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SOLID COMPLEXES FROM 2-BENZYLIDENIMINOBENZOHYDROXAMIC, 2-PYRILIDENIMINOBENZOHYDROXAMIC AND 2-SALICYLIDENIMINOBENZOHYDROXAMIC ACIDS WITH Fe(III) AND Cu(II)

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ABSTRACT

The solid complexes that 2-benzylideniminobenzohydroxamic, 2-pyrilideniminobenzohydroxamic and 2-salicylideniminobenzohydroxamic acids form with Fe(III) and Cu(II) ions have been isolated. The six complexes have been characterized by chemical analysis and IR spectroscopy. Their thermal behaviour has also been studied.

INTRODUCTION

2-Benzylideniminobenzohydroxamic acid (BIBHA), 2-pyrilideniminobenzohydroxamic acid (PIBHA) and 2-salicylideniminobenzohydroxamic acid (SIBHA) have been used as reagents in several spectrophotometric and extractive spectrophotometric determinations of Fe(III) [1,2], Ti(IV) [3–5], V(V) [5–7] and Mo(VI) [8,9].

There are a few papers describing the thermal behaviour and stability of the solid complexes of hydroxamic acid with metallic ions [10–14]. In this paper, we present a study of the thermal stability of the solid complexes formed by BIBHA, PIBHA and SIBHA with Fe(III) and Cu(II) ions.

EXPERIMENTAL

Preparation of reagents and chelates

All experiments were performed using analytical reagent grade chemicals.

The BIBHA, PIBHA and SIBHA were prepared using the method reported earlier [15–17], by reacting *o*-aminobenzohydroxamic acid with benzaldehyde 2-pyridinecarboxaldehyde or salicylaldehyde, respectively.

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The metal chelates were prepared by precipitation from 50 ml of solution containing between 0.5 and 4.0 mmol of metal ions and between 1.0 and 4.0 mmole of ligand, at pH 6–8, and stirring for 30 min.

The precipitates were immediately filtered off, washed with cold water and dried over calcium carbonate.

Apparatus

The elemental analyses were carried out using a Perkin–Elmer 240 C.

Thermal studies were carried out on a Mettler MTA 3000 system provided with a Mettler TG 50 thermobalance and a Mettler differential scanning calorimeter. The TG curves were obtained in a static air atmosphere, using sample weights of 10.23–12.80 mg and at a heating rate of 10 °C min^{-1}. The temperature range studied was 35–600 °C.

IR spectra were obtained on a Beckman IR 33 spectrophotometer as KBr pellets prepared with the solids as obtained and after 1 h heating between 200 and 350 °C.

RESULTS AND DISCUSSION

The solid complexes prepared under the experimental conditions indicated above have a stoichiometry of 2 : 1 (ligand : metal) in all cases except the complex Fe–BIBHA which has a 1 : 1 stoichiometry. The complexes of Fe(III) are red and the complexes of Cu(II) are green. Table 1 contains the elemental analysis data for the reagents, BIBHA, PIBHA and SIBHA, and the complexes with Fe(III) and Cu(II). The results obtained show that the

TABLE 1

Elemental analysis data

Compound	C (%)		H (%)		N (%)		H_2O (%)	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found [a]
BIBHA	69.98	69.73	5.02	4.77	11.65	11.59		
$FeBIB(OH)_2$	51.09	50.98	3.97	3.61	8.51	8.83	–	–
$Cu(BIB)_2 \cdot H_2O$	60.65	60.49	4.30	4.07	10.11	10.12	3.00	1.60
PIBHA	64.71	64.86	4.60	4.65	17.42	17.32	–	–
$Fe(PIB)_2OH \cdot 2H_2O$	53.00	54.53	4.25	3.61	14.26	15.11	6.10	7.66
$Cu(PIB)_2 \cdot H_2O$	55.60	56.28	3.90	3.88	14.96	15.16	3.21	2.83
SIBHA	65.60	65.51	4.72	4.80	10.93	10.83	–	–
$Fe(SIB)_2OH$	57.60	56.11	3.95	3.65	9.60	9.58	–	–
$Cu(SIB)_2 \cdot 2H_2O$	55.13	55.40	4.20	3.57	9.18	9.26	5.91	2.60

[a] Water percentages measured from TG data.

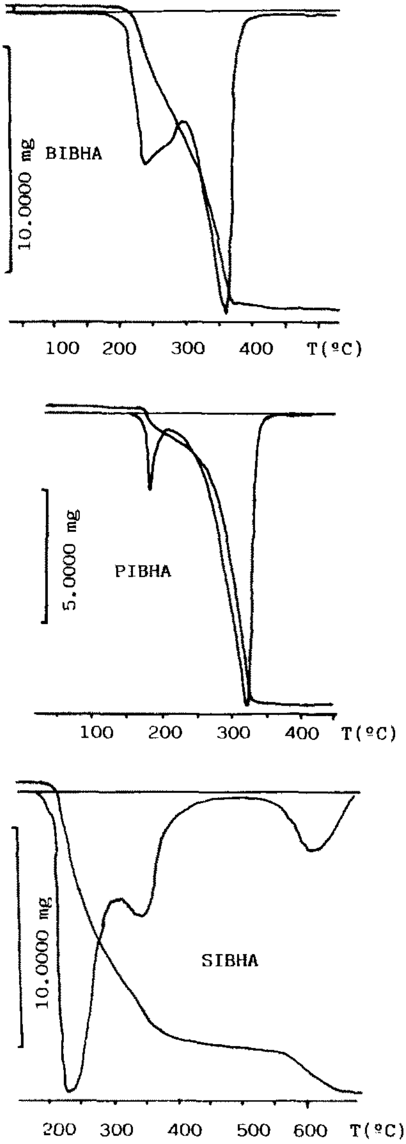

Fig. 1. Thermogravimetric curves of 2-benzylideniminobenzohydroxamic acid (BIBHA), 2-pyrilideniminobenzohydroxamic acid (PIBHA) and 2-salicylideniminobenzohydroxamic acid (SIBHA).

complexes obtained from Cu(II), as well as the Fe–PIBHA complex, contain crystallization or coordination water, or both.

The TG of the reagents, Fig. 1, show one step for the decomposition of anhydrous hydroxamic acids. This process takes place between 350 and 400 °C.

Dehydration processes

At the first stage of the thermal decomposition of the hydrated complexes, water is eliminated with a corresponding mass loss on the TG curves occurring between 40 and 150 °C (Fig. 2). The data for calculated and observed weight loss and the corresponding temperature, for the dehydration processes, are given in Table 2.

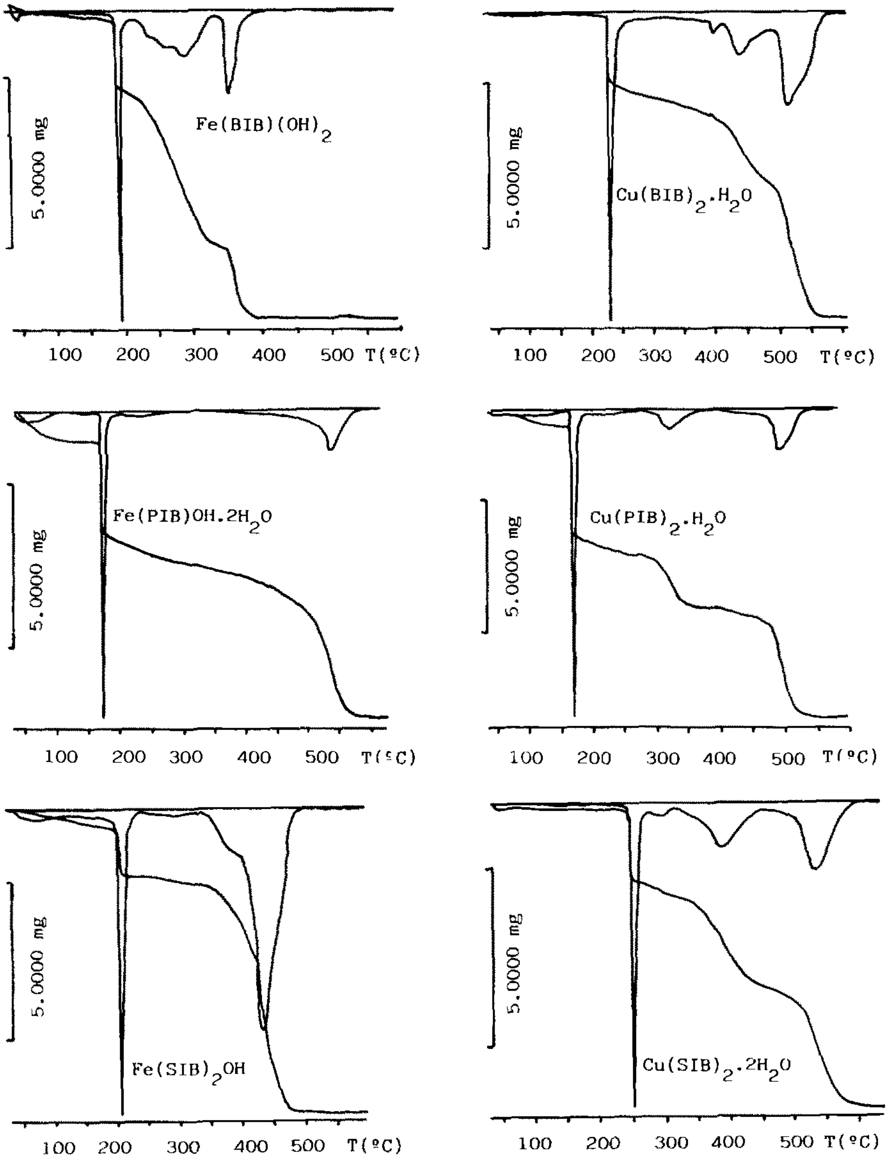

Fig. 2. Thermogravimetric curves of the complexes with Fe(III) and Cu(II).

TABLE 2

TG assignations for the dehydration process

Process	Temperature (° C)	Weight loss (%)	
		Calc.	Found.
$Cu(BIB)_2 \cdot H_2O \rightarrow Cu(BIB)_2$	200	3.20	–
$Fe(PIB)_2OH \cdot 2H_2O \rightarrow Fe(PIB)_2OH$	100	6.10	7.60
$Cu(PIB)_2 \cdot H_2O \rightarrow Cu(PIB)_2$	100	3.21	2.83
$Cu(SIB)_2 \cdot 2H_2O \rightarrow Cu(SIB)_2 \cdot H_2O$	150	2.90	2.60

The TG curves of these compounds (Fig. 2) have one step for the Fe–PIBHA and Cu–PIBHA complexes in the temperature range 40–100 ° C, which can be ascribed to the loss of 2 and 1 molecules of water, respectively.

For the $Cu(BIB)_2 \cdot H_2O$ complex, mass loss is not observed below 220 ° C on the TG curve. In this case, the loss corresponding to a water molecule overlaps with the pyrolysis process.

For the $Cu(SIB)_2 \cdot 2H_2O$ complex, two dehydration steps are observed. The first takes place at 150 ° C with the loss of one molecule of water, and the second dehydration step is accompanied by partial decomposition of the hydroxamic complex.

Decomposition of anhydrous complexes

All complexes undergo a strong two-stage decomposition as can be seen in Fig. 2. The experimental and calculated residues at different temperatures are shown in Table 3. In this table, are also included the metal contents, determined gravimetrically as oxides.

The first step (between 220 and 400 ° C) suggests that the complex molecule is fracturing at the azomethinic bond. This step generally corresponds to a mass loss of about 35%. According to the measured percentages, the residual masses are in good agreement with the calculated values.

After this, a progressive decomposition is observed, finally leaving a residue of the corresponding oxide (over 500 ° C). The measured percentages of residual masses for temperatures between 500 and 600 ° C are in good agreement with the calculated values after calcination of the solid.

IR spectra

The IR spectra of reagents and complexes (Table 4) show that the bands of NH, C=O and C=N are unchanged.

The IR spectra of BIBHA, PIBHA and SIBHA show OH bands at 3220, 3080 and 3240 cm^{-1}, respectively. In the complexes, a broad band appears between 3300 and 3410 cm^{-1} and is probably due to –OH or water. Also, in

TABLE 3

Pyrolysis processes

Complex	T (° C)	Residue (%)		Calcined at 600 ° C
		Calc.	Found	
$FeBIB(OH)_2$	250	72.63	72.35	–
	500	24.21	25.57	23.8
$Cu(BIB)_2 \cdot H_2O$	390	71.46	68.77	–
	600	14.21	13.85	13.4
$Fe(PIB)_2OH \cdot 2H_2O$	250	60.36	59.38	–
	600	13.56	12.59	10.0
$Cu(PIB)_2 \cdot H_2O$	220	64.38	60.39	–
	600	14.16	10.02	11.1
$Fe(SIB)_2OH$	400	69.11	68.36	–
	600	13.70	13.68	12.6
$Cu(SIB)_2 \cdot 2H_2O$	390	62.26	61.11	–
	600	13.04	15.39	14.7

TABLE 4

IR absorption bands (cm^{-1})

Compound	N-H	C=O	C=N
BIBHA	3310	1610	1640
$FeBIB(OH)_2$	3320 [a]	1595	1600
$Cu(BIB)_2 \cdot H_2O$	3310 [a]	1600	1615
PIBHA	3220	1610	1650
$Fe(PIB)_2OH \cdot 2H_2O$	3250 [a]	1600	1620
$Cu(PIB)_2 \cdot H_2O$	3280 [a]	1610	1650
SIBHA	3410	1635	1616
$Fe(SIB)_2OH$	3400 [a]	1600	1615
$Cu(SIB)_2 \cdot 2H_2O$	3410 [a]	1605	1620

[a] Bands overlap with the –OH band.

the complex, we believe that the OH band of the hydroxamic group does not appear, as occurs with other hydroxamic acids [14, 18–20].

Most absorption bands are strongly affected by temperature. In consequence, the whole spectrum changes and the bands disappear or become much weaker on heating.

REFERENCES

1 F. Salinas, M.C. Mahedero and J.P. García-Martín, Bull. Soc. Chim. Belg., 96(1) (1987) 75.

2 F. Salinas, M. Jiménez Arrabal and I. Durán-Merás, Quim. Anal., 6(2) (1987) 144.
3 F. Salinas, M.C. Mahedero, M. Jiménez Arrabal and M.F. Fernández, Afinidad, XLV (412) (1988) 63.
4 F. Salinas, M. Jiménez Arrabal and I. Durán-Merás, Bull. Soc. Chim. Belg., 94(10) (1985) 713.
5 F. Salinas, M.C. Mahedero and J.P. García-Martín, Bull. Soc. Chim. Belg., 95(2) (1986) 89.
6 F. Salinas, M.C. Mahedero and F. Vinagre Arias, Quim. Anal., in press.
7 F. Salinas, M. Jiménez Arrabal and I. Durán-Merás, Bull. Soc. Chim. Belg., 94(2) (1985) 101.
8 F. Salinas, M.C. Mahedero, J.P. García-Martín and M.F. Fernández, Anal. Lett., 19 (13 & 14) (1986) 1359.
9 F. Salinas, M. Jiménez Arrabal and I. Durán-Merás, Ann. Chim. (Rome), 77 (1977) 705.
10 A Cueto, Thermochim. Acta, 15 (1974) 23.
11 L.F. Capitán-Vallvey, A. Gázquez and F. Salinas, Thermochim. Acta, 15 (1974) 23.
12 B. Chatterjee, J. Indian. Chem. Soc., 53 (1976) 721.
13 W.W. Wendlandt and A.J. Holberg, Anal. Chim. Acta, 29 (1963) 539.
14 F. Salinas, I.J. Pérez Alvarez, J.L. Martínez Vidal and A.R. Fernández Alba, Thermochim. Acta, 127 (1988) 285.
15 F. Salinas, M.C. Mahedero, J.P. García-Martín and J. Rodríguez Flores, An. Quim., 83(B) (1987) 293.
16 F. Salinas, M. Jiménez Arrabal and I. Durán-Merás, Proc. Indian Acad. Sci. (Chem. Sci.), 97 (1986) 159.
17 F. Salinas, M.C. Mahedero and J.P. García-Martín, Quim. Anal., 5(4) (1986) 477.
18 C.K. Pal and A.K. Chakraburtty, J. Indian Chem. Soc., 52(9) (1975) 869.
19 S.K. Brahma and A.K. Chakraburtty, J. Inorg. Nucl. Chem., 39 (1977) 1723.
20 M. Koeva, N. Jordanov and St. Mareva, Anal. Chim. Acta, 104 (1979) 161.