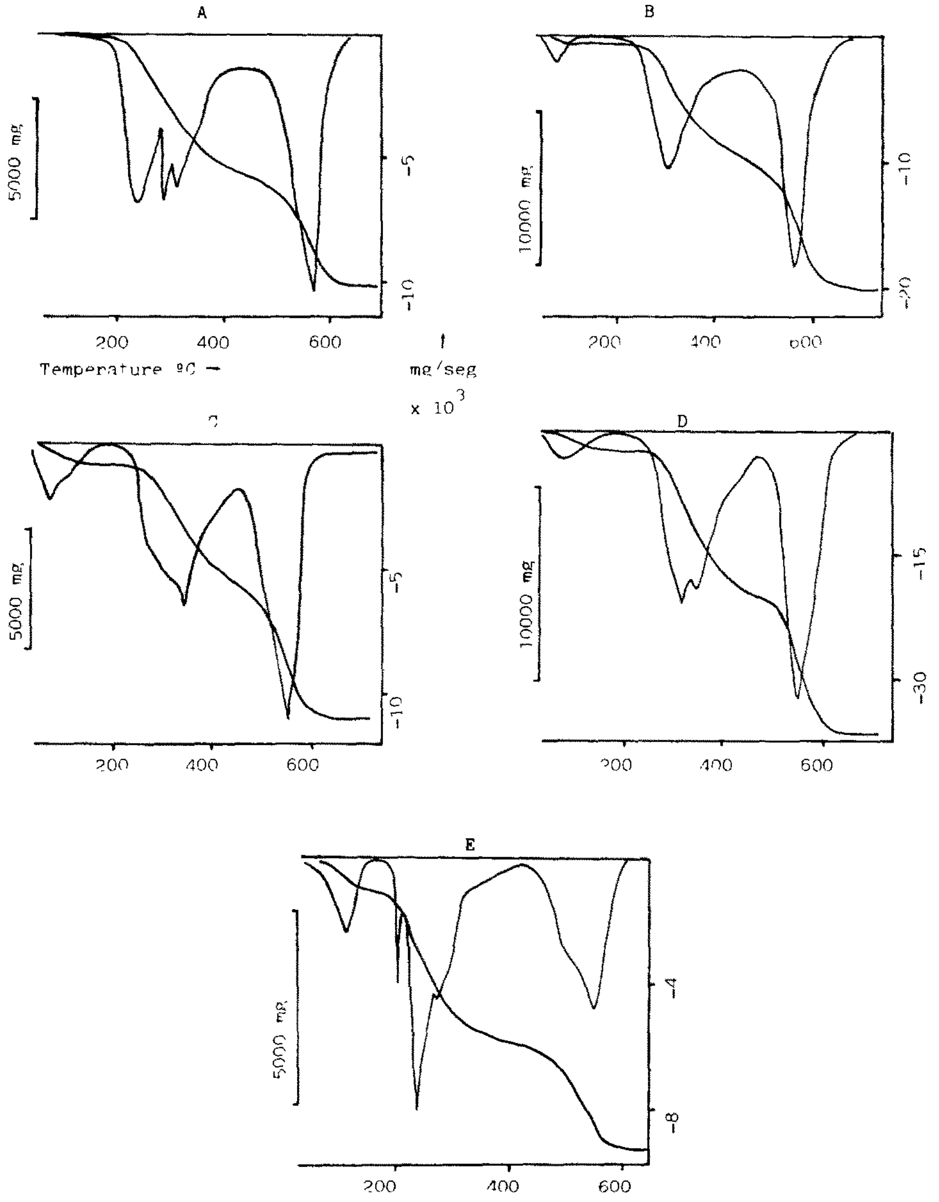

Fig. 1. TG and DTG curves of (A) CM; (B) $Co(CM)_2Cl_2 \cdot H_2O$; (C) $Ni(CM)_2Cl_2 \cdot 2H_2O$; (D) $Cu(CM)_2Cl_2 \cdot 2H_2O$; (E) $Cu(CM)SO_4 \cdot 2H_2O$.

The lower values of the dehydration enthalpies of $Ni(CM)_2Cl_2 \cdot 2H_2O$ and $Co(CM)_2Cl_2 \cdot H_2O$ indicate water of crystallization. The high value of the dehydration enthalpy and temperature peak values for $Cu(CM)SO_4 \cdot 2H_2O$ suggest that the two water molecules are directly coordinated to Cu(II).

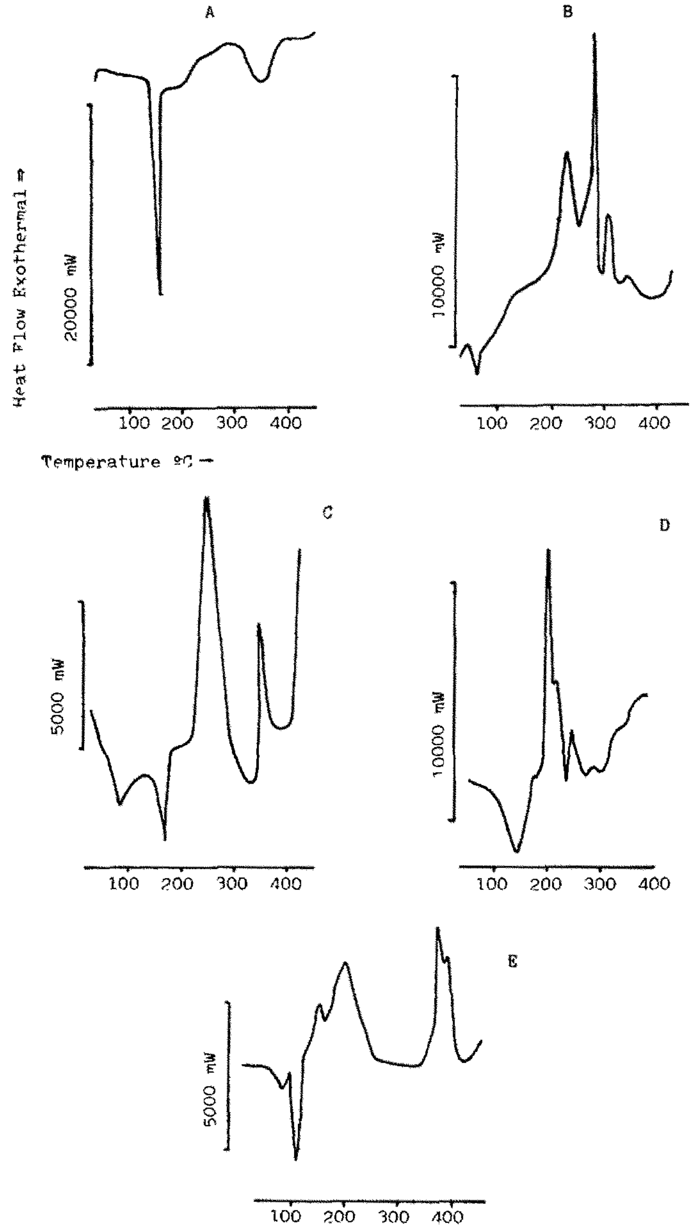

Fig. 2. DSC curves of (A) CM: (B) $Co(CM)_2Cl_2 \cdot H_2O$; (C) $Ni(CM)_2Cl_2 \cdot 2H_2O$; (D) $Cu(CM)SO_4 \cdot 2H_2O$; (E) $Cu(CM)_2Cl_2 \cdot 2H_2O$.

Non-isothermal kinetics analyses of the dehydration processes were carried out using the Coats and Redfern method [4,5]. In all cases, dehydration takes place by means of a nucleation mechanism, controlled by monodimensional diffusion, which corresponds to the F_1 model (Sharp et al. notation) [6]. The activation energy values are shown in Table 2.

TABLE 1

Temperatures and weight losses of the complexes studied

Compound	Dehydration					Decomposition		
	Temperature range (°C)	Peak temperature DSC (°C)	Weight loss%		Enthalpy (kJ mol^{-1})	Temperature range (°C)	Weight loss%	
			Calcd.	Obs.			Calcd.	Obs.
Co(CM)$_2$Cl$_2$·H$_2$O	50– 80	60	2.9	3.1	13	280–610	88	86
Ni(CM)$_2$Cl$_2$·2H$_2$O	50–140	85	5.4	5.6	15	250–620	89	87
Cu(CM)$_2$Cl$_2$·2H$_2$O	50–140	80	5.3	5.6	–	260–600	88	88
Cu(CM)SO$_4$·2H$_2$O	60–140	142	8.0	7.7	72	200–580	–	75

TABLE 2

Activation energies of the complexes

Compound	Dehydration temperature (°C)	Activation energy (kJ mol^{-1})
$Co(CM)_2Cl_2 \cdot H_2O$	60	17.9
$Ni(CM)_2Cl_2 \cdot 2H_2O$	85	21.5
$Cu(CM)_2Cl_2 \cdot 2H_2O$	80	12.7
$Cu(CM)SO_4 \cdot 2H_2O$	142	41.2

Pyrolytic decomposition

The anhydrous chloride complexes are stable below 250°C, while the $Cu(CM)SO_4 \cdot 2H_2O$ is stable below 200°C. At 110 and 170°C melting takes place of the $Cu(CM)_2Cl_2 \cdot 2H_2O$ and $Ni(CM)_2Cl_2 \cdot 2H_2O$ complexes respectively, which correspond with endothermic peaks, as shown in the DSC curves (Fig. 2).

The pyrolytic decomposition of the chloride complexes takes place in two steps. For the chloride complexes we observe: (1) 250–450°C temperature range with a corresponding 40% weight loss, and (2) 510–620°C temperature range with a corresponding 37% weight loss.

The DTG curves of all the complexes suggest some processes which overlap. The DSC curves show two exothermic peaks for that first decomposition process.

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

The $Cu(CM)SO_4 \cdot 2H_2O$ complex shows the steps: (1) 200–325°C temperature range, whose weight loss is of 35% and (2) 460–580°C temperature range, whose weight loss is of 25%.

The DTG curve of this complex suggests some processes which overlap. The DSC curves show exothermic peaks at 202, 215 and 250°C temperature ranges.

The residual weight loss is 75% of the original weight, which corresponds to a $CuO–CuSO_4$ mixture.

ACKNOWLEDGEMENT

We thank to Dr. Salas-Pelegrin for the thermal analyses.

REFERENCES

1 A. Sancho, J. Borrás, L. Soto-Tuero, C. Esteban-Calderon, M. Martínez-Ripoll and S. García-Blanco, Polyhedron, 4 (1985) 539.
2 L. Soto, J. Borrás, A. Sancho, A. Fuertes and C. Miravitlles, Acta Crystallogr., Sect. C, 41 (1985) 1431.
3 A. Sancho, L. Soto and J. Borrás, Transition Met. Chem., 10 (1985) 214.
4 A.W. Coats and J.P. Redfern, Nature (London), 68 (1964) 201.
5 C.S.R. Murthy, G.N. Rao and A. Prabhakara Rao. Thermochim. Acta, 55 (1982) 19.
6 J.H. Sharp, G.W. Broudley and B.N.N. Achar, J. Am. Ceram. Soc., 49 (1966) 379.