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THIOPHENEHYDROXAMIC ACID (THA) AND ITS SOLID COMPLEXES WITH SEVERAL METALLIC DIVALENT CATIONS: A SPECTROSCOPIC AND THERMAL STUDY

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ABSTRACT

THA and nine complexes with the cations Cu(II), Cd(II), Ni(II), Pb(II), Co(II), Zn(II), Sr(II), Ca(II), Ba(II) and Mg(II) have been prepared and characterized. These compounds have the general formula $M(\mathrm{THA})_2$ with a variable amount of water. The thermal behaviour of these complexes has been studied by TG, DTG and DSC techniques developed in a dynamic atmosphere of air. IR data show a tautomeric transformation and the formation of an ionic oxygen–metal bond.

INTRODUCTION

The hydroxamic acids are excellent complexing agents for most cations, generally forming complexes of $2R:1M$ stoichiometries [1]. The chelation takes place on the carbonylic oxygen and the hydroxamic nitrogen.

A small number of papers on the TG, DTG and DSC analysis of the complexes obtained from hydroxamic acids and divalent cations has been published, which include data on their thermal stabilities in the solid state [2–4]. In a previous work [5], the behaviour of the complexes formed between mandelohydroxamic acid and divalent cations was described.

The purpose of this paper is the synthesis of the complexes obtained from THA and several divalent metallic cations and their study using elemental analysis and TG, DTG and DSC techniques. The thermal decomposition processes have been followed by IR spectroscopy.

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EXPERIMENTAL

Materials

A 0.5 M solution of sodium thiophenehydroxamate (Na-THA) in distilled water was prepared [6]. 0.1 M solutions of Cu(II), Cd(II), Pb(II), Ni(II), Co(II), Zn(II), Sr(II), Ca(II), Ba(II), Mg(II) as nitrates (Merck R.A.) were prepared in distilled water.

To prepare the solid complexes, 10 ml of a 0.1 M solution of the metal cation were added to 10 ml of a hot 0.5 M solution of Na-THA with stirring. The precipitate obtained was heated at 50 ° C for 1 hour, then filtered and washed with hot water. The complexes were dried on P_2O_5 in a vacuum.

Apparatus

Carbon, nitrogen, hydrogen and sulphur contents were determined by elemental analyses at the Institute of Bio-organic Chemistry of Barcelona. Infrared spectra of the compounds were recorded as KBr pellets made with the freshly prepared complexes and after one hour of heating at 120, 160, 200 and 250 ° C, in the region 4000–600 cm^{-1} using a Perkin–Elmer 297 spectrophotometer. The TG studies were carried out in air on a Mettler TG-50 thermobalance, using samples varying in weight from 5.8 to 12.3 mg at a heating rate of 10 ° C min^{-1}. The DSC curves were recorded in a Mettler differential scanning calorimeter DSC-20 at a heating rate of 5 ° C min^{-1} in a temperature range of 40–550 ° C using sample weights varying from 2.8 to 5.6 mg.

RESULTS AND DISCUSSION

The stoichiometry of the solid complexes obtained from THA and the divalent cations Ca(II), Sr(II), Ba(II), Ni(II), Co(II), Cu(II), Zn(II), Cd(II) and Pb(II) was found to be 2 : 1 in each case. The Pb(II), Cd(II) and Cu(II) complexes formed anhydrous crystals whereas the other complexes are hydrated as can be seen from the results of the elemental analysis (Table 1).

Among these values there is an interesting deviation in the sulphur contents. The measured percentages are virtually half the calculated amount in the complexes of Pb(II), Cd(II), Ca(II), Sr(II), Ba(II) and Zn(II). This fact could be due to a possible formation of the corresponding metallic sulphide during the process.

The TG analyses of the complexes of Ba(II), Ca(II), Sr(II) and Zn(II) indicate that the first loss occurs between 112 and 160 ° C, corresponding to a dehydration process, as can be seen by comparing the calculated and lost percentages (Fig. 1). In the complexes of Ni(II) and Co(II), this dehydration

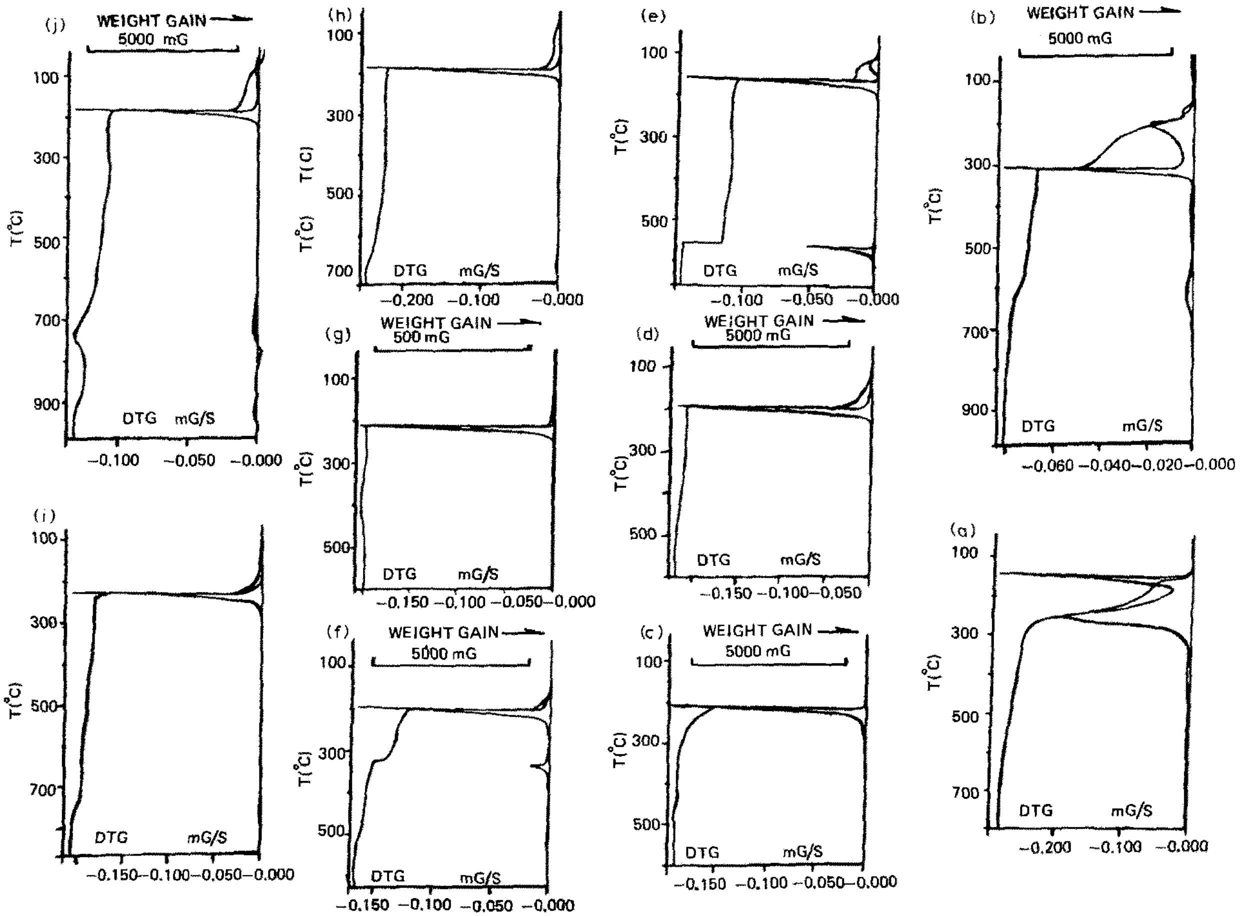


Fig. 1. Thermogravimetric curves for (a) THA and for THA complexes of (b) Zn(II), (c) Cu(II), (d) Pb(II), (e) Ba(II), (f) Cd(II), (g) Co(II), (h) Ca(II), (i) Ni(II) and (j) Mg(II).

TABLE 1

Elemental analysis

Compound	%C		%H		%N		%S		$\%H_2O$ [a]	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$Pb(THA)_2$	24.43	24.45	1.64	1.37	5.70	5.75	13.05	7.97		
$Cd(THA)_2$	30.27	29.33	2.03	2.00	7.06	6.99	16.16	7.30		
$Cu(THA)_2$	34.53	34.95	2.32	2.11	8.05	8.10	18.43	-		
$Ca(THA)_2 \cdot 0.5H_2O$	36.02	35.91	2.72	2.61	8.40	9.10	19.23	10.18	2.70	3.03
$Sr(THA)_2 \cdot 0.5H_2O$	31.53	31.66	2.38	2.47	7.35	7.28	16.83	7.87	2.36	-
$Ni(THA)_2 \cdot H_2O$	33.26	33.27	2.79	2.42	7.76	7.71	17.76	11.71	4.99	5.09
$Co(THA)_2 \cdot H_2O$	33.25	33.60	2.79	2.66	7.75	7.75	17.75	16.00	4.99	-
$Zn(THA)_2 \cdot H_2O$	32.66	32.64	2.74	2.42	7.62	7.58	17.44	7.00	4.90	6.55
$Ba(THA)_2 \cdot 2H_2O$	26.24	26.21	2.64	2.37	6.12	6.06	14.01	7.81	7.87	8.28

[a] Water percentages measured from TG data.

process seems to occur below 190 °C in a gradual way, overlapping with the first decomposition of the complex; therefore the mass loss corresponding to dehydration became difficult to quantify. We have observed that the higher the dehydration temperature, the greater the deviation between the percentages of loss and theoretical values (Table 2). In the complexes of alkaline earth cations, an inverse proportionality between dehydration temperature and ionic radius was noted.

Two or more further steps are observed. The highest occurs between 157 and 220 °C and involves a loss of 150–200 g mol^{-1} in the complexes, indicating the occurrence of a strong decomposition which we have studied, following the process using IR spectroscopy.

Anhydrous complexes are stable within a short temperature interval. In Table 2, the different temperatures corresponding to mass losses, and the experimental and calculated residues (as percentages) are shown for the decomposition processes. The complexes derived from Cu(II), Zn(II), Ni(II) and Co(II) follow the thermal stability order proposed by Irving and Williams [7]: $Co < Ni < Cu > Zn$.

The TG residues can be classified in two groups: the complexes of Pb(II), Ni(II), Cd(II), Ba(II) and Zn(II) which give mass percentages that correspond to the transformation to the metallic oxides, and the Ca(II), Sr(II), Co(II) and Cu(II) complexes which give percentages corresponding to the transformation to the metallic sulphide.

The IR spectra (Table 3) of the free acid show a strong absorption at about 1608 cm^{-1} assigned to C=O stretching, and a broad band at 3200 cm^{-1} corresponding to N–H stretch. The complexes with THA show a deviation of less than 20 cm^{-1} in the first band and a new shoulder at higher wavelengths. If a salt (a hydroxamate) was formed, a deviation of some -50 cm^{-1} in the first band could be expected [8,9]. In a previous paper [5], we

TABLE 2

Thermogravimetric data

Compound	T_1 [a]	m_1 [b]	T_2	m_2	T_3	m_3	T_4	m_4	Found Res.	Calculated [c]	
										Oxide	Sulphide
$Pb(THA)_2$			220	57.46	410	1.65			41.44	45.41	48.68
$Cu(THA)_2$			220	69.75	350	4.79			26.98	22.86	27.48
$Cd(THA)_2$	165	5.09	192	61.52	550	2.76			30.08	32.37	36.42
$Ca(THA)_2 \cdot 0.5H_2O$	150	3.03	187	68.28	650	7.45			20.43	16.82	21.64
$Sr(THA)_2 \cdot 0.5H_2O$	140	6.32	180	47.84	700	9.40			33.72	27.20	31.42
$Ni(THA)_2 \cdot H_2O$			220	69.75	680	4.79			19.21	20.69	25.14
$Co(THA)_2 \cdot H_2O$			190	56.58	323	7.68	550	3.05	26.18	20.74	25.19
$Zn(THA)_2 \cdot H_2O$	160	6.55	190	34.89	305	29.15	600	6.79	22.20	22.13	26.50
$Ba(THA)_2 \cdot 2H_2O$	112	8.28	157	42.13	550	14.20			32.41	33.51	37.02

[a] T_i, temperatures (°C) at which mass loss occurs.

[b] m_i, mass lost (%).

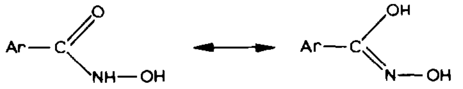
[c] The theoretical percentages are given for oxides and sulphides.

TABLE 3

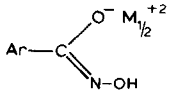
IR absorption wavenumbers

Compound	Wavenumbers (cm^{-1})										
	O-H	N-H	C=O	N-H			C-N		N-O		
THA		3240	1608	1545	1490	1415	1354	1315	1000	840	720
$Ba(THA)_2 \cdot 2H_2O$	3500	3280	1590		1500	1420	1358	1305	1060	842	700
$Ca(THA)_2 \cdot 0.5H_2O$		3280	1600	1550	1500	1420	1380	1300	1080	850	700
$Sr(THA)_2 \cdot 0.5H_2O$		3260	1590	1545	1500	1420	1360	1300	1080	850	705
$Cd(THA)_2$	3460	3300	1590	1550	1500	1420	1360	1315	1062	855	705
$Pb(THA)_2$		3150	1590	1558	1500	1425	1360	1305	1060	840	705
$Co(THA)_2 \cdot H_2O$	3460	3300	1600	1559	1505	1422	1365	1340	1070	855	715
$Ni(THA)_2 \cdot H_2O$		3200	1592	1560	1500	1420	1362	1338	1060	852	710
$Cu(THA)_2$	3460	3200	1590	1568	1490	1425	1375	1335	1080	860	700
$Zn(THA)_2 \cdot H_2O$		3180	1592	1560	1500	1420	1365	1335	1075	860	712

reported a shorter deviation of this absorption band (about -25 cm^{-1}) in a series of mandelohydroxamic acid–divalent cation complexes, which was correlated with the protonation at the hydroxamic OH group. There is also a visible modification between 3500 and 3000 cm^{-1} in all the complexes, anhydrous or hydrated, and the bands assigned to C–N and N–O, 1340 and 1080 cm^{-1} respectively, are shifted to lower wavelengths. Therefore, the hydroxamic acid has not formed a salt but it has probably undergone a structural alteration according to the tautomeric scheme



and the complex formation in some way stabilizes the oxygen-charged anion better than the nitrogen-charged one. So, the complexes can be represented by the formula



The DSC study of free THA shows two steps: an endothermic one at 127.6 ° C ($\Delta H = 22.07$ kJ mol^{-1}) assigned to the melting which occurs in the range (126–127 ° C); and a second exothermic step ($\Delta H = 215.79$ kJ mol^{-1}) corresponding to a structural modification of the molecule.

The first loss of mass of THA in the TG study is 30.6 g mol^{-1} (below 140 ° C) and it can be correlated with the above-mentioned structural change detected in DSC. There is a second loss (about 87.5 g mol^{-1}) below 250 ° C and the organic material is totally destroyed above this temperature.

In the IR spectra registered after heating the complexes at moderate temperatures, a modification of the shape and strength of the absorption band appearing at 1590–1600 cm^{-1} can be observed; meanwhile the wavenumber remains constant (with the complexes of Sr and Ca) or else is shifted to a value greater by some 50 cm^{-1}. The rest of bands become weaker at the same wavenumber, except for the absorption at 3200 cm^{-1} which is shifted to 3300–3400 cm^{-1} (in the case of the complexes of Zn, Sr, Pb and Co).

Dehydration processes were also detected by comparing the spectra obtained at different temperatures.

The spectra of complexes heated at 250°C show a total decomposition with a weak band at 1640 cm^{-1} and four strong absorptions at 1560, 1380, 860 and 700 cm^{-1}, which are very similar in all the complexes.

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