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THERMAL STUDY OF TERNARY COMPLEXES OF Cu(II), CIMETIDINE AND PHENOBARBITONE

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ABSTRACT

A study of the thermal decomposition of ternary complexes of Cu(II), cimetidine (CM) and phenobarbitone (HL) is reported. All the complexes decompose by two processes: dehydration and pyrolytic decomposition. The activation energies of dehydration processes were determined and we conclude that the water molecules interact weakly with the metallic ion.

INTRODUCTION

The ternary complexes of Cu(II) with 5,5 di-substituted barbituric acids were used for the identification and determination of these drugs and have been studied extensively more recently [1,2]. Pezeshk et al. [3] studied the synthesis and properties of the ternary complexes of Cu(II), imidazole and phenobarbitone. In earlier work, we have synthesized and characterized the ternary complexes of Cu(II) CM and HL [4], and tentatively proposed structures in which the Cu(II) ion was distorted octahedrally and surrounded by the N and O donor atoms of HL and by the N and S donor atoms of CM. We have also reported a study of the stability constants of the ternary complexes in methanolic solution [5].

There is no information in the literature on the thermal behaviour of these compounds, although a thermal study of the ternary complexes of Cu(II), thiobarbiturates and pyridine has been reported [6].

EXPERIMENTAL

Methods

The thermal analyses were made with a RAX 1200 simultaneous TG-DTA thermobalance at a heating rate of 5°C min^{-1} under a dynamic oxygen atmosphere. Calcined Al_2O_3 was used as reference. In the non-isothermal

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kinetic study of dehydration processes, a 1.3°C min^{-1} heating rate was used.

Infrared spectra were obtained using KBr pellets on a Pye-Unicam SP 2000 spectrophotometer. X-ray powder diffraction patterns were obtained by means of a Kristalloflex 810 Siemens diffractometer using Cu–Kα radiation.

Samples

The ternary complexes $Cu(CM)L_2 \cdot 2H_2O$, $Cu(CM)_2L_2 \cdot 2H_2O$, $Cu_2(CM)L(OH)_3$ and $Cu_2(CM)_2L(OH)_3 \cdot 2H_2O$ were prepared as previously described [4].

RESULTS AND DISCUSSION

TG and DTA curves for the complexes are given in Fig. 1 and Fig. 2 respectively. The analytical data calculated from the curves in Fig. 1 are summarized in Table 1.

The thermal decomposition of all the compounds takes place in two stages: (a) dehydration; (b) pyrolytic decomposition and metal oxide formation.

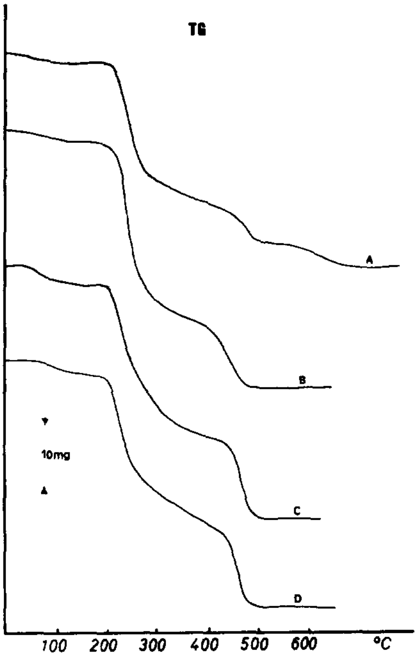

Fig. 1. TG curves of: (A) $Cu(CM)L_2 \cdot 2H_2O$; (B) $Cu(CM)_2L_2 \cdot 2H_2O$; (C) $Cu_2(CM)_2L(OH)_3 \cdot 2H_2O$; (D) $Cu_2(CM)L(OH)_3$.

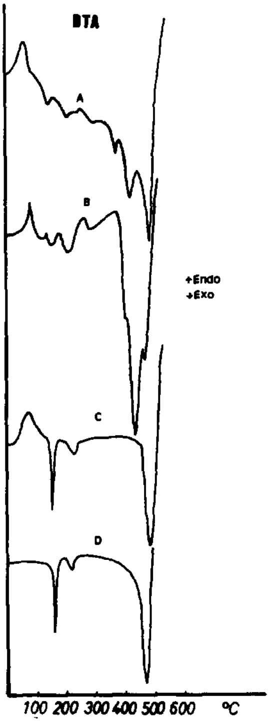

Fig. 2. DTA curves of: (A) $Cu(CM)L_2 \cdot 2H_2O$; (B) $Cu(CM)_2L_2 \cdot 2H_2O$; (C) $Cu_2(CM)_2L(OH)_3 \cdot 2H_2O$; (D) $Cu_2(CM)L(OH)_3$.

TABLE 1

Dehydration temperatures and weight losses of the complexes studied

Compound	Dehydration			Decomposition		
	Temp. (°C)	Weight loss (%)		Temp. range (°C)	Weight loss (%)	
		obs.	calcd.		obs.	calcd.
$Cu(CM)L_2 \cdot 2H_2O$	101	4.50	4.42	200–650	85.62	85.37
$Cu(CM)_2L_2 \cdot 2H_2O$	111	3.46	3.37	190–470	89.07	89.17
$Cu_2(CM)_2L(OH)_3 \cdot 2H_2O$	180	6.44	6.62	225–650	77.01	76.65
$Cu_2(CM)L(OH)_3$	180	4.12	4.08	225–600	71.17	71.89

Dehydration

The TG curves of $Cu(CM)L_2 \cdot 2H_2O$ and $Cu(CM)_2L_2 \cdot 2H_2O$ show that the loss of water molecules takes place in one step only (Fig. 1), corresponding to an endothermic peak at 70°C and 88°C respectively in the DTA curves (Fig. 2).

The dehydration process of $Cu_2(CM)_2L(OH)_3 \cdot 2H_2O$ takes place in two

TABLE 2

Activation energies of the complexes studied

Compound	Dehydration temp. (°C)	Activation energy (kJ mol^{-1})
$Cu(CM)L_2 \cdot 2H_2O$	101	19.23
$Cu(CM)_2L_2 \cdot 2H_2O$	111	31.35
$Cu_2(CM)_2L(OH)_3 \cdot 2H_2O$	119	58.10

clearly-defined steps, the first finishing at 119°C with the weight loss indicating the elimination of one molecule of water. The observed weight loss at the second step (180°C) corresponds to a loss of OH groups. The DTA curve at 80°C shows an endothermic peak associated with the first step and an exothermic peak for the second step. The exothermic peak is consistent with two processes which take place in the same temperature range: one endothermic dehydration, and the other exothermic corresponding to a structural change of higher intensity than the first.

The dehydration process of $Cu_2(CM)L(OH)_3$ presents a single step at 180°C corresponding to an OH condensation. The DTA curve shows an exothermic peak which corresponds to a similar stage for $Cu_2(CM)_2L(OH)_3 \cdot 2H_2O$.

Non-isothermal kinetic analysis of these processes was carried out using the Coats and Redfern method [7,8]. In all cases, dehydration takes place by means of a nucleation mechanism, controlled by monodimensional diffusion, which corresponds to the F_1 model (Sharp notation) [9]. The activation energy values shown in Table 2 allow us to conclude that the water molecules present in $Cu(CM)L_2 \cdot 2H_2O$, $Cu(CM)_2L_2 \cdot 2H_2O$ and $Cu_2(CM)_2L(OH)_3 \cdot 2H_2O$ interact weakly with the metallic ion. These results suggest that the structural role played by the water molecules is essentially similar.

Pyrolytic decomposition

The DTA curves of $Cu(CM)L_2 \cdot 2H_2O$ and $Cu(CM)_2L_2 \cdot 2H_2O$ show an exothermic peak at 150°C which does not correspond to a weight loss. To study the nature of this process IR spectra of the samples at 180°C were obtained. The differences between the IR spectra of the original and heated samples are: (i) the band at 2160 cm^{-1} attributed to a $\nu(C{\equiv}N)$ and the band at 1600 cm^{-1} assigned to a combination of $\nu(C{=}N)$, $\nu(C{=}O)$ and $\delta(N{-}H)$ are strongly reduced; (ii) the band at 1040 cm^{-1} characteristic of the barbiturate skeleton is enhanced; (iii) in the 600–400 cm^{-1} range, the bands are similar to the IR spectrum of phenobarbitone [10].

The X-ray diffraction pattern could not be obtained since the solids are amorphous.

We conclude that the exothermic processes occurring at 150°C in the complexes $Cu(CM)L_2 \cdot 2H_2O$ and $Cu(CM)_2L_2 \cdot 2H_2O$ consist of a dissociation process to convert them, at least partially, to the binary complexes Cu(II)-CM and to HL. This dissociation process also occurs in the thermal behaviour of hydroxoternary complexes and allows us to explain the exothermic peak at 150°C. Effectively, the IR spectra of the products from these complexes when heated at 180°C, show they are the ternary complexes. Moreover the bands corresponding to the O–H group have disappeared.

All the dehydrated compounds decompose in the temperature range 190–650°C.

The TG curve of $Cu(CM)L_2 \cdot 2H_2O$ shows a loss of weight in three steps (at 200–300°C, 300–450°C, and 450–650°C) which corresponds to the formation of CuO as shown by X-ray diffraction methods and IR spectroscopy. The DTA curve shows a complex process with exothermic peaks at 210, 295, 375, 420 and 458°C. The IR spectra of the samples at 280°C, 310°C and 365°C show band elimination at 2160 cm^{-1} characteristic of $\nu(C{\equiv}N)$ whilst the band at 1600 cm^{-1} appears. The IR spectrum of the sample at 470°C is very different from the others and shows broad bands at 1200, 1100, 1050 and 620 cm^{-1} indicating that a sulphate group is present in the sample. This was also observed by Paulik [6] in the thermal decomposition of the ternary complexes of Cu(II), thiobarbiturates and pyridine.

The TG curve of $Cu(CM)_2L_2 \cdot 2H_2O$ shows a weight loss of 89.07% corresponding to CuO formation. The pyrolytic decomposition takes place in two steps (at 200–300°C and 300–500°C). The DTA curve show a complex process, with exothermic peaks at 210, 280, 390, 430 and 460°C.

The pyrolytic decomposition of hydroxoternary complexes is similar to that observed for $Cu(CM)_2L_2 \cdot 2H_2O$, showing exothermic peaks at 220°C and 470°C.

REFERENCES

1 M.R. Caira, G.V. Fazakerley, P.W. Linder and L.R. Nassimbeni, Acta Crystallogr., Sect. B, 29 (1973) 2898.
2 G.V. Fazakerley, P.W. Linder, L.R. Nassimbeni and A.L. Rodgers, Inorg. Chim. Acta, 9 (1974) 193.
3 A. Pezeshk, F.T. Greenaway and J.R. Sorenson, Inorg. Chim. Acta, 80 (1983) 191.
4 R. Ortiz, J. Borrás, L. Perelló and J. Jiménez, Synth. React. Inorg. Met.-Org. Chem., 8 (1985).
5 R. Ortiz, J. Borrás, L. Perelló and H. Jiménez, Monatsh. Chem., 878 (1985) 1180.
6 J. Morvay, Study of Transition Metal Thiobarbiturate Complexes. Studia Medica Series, Szeged, 1972.
7 A.W. Coats and J.P. Redfern, Nature (London), 68 (1964) 201.
8 C.S.R. Murthy, G.N. Rao and A. Prabhakara Rao, Thermochim. Acta, 55 (1982) 19.
9 J.H. Sharp, G.W. Broudley and B.N.N. Achar, J. Am. Ceram. Soc., 49 (1966) 379.
10 A. Jiménez, H. Jiménez J. Borrás and R. Ortiz, Synth. React. Inorg. Met.-Org. Chem., 14(8) (1984) 1099.