

**THERMAL AND SPECTROSCOPIC STUDY  
OF THE SOLID COMPLEXES  
OF FURAN-2-HYDROXAMIC ACID  
AND SEVERAL DIVALENT METALLIC CATIONS**

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Solid crystalline complexes of furan-2-hydroxamic acid (FHA) and six metallic divalent cations (Ca(II), Ba(II), Co(II), Ni(II), Cu(II), and Cd(II)) were prepared. In all cases the stoichiometry was 2(FHA) : 1 (cation). The solids were characterized by elemental analysis, TG, DSC and IR techniques.

Hydroxamic acids generally form complexes of 2 : 1 stoichiometry with divalent metallic cations in neutral and alkaline media [1–3], but few of them have been studied in the solid state [4–6]. The chelation takes place with the carbonyl and the hydroxy of the hydroxamic group, with a partial loss of double bond character of the C=O group and a large increase of this character in the C—N group [6].

The aim of this work was to synthesize complexes of furan-2-hydroxamic acid (FHA) and several divalent metallic cations, and to investigate the thermal behaviour of these solids by means of TG–DTG, DSC and IR techniques.

### **Experimental**

FHA was synthesized by the method of described by Hauser and Renfrow [7]. The isolated acid was recrystallized from petroleum ether-methanol 2 : 1.

All the FHA—divalent cation complexes were prepared in the following general way: to 10 ml of a hot solution of 0.5 M FHA (as potassium salt), 10 ml of a 0.1 M solution of the metal salt was added with stirring. The precipitate was immediately

**Table 1** Elemental analysis data

Compound	C, %		H, %		N, %		H <sub>2</sub> O*, %	
	calc.	found	calc.	found	calc.	found	calc.	found
K-FHA	36.57	35.72	2.45	2.88	8.53	8.32	—	—
Ca(FHA) <sub>2</sub> ·2H <sub>2</sub> O	36.58	35.94	3.40	3.15	8.53	8.42	10.9	10.3
Ba(FHA) <sub>2</sub> ·H <sub>2</sub> O	29.47	30.38	2.47	2.08	6.87	6.43	4.4	4.5
Co(FHA) <sub>2</sub> ·H <sub>2</sub> O	36.49	35.45	3.05	2.49	8.51	8.01	5.4	4.9
Ni(FHA) <sub>2</sub> ·2H <sub>2</sub> O	34.61	33.31	3.48	3.00	8.07	7.99	11.0	10.3
Cd(FHA) <sub>2</sub> ·2H <sub>2</sub> O	29.98	30.80	3.01	2.69	6.99	6.97	8.9	7.7
Cu(FHA) <sub>2</sub> ·H <sub>2</sub> O	35.98	37.18	2.99	2.91	8.39	9.03	6.4	5.4

\* Water percentages measured from TG data.

filtered off, washed with cold water and dried over calcium carbonate. Analytical data are given in Table 1.

Elemental analysis were carried out at the Institute of Bio-organic Chemistry, Barcelona.

Thermal studies were carried out on a Mettler TA 3000 System provided with a Mettler TG 50 thermobalance and a Mettler differential scanning calorimeter. TG curves were obtained at a heating rate of 10 deg/min in a static air atmosphere, with sample weights between 4.42 and 11.67 mg. The temperature range studied was 40–1000°. The DSC curves were registered at a heating rate of 10 deg/min in a static atmosphere of air, within the range 30–600°; the sample weights ranged from 1.33 up to 1.86 mg in these cases.

IR spectra were produced on a Perkin-Elmer 297 spectrophotometer; KBr pellets were prepared with the solids obtained after heating for 1 hour at 25, 80 and 150°.

## Results and discussion

The solid FHA—metal complexes prepared under the specified experimental conditions have a stoichiometry of 2:1, all of them containing one or two water molecules of crystallization or coordination as a difference from FHA and its potassium salt (K-FHA), which crystallize in anhydrous form (Table 1).

The hydrated complexes undergo dehydration between 80 and 130°, the experimental mass losses being in good agreement with the theoretical ones. As expected, the dehydration is accompanied by an endothermic peak in the DSC curves (Fig. 1).

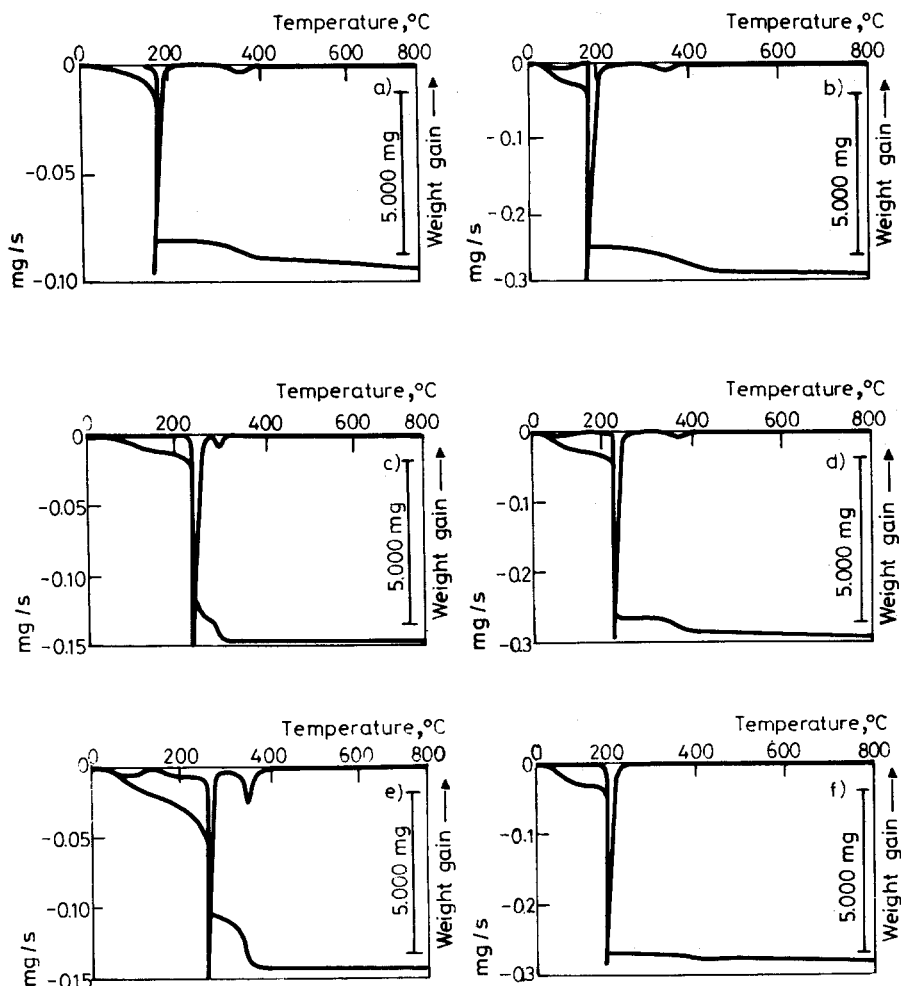


Fig. 1 TG and DSC curves of furan-2-hydroxamic acid complexes of Ba(II) (A); Cd(II) (B); Co(II) (C); Cu(II) (D); Ni(II) (E) and Ca(II) (F)

The anhydrous complexes undergo thermal decomposition in one or two steps; the first one takes place at about  $200^{\circ}$  with considerable mass loss. The total decomposition leads to the formation of the corresponding oxides, the experimental mass loss being in good agreement with the theoretical one (Table 2).

Table 3 gives IR data for K-FHA and the complexes before and after heating for an hour at the decomposition temperature ( $200\text{--}250^{\circ}$ ).

Appreciable shifts in the C—N and N—O bands ( $1300$  and  $720\text{ cm}^{-1}$ , respectively, for K-FHA) can be observed. Both absorptions are shifted towards

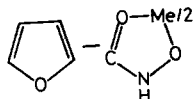
**Table 2** TG assignments for the pyrolysis processes

Compound	End-product	Weight loss, %		Temperature, °C
		calc.	found	
Ca(FHA) <sub>2</sub> ·2H <sub>2</sub> O	CaO	82.9	81.3	600
Ba(FHA) <sub>2</sub> ·H <sub>2</sub> O	BaO	62.3	59.6	900
Co(FHA) <sub>2</sub> ·H <sub>2</sub> O	CoO	76.4	77.2	350
Ni(FHA) <sub>2</sub> ·2H <sub>2</sub> O	NiO	76.2	74.1	400
Cd(FHA) <sub>2</sub> ·2H <sub>2</sub> O	CdO	67.9	69.3	500
Cu(FHA) <sub>2</sub> ·H <sub>2</sub> O	CuO	76.2	76.7	400

higher frequencies by about 15–40 cm<sup>-1</sup> for the former and 20–30 cm<sup>-1</sup> for the latter.

The presence of a new band (about 945–958 cm<sup>-1</sup>) for all the solids except the reactive salt indicates a structural modification in which the C=O group must be involved. FHA presents an unique carbonyl band in this zone (1630 cm<sup>-1</sup>), whereas it is duplicated in the spectra of the solid complexes, with a second band of the same intensity at 1580 cm<sup>-1</sup>. It was seen previously [6], that such shifts and modifications correspond to coordination in which the carbonyl group is involved.

A general formula can be proposed:

**Scheme 1** Structure of the complexes [M(II)-FHA]

where a partial loss of the double bond character of the C=O group justifies the spectral data [8].

The spectra registered after heating at low temperatures (120°) show some variation in the shapes of the bands between 3200 and 3500 cm<sup>-1</sup>, except in the Cu(II) complex. This modification is due to the corresponding dehydration process and is not involved in the anhydrous Cu(II) complex. On the other hand, the spectra present no important modification except that the band between 1600 and 1400 cm<sup>-1</sup> become broader and overlap in very broad absorption when total decomposition is achieved.

The thermal decomposition leads to a new band (about 2175–2200 cm<sup>-1</sup>) in the spectra of the Cd(II), Ba(II), Ni(II) and Ca(II) complexes, which may be assigned to the formation of an isocyanate group as proposed in [9].

Table 3 IR absorption bands,  $\text{cm}^{-1}$ 

Compound	O—H		SCN		C=O		NH		C—N		NO	
	20 °C	T, °C	20 °C	T, °C	20 °C	T, °C	20 °C	T, °C	20 °C	T, °C	20 °C	T, °C
K-FHA	3200	—	—	—	1630	—	1335	—	1300	—	1015	—
Ca(FHA) <sub>2</sub> ·2H <sub>2</sub> O	3360	3300	—	2200	1612	1598	1590	—	1320	—	958	740
Ba(FHA) <sub>2</sub> ·H <sub>2</sub> O	3330	3300	—	2180	1600	1580	1560	—	1315	—	945	742
Co(FHA) <sub>2</sub> ·H <sub>2</sub> O	3340	3400	—	—	1660	1600	—	—	1342	—	951	742
Ni(FHA) <sub>2</sub> ·2H <sub>2</sub> O	3400	3300	—	2180	1608	1580	1580	—	1330	—	958	750
Cd(FHA) <sub>2</sub> ·2H <sub>2</sub> O	3200	3200	—	2175	1600	1580	1540	—	1320	—	950	741
Cu(FHA) <sub>2</sub> ·H <sub>2</sub> O	3400	3400	—	—	1600	1590	1600	—	1360	—	958	742

K-FHA: Potassium furan-2-hydroxamate.

T = 200 °C for Cd, Ba and Cu cations; T = 250 °C for Co, Ni and Ca cations.

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**Zusammenfassung** — Es wurden feste, kristalline Komplexe von Furan-2-hydroxamsäure (FHA) und sechs verschiedenen bivalenten Metallkationen hergestellt: Ca(II), Ba(II), Co(II), Ni(II), Cu(II) und Cd(II). Die stöchiometrische Zusammensetzung betrug in allen Fällen 2(FHA):1(Kation). Die Feststoffe wurden mittels Elementaranalyse, TG-, DSC- und IR-Techniken charakterisiert.

**Резюме** — Получены твердые кристаллические комплексы фуран-2-гидроksamовой кислоты с двухвалентными катионами кальция, бария, кобальта, никеля, меди и кадмия. Для всех комплексов стехиометрический состав лиганд : катион составлял 2 : 1. Полученные комплексы изучены методом ТГ, ДСК, ИК спектроскопии и элементарным анализом.