

## STUDY OF THE THERMAL DECOMPOSITION OF CINOXACIN COMPLEXES WITH Co(II), Ni(II) AND Cu(II)

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### ABSTRACT

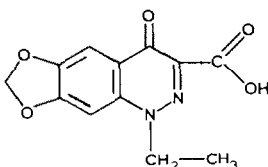
The complexes of cinoxacin with Co(II), Ni(II) and Cu(II) have been prepared and their thermal behaviour studied by thermogravimetry (TG), differential thermal analysis (DTA) and IR spectroscopy.

The complexes decompose in two steps: dehydration and decomposition of the anhydrous complexes to metal or metal oxide. The activation energies of dehydration processes were determined and we can conclude that the water molecules interact weakly with the metallic ion.

### INTRODUCTION

Cinoxacin (1-ethyl-4(1*H*)-oxo-(1,3)dioxolo(4,5-*g*)cinnoline-3-carboxylic acid) is a synthetic cinnoline derivative of pharmaceutical interest owing to its potent antibacterial activity [1-3].

The molecular structure of cinoxacin (HCx) is:



There is no information in the literature about the complexes of HCx with metal ions. In the present paper a description is given of the preparation of some complexes of HCx with Co(II), Ni(II) and Cu(II) which have been obtained in order to study their thermal behaviour by TG and DTA techniques.

### EXPERIMENTAL

#### *Materials*

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

## Methods

Chemical analysis of C, H, Cl and N were determined by an elemental analyser (Carlo-Erba model M.O.V.). The determination of metal ions was carried out in a Perkin-Elmer 290 absorption spectrometer.

The IR spectra of the compounds studied were recorded on a Pye-Unicam SP 2000 spectrometer. Samples were prepared as KBr discs for the range 4000–600  $\text{cm}^{-1}$  and CsI discs for the range 600–200  $\text{cm}^{-1}$ .

X-ray powder diffraction patterns were obtained by means of Kristalloflex 810 Siemens diffractometer using  $\text{Cu-K}\alpha$  radiation.

The thermal analyses were made using a RAX 1200 simultaneous TG-DTA thermobalance at a heating rate of 5°C  $\text{min}^{-1}$  under dynamic oxygen atmosphere. Calcined  $\text{Al}_2\text{O}_3$  was used as reference. In the non-isothermal kinetic study of dehydration processes a 1.3°C  $\text{min}^{-1}$  heating rate was maintained.

## Preparation of the complexes

Cinoxacin complexes of Co(II) and Cu(II) were obtained in DMSO medium, by mixing solutions containing 6 mmol of cinoxacin and 2 mmol of  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , respectively. To the resulting solution 2.5 ml of a 1 M aqueous solution of NaOH were added with stirring. After 1 h an orange precipitate was obtained for the cobalt complex. In the case of the copper compound, a greyish precipitate was formed immediately.

The compounds were filtered, washed with DMSO solution and dried in vacuum at 50°C to constant weight.

The Ni(II) compound was obtained in methanolic medium, by mixing solutions containing 3 mmol of cinoxacin and 3 mmol of  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ . Then 2.1 ml of a 1 M NaOH solution were added with stirring. On evaporation at room temperature for several days a green powder was

TABLE 1  
Analytical data for some complexes of cinoxacin

Compound	M% Found (Calcd.)	N% Found (Calcd.)	C% Found (Calcd.)	H% Found (Calcd.)	Cl% Found (Calcd.)	Na% Found (Calcd.)	Colour
$\text{Co}(\text{Cx})_3\text{Na} \cdot 10\text{H}_2\text{O}$	5.42 (5.60)	8.18 (8.03)	41.62 (41.34)	4.59 (4.78)	–	2.48 (2.20)	orange
$\text{Ni}_2(\text{Cx})_3\text{ClO}_4 \cdot 8\text{H}_2\text{O}$	10.10 (10.26)	7.25 (7.30)	37.20 (37.76)	3.89 (4.02)	3.60 (3.10)	–	green
$\text{Cu}(\text{Cx})_2\text{H}_2\text{O}$	10.35 (10.52)	9.28 (9.27)	47.76 (47.72)	3.57 (3.64)	–	–	greyish

obtained. It was filtered and washed with a methanolic solution and dried in vacuum at 50°C to constant weight.

Analytical data of the complexes are presented in Table 1.

## RESULTS AND DISCUSSION

The IR data of the isolated compounds are tabulated in Table 2, together with those corresponding to free cinoxacin. The principal IR bands have been assigned by comparison with the IR spectrum of free cinoxacin.

The band at 1735  $\text{cm}^{-1}$  in the spectrum of the ligand may be assigned to the antisymmetric stretching frequency of the  $-\text{COOH}$  group [4]. Shifting of this band to higher frequencies in the complexes indicates the coordination of the ligand through the carboxylic group.

In addition, the bands corresponding to  $\nu(\text{C}=\text{N})$  are displaced to higher frequencies with respect to the position of the bands in the free ligand. This fact suggests that the ligands coordinate through the nitrogen [4].

Likewise, the IR spectrum of the complexes also presents new bands in the 560–480 and 340–260  $\text{cm}^{-1}$  regions attributed to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$ , respectively [5].

The TG and DTA curves for cinoxacin and the isolated complexes are given in Figs. 1 and 2, respectively.

The TG curve of anhydrous cinoxacin shows a weight loss in two steps (270–330, 330–550°C). At 550°C no cinoxacin remains in the reaction crucible. On the other hand, the DTA curve of anhydrous cinoxacin exhibits one endothermic effect centred at 260°C corresponding to fusion of the sample. The value found for the melting point (257°C) is in good agreement with the literature data [6]. The DTA curve shows at 290°C an exothermic peak associated with the first step at decomposition and a complex exothermic process at 475°C associated with the second step.

The thermal decomposition of all isolated complexes, takes place in two processes: (a) dehydration, (b) decomposition of the corresponding anhydrate

TABLE 2  
Infrared data of some complexes of cinocacin

Compound	$\nu(\text{O}-\text{H})$ acid	$\nu(\text{C}=\text{O})$		$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
		Carboxylic group	Cetonic group			
Cinoxacin	2600	1735	1620	1560	—	—
$\text{Co}(\text{Cx})_3\text{Na}\cdot 10\text{H}_2\text{O}$	—	1620	1600	1540	490	270
$\text{Ni}_2(\text{Cx})_3\text{ClO}_4\cdot 8\text{H}_2\text{O}$	—	1600	1590	1520	540	330
$\text{Cu}(\text{Cx})_2\cdot \text{H}_2\text{O}$	—	1630	1600	1520	540	250

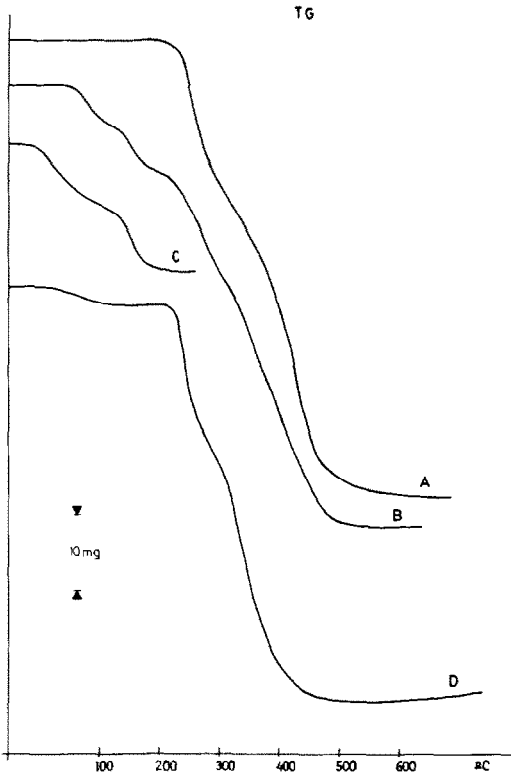


Fig. 1. TG curves of: (A) cinocaxin; (B)  $\text{Co}(\text{Cx})_3\text{Na} \cdot 10\text{H}_2\text{O}$ ; (C)  $\text{Ni}_2(\text{Cx})_3\text{ClO}_4 \cdot 8\text{H}_2\text{O}$ ; (D)  $\text{Cu}(\text{Cx})_2 \cdot \text{H}_2\text{O}$ .

complexes. Perchlorate complexes decompose violently once dehydrated at temperatures of 250–350°C.

### *Dehydration processes*

The first step taking place in the thermal decomposition of the complexes is the elimination of water molecules. Data for calculated and observed weight losses, dehydration temperatures and activation energy values are tabulated in Table 3.

Under conditions used in the present work, the dehydration process takes place in two steps for  $\text{Co}(\text{Cx})_3\text{Na} \cdot 10\text{H}_2\text{O}$  and  $\text{Ni}_2(\text{Cx})_3\text{ClO}_4 \cdot 8\text{H}_2\text{O}$  complexes, and in a single step for the  $\text{Cu}(\text{Cx})_2 \cdot \text{H}_2\text{O}$  complex, as shown by the corresponding DTA curve.

The dehydration processes of  $\text{Co}(\text{Cx})_3\text{Na} \cdot 10\text{H}_2\text{O}$  and  $\text{Ni}_2(\text{Cx})_3\text{ClO}_4 \cdot 8\text{H}_2\text{O}$  are very similar. At the first step, the observed weight loss indicates the elimination of 5 and 4 molecules of water, respectively. The observed weight loss at the second step corresponds to the loss of 5 and 4 molecules of water, respectively.

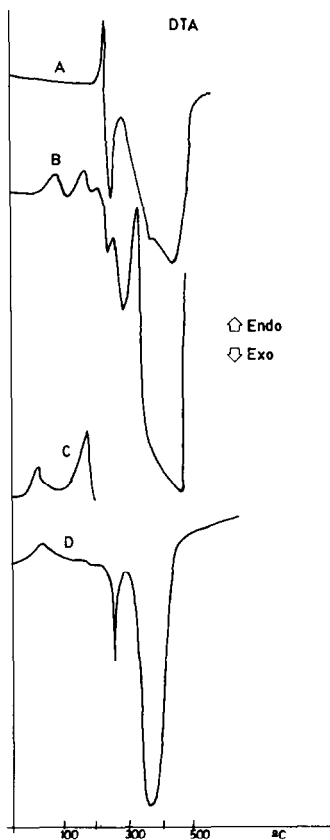


Fig. 2. DTA curves of: (A) cinoxacin; (B)  $\text{Co}(\text{Cx})_3\text{Na} \cdot 10\text{H}_2\text{O}$ ; (C)  $\text{Ni}_2(\text{Cx})_3\text{ClO}_4 \cdot 8\text{H}_2\text{O}$ ; (D)  $\text{Cu}(\text{Cx})_2 \cdot \text{H}_2\text{O}$ .

Non-isothermal kinetic analyses of these processes were carried out using Coats and Redfern and Dharwadkar and Karkhanavala's methods [7–9]. In all cases dehydration takes place by means of a nucleation mechanism, which corresponds to the  $F_1$  model (Sharp notation [10]). The activation energy values allow us to conclude that the water molecules present in all complexes interact weakly with the metal ion. On the other hand, the existence of two different types of water molecules can be explained either by the different binding sites of each molecule of water in the initial structure or by the consecutive structural changes that can take place during the heating process.

#### *Pyrolytic decomposition*

The TG curve of  $\text{Co}(\text{Cx})_3\text{Na} \cdot 10\text{H}_2\text{O}$  shows a weight loss in two overlapping steps (270–345, 345–550°C). Furthermore, the DTA curve shows a

TABLE 3  
Thermoanalytical data for dehydration processes

Process	Weight loss (%)		Dehydration temp. (°C)	Activation energy (kcal mol <sup>-1</sup> )	
	Calcd.	Found		Coats and Redfern's method	Karkhanavala's method
$\text{Co(Cx)}_3\text{Na} \cdot 10\text{H}_2\text{O} \rightarrow \text{Co(Cx)}_3\text{Na} \cdot 5\text{H}_2\text{O} + 5\text{H}_2\text{O}$	8.6	8.51	130	4.23	3.33
$\text{Co(Cx)}_3\text{Na} \cdot 5\text{H}_2\text{O} \rightarrow \text{Co(Cx)}_3\text{Na} + 5\text{H}_2\text{O}$	8.6	8.52	240	6.17	5.59
$\text{Ni}_2(\text{Cx})_3\text{ClO}_4 \cdot 8\text{H}_2\text{O} \rightarrow \text{Ni}_2(\text{Cx})_3\text{ClO}_4 \cdot 4\text{H}_2\text{O} + 4\text{H}_2\text{O}$	6.29	6.39	90	7.16	7.79
$\text{Ni}_2(\text{Cx})_3\text{ClO}_4 \cdot 4\text{H}_2\text{O} \rightarrow \text{Ni}_2(\text{Cx})_3\text{ClO}_4 + 4\text{H}_2\text{O}$	6.29	6.38	205	3.72	3.35
$\text{Cu(Cx)}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Cu(Cx)}_2 + \text{H}_2\text{O}$	2.98	3.07	140	3.45	3.01

TABLE 4

TG and DTA data for pyrolytic processes

Compound	Temp. range (°C)	Weight loss (%)		DTA peak temp. (°C)	
		Found	Calcd.	Endo	Exo
Cinoxacin	270–550	99.49	100	–	290, 475
Cu(Cx) <sub>2</sub> → CuO	290–500	86.65	86.9	–	300, 400
(Co(Cx) <sub>3</sub> )Na → Co	270–1000	94.93	94.36	–	300, 340, 500

complex process with exothermic peaks at 300, 340 and 500°C. This must be attributed to the combustion of the organic matter. The weight percentage of the residue (5.57%) corresponds to Co as revealed by X-ray diffraction methods and IR spectroscopy.

The anhydrous copper complex is stable up to 298°C; from this temperature to the end of the run a very rapid weight loss occurs in two steps (290–340, 340–500°C). The DTA curve shows a complex process with exothermic peaks at 300 and 400°C. The percentage weight of the residue at 500°C (13.35%) corresponds to CuO characterized by X-ray diffraction and IR spectroscopy.

The thermogravimetric and DTA data for the pyrolytic processes are given in Table 4.

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