Thermochimica Acta, 156 (1989) 393–398
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL STUDIES ON CINOXACIN COMPLEXES. PART II. THERMAL BEHAVIOUR OF SOME METAL COMPLEXES OF CINOXACIN

C. CHULVI, R.M. ORTIZ and L. PERELLO

Departamento de Química Inorgánica, Facultad de Farmacia, Universidad de Valencia (Spain)

M.A. ROMERO

Departamento de Química Inorgánica, Fucaltad de Ciencias, Universidad de Granada (Spain)

(Received 5 May 1989)

ABSTRACT

The thermal behaviour of complexes of cinoxacin with Co(II), Zn(II) and Cd(II) was studied using thermogravimetry (TG) and differential scanning calorimetry (DSC). The complexes decompose in two steps: dehydration and pyrolitic decomposition. Dehydration enthalpies have been calculated from the DSC curves.

INTRODUCTION

Cinoxacin (HCx = 1-ethyl-4(1H)-oxo-(1,3)dioxolo(4,5-g) cinnoline-3-carboxylic acid) is an anti-microbial agent related to oxolinic acid. It is also active, both in vitro [1] and in vivo [2], against a large variety of Gram-negative bacteria, especially those often associated with infections of the urinary tract (*Escherichia coli, Klebsiella sp., Enterobacter sp.*, etc). It has been suggested that the compound acts via interaction with DNA-gyrase [3].

In our previous paper [4] we reported on the synthesis, IR spectral studies and thermal behaviour of Co(II), Ni(II) and Cu(II) complexes of cinoxacin (HCx). Those studies were extended to the synthesis and spectroscopic characterization of some new divalent metal complexes of cinoxacin [5]. In continuation of this work, the present communication reports a TG and DSC thermal study of the complexes synthesized in our previous work.

EXPERIMENTAL

Materials

Cinoxacin was kindly provided by Lilly Indiana de España, S.A. All reagents used in this work were of analytical grade.

Methods

Infrared spectra were obtained using KBr pellets on a Perkin–Elmer 843 spectrophotometer. X-ray powder diffraction patterns were obtained by means of a Kristalloflex 810 Siemens diffractometer using Cu *Kα* radiation. Solid reflectance spectra were obtained on a Perkin–Elmer model Lamda 15 spectrophotometer with a reflectance attachment.

TG studies were carried out in a Mettler TG-50 thermobalance in dynamic pure air atmosphere (100 ml min^{-1}) and at a heating rate of 20 °C min^{-1}. DSC curves were recorded in a Mettler differential scanning calorimeter (model DSC-20) in a static air atmosphere and at a heating rate of 10 °C min^{-1}.

Samples

The complexes studied, whose synthesis and characterization have been previously described [5], were the following: $Co_2Cx_3(OH) \cdot H_2O$, $(Co_2Cx_5)Na \cdot 4H_2O$, $Zn_2Cx_3(OH)$, $ZnCx_2 \cdot 4H_2O$, $(CdCx)Cl \cdot 4H_2O$, $CdCx_2 \cdot 2H_2O$ and $(Cd_2Cx_5)Na \cdot 4H_2O$.

RESULTS AND DISCUSSION

The thermal behaviour of the isolated complexes consists of two major processes: dehydration of hydrated compounds and decomposition of the anhydrous complexes to give the respective metal oxides.

Dehydration processes

The data for calculated and observed weight losses and the corresponding temperature ranges for the dehydration processes are given in Table 1.

In Fig. 1, it can be observed that the dehydration processes of $CdCx_2 \cdot 2H_2O$ and $(Cd_2Cx_5)Na \cdot 4H_2O$ take place in two clearly defined steps suggesting a marked difference in the bonding of the water molecules.

In the other compounds, it can be seen that the dehydration processes occur in a single step in the temperature range 80–150 °C, except for the Co(II) and Zn(II) hydroxo complexes. In these two species, the temperature range is 110–220 °C because it includes condensation of the OH^- groups.

Fig. 1. TG and DTG curves of: (A) $Co_2Cx_3(OH) \cdot H_2O$; (B) $(Co_2Cx_5)Na \cdot 4H_2O$; (C) $Zn_2Cx_3(OH)$; (D) $ZnCx_2 \cdot 4H_2O$; (E) $(CdCx)Cl \cdot H_2O$; (F) $CdCx_2 \cdot 2H_2O$; and (G) $(Cd_2Cx_5)Na \cdot 4H_2O$.

TABLE 1

Thermoanalytic data for dehydration processes of isolated complexes

Process	Weight loss (%)		Temperature range (° C)	Peak temperature DSC (° C)	ΔH (kJ mol^{-1})
	Calc.	Found			
$Co_2Cx_3(OH)\cdot H_2O \rightarrow$ "Co_2Cx_3" $+ H_2O$	3.74	3.80	110–190	128 170	52.1
$(Co_2Cx_5)Na\cdot 4H_2O \rightarrow (Co_2Cx_5)Na + 4H_2O$	4.74	4.83	120–150	134	275.7
$Zn_2Cx_3(OH) \rightarrow$ "Zn_2Cx_3"	1.82	1.86	160–220	195	27.6
$ZnCx_2\cdot 4H_2O \rightarrow ZnCx_2 + 4H_2O$	11.01	10.92	80–130	93	108.9
$(CdCx)Cl\cdot H_2O \rightarrow (CdCx)Cl + H_2O$	4.21	4.11	80–150	121	11.2
$CdCx_2\cdot 2H_2O \rightarrow CdCx_2\cdot H_2O + H_2O$	2.68	2.73	80–120	90	–
$CdCx_2\cdot H_2O \rightarrow CdCx_2 + H_2O$	2.68	2.73	180–220	192	55.7
$(Cd_2Cx_5)Na\cdot 4H_2O \rightarrow (Cd_2Cx_5)Na\cdot 3H_2O + H_2O$	1.10	1.15	110–140	123	22.7
$(Cd_2Cx_5)Na\cdot 3H_2O \rightarrow (Cd_2Cx_5)Na + 3H_2O$	3.33	3.20	170–210	185	115.3

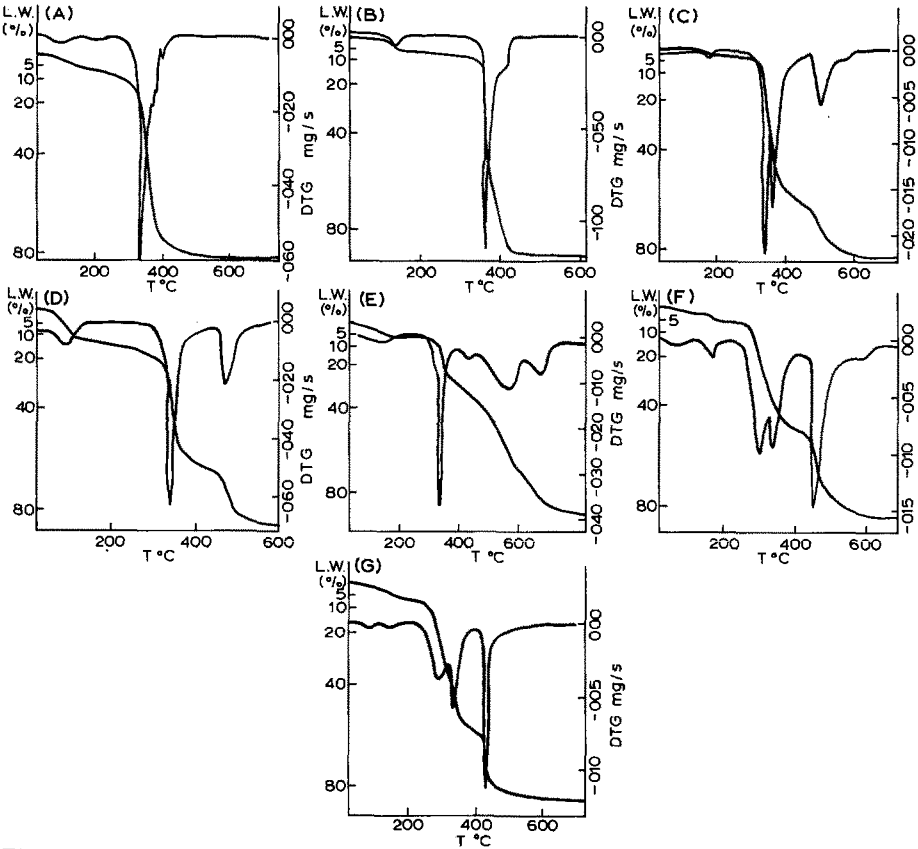

Fig. 1.

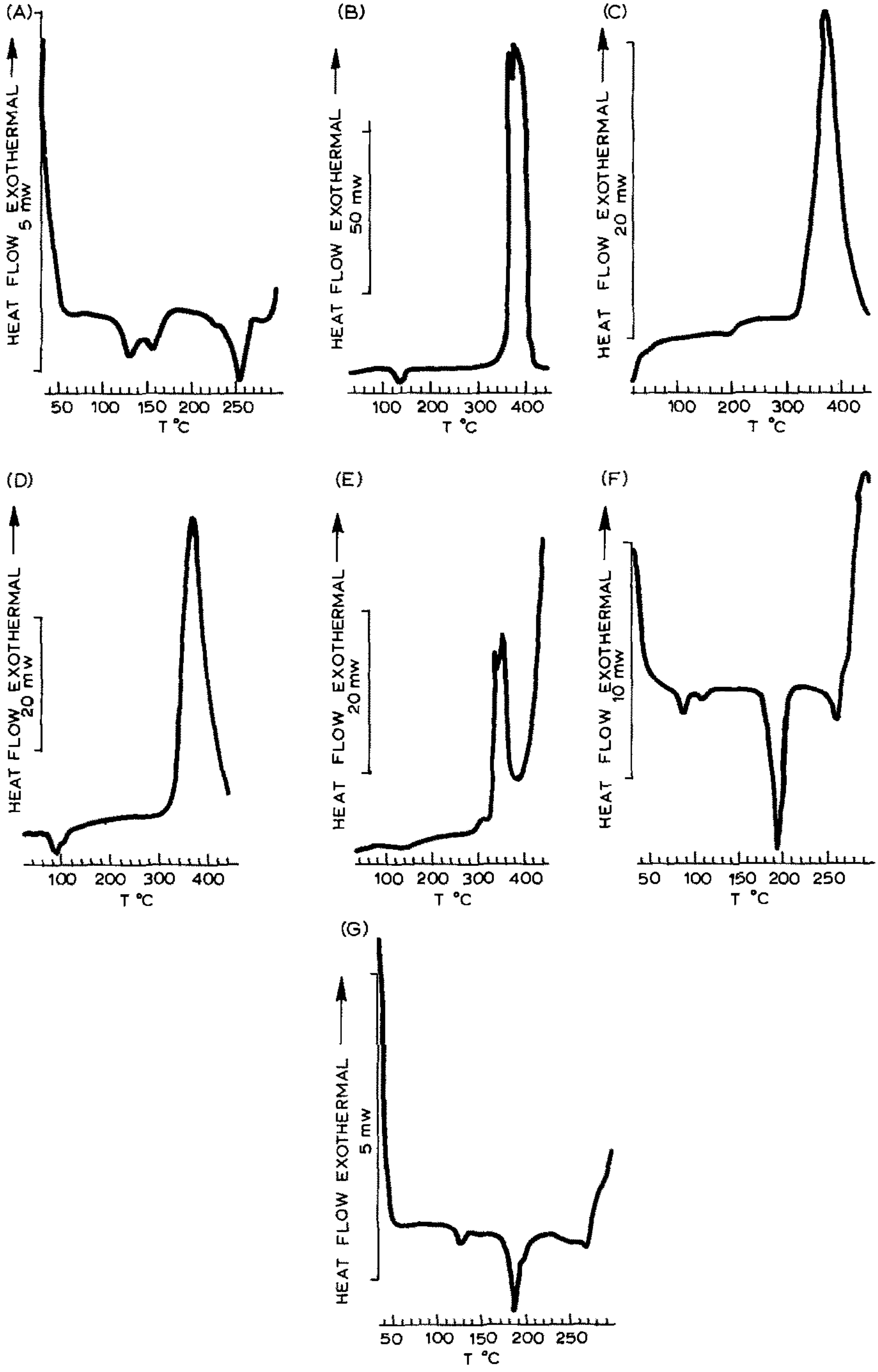

Fig. 2. DSC curves of: (A) $Co_2Cx_3(OH) \cdot H_2O$; (B) $(Co_2Cx_5)Na \cdot 4H_2O$; (C) $Zn_2Cx_3(OH)$; (D) $ZnCx_2 \cdot 4H_2O$; (E) $(CdCx)Cl \cdot H_2O$; (F) $CdCx_2 \cdot 2H_2O$; and (G) $(Cd_2Cx_5)Na \cdot 4H_2O$.

TABLE 2

Thermogravimetric and DSC curves for the pyrolytic processes

Process	Temperature range TG (°C)	Weight loss (%)		DSC Peaks (°C)	
		Calcd.	Found	Endo	Exo
3"Co_2Cx_3" $\rightarrow 2Co_3O_4$	250–450	79.13	78.76	252	350, 380
$3(Co_2Cx_5)Na \rightarrow 2Co_3O_4 + 3/2Na_2O$	330–450	84.00	83.87	–	360, 380
"Zn_2Cx_3" $\rightarrow 2ZnO$	275–650	80.71	80.83	–	380, > 440
$ZnCx_2 \rightarrow ZnO$	225–550	71.02	71.50	–	380, > 440
$2(CdCx)Cl \rightarrow CdO + CdCl_2$	320–550	59.27	59.83	–	310, 330, 370, > 440
$CdO + CdCl_2 \rightarrow 2CdO$	550–800	21.48	22.07	–	–
$CdCX_2 \rightarrow CdO$	260–600	75.48	76.10	261	350, 440, > 440
$(Cd_2Cx_5)Na \rightarrow 2CdO + 1/2Na_2O$	260–560	76.18	76.75	270	350, 430

The RD spectrum of $Co_2Cx_3(OH) \cdot H_2O$ compound obtained at 200 °C shows a structural change associated with removal of the OH^- group, which seems to indicate that this group is directly linked to the Co(II) ion.

The expected endothermic behaviour for the dehydration processes of these complexes was observed in the DSC curves over the same temperature range (Fig. 2). The corresponding dehydration enthalpies and DSC peak temperatures are also given in Table 1.

The high ΔH values of the corresponding $(Co_2Cx_5)Na \cdot 4H_2O$ dehydration and the second step of the $CdCx_2 \cdot 2H_2O$ and $(Cd_2Cx_5)Na \cdot 4H_2O$ dehydration, at 134, 192 and 185 °C respectively, suggest that these water molecules are strongly linked. For the remaining complexes, the respective endothermic events can be assigned to the release of crystallization water.

Pyrolytic decomposition

Thermogravimetric and DSC data for the pyrolytic processes are given in Table 2. All the dehydrated compounds decompose in the 225–800 °C temperature range. In the DSC plots (Fig. 2), two, three or four exothermic effects can be observed.

Likewise, the DSC curves of $Co_2Cx_3(OH) \cdot H_2O$, $CdCx_2 \cdot 2H_2O$ and $(Cd_2Cx_5)Na \cdot 4H_2O$ show one endothermic process centred at 252, 261 and 270 °C, respectively, corresponding to the decarboxylation of the samples [6]. There is an intense exothermic effect overlapping with these peaks, due to the beginning of the pyrolytic decomposition. This interferes with the integration of the endothermic event, and must be taken into account when considering the calculated decarboxylation enthalpy (36.6, 14.1 and 3.2 kJ mol^{-1} respectively).

IR spectra of the samples obtained at 290 ° C were recorded to study the nature of the decarboxylation processes. A comparison between the IR spectra of the original and the heated samples shows a strong reduction of the $\nu_{ax}(COO^-)$, $\nu(C{=}O)_{ceto}$ and $\nu(C{=}N)$ bands. This leads to the conclusion that the pyrolysis process starts with the ligand decarboxylation, which implies a modification of the $\nu(C{=}N)$ vibration.

Although the IR spectra of the other samples at 300 ° C suggests that ligand pyrolysis also begins with decarboxylation, it is not possible to observe any endothermic event in the DSC curve, probably because it is included in the exothermic process.

The final residues of pyrolytic decomposition of the complexes were characterized by IR spectroscopy and X-ray powder diffraction patterns [7]; the results are summarized in Table 2. For $(CdCx)Cl \cdot H_2O$, CdO and $CdCl_2$ are formed at 550 ° C, the halide being eliminated at higher temperatures [8].

ACKNOWLEDGEMENT

The authors wish to thank CAICYT, Spain (932/84) for financial support.

REFERENCES

1 H. Giamarellon and G.G. Jackson, Antimicrob. Agents Chemother., 7 (1975) 688.
2 D. Genwood and F. O'Grady, Antimicrob. Agents Chemother., 12 (1978) 678.
3 K. Timmers and R. Sternglanz, Bioinorg. Chem., 9 (1978) 145.
4 L. Perelló, M.I. Roselló and R. Ortiz, Thermochim. Acta, 106 (1986) 333.
5 C. Chulvi, R. Ortiz and L. Perelló, Reunión Científica Plenaria de Química Inorgánica de la R.S.E.Q., Salamanca, 1987.
6 A. Mederos, J.V. Herrera, A. Benitez and A. Rancel, An. Quím., 84 (1988) 5.
7 R.A. Nyquist and R. Kagel, Infrared Spectra of Inorganic Compounds, 2nd edn., Academic Press, New York, 1971.
8 M.H. Moreno Carretero and J.M. Salas-Peregrin, J. Therm. Anal., 29 (1971) 1053.