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SOLID COMPLEXES FROM *N*-PHENYL-*O*-ACETYL-MANDELOHYDROXAMIC ACID (*N*-PAMHA) AND SEVERAL DIVALENT METALLIC CATIONS: A THERMAL AND SPECTROSCOPIC STUDY

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ABSTRACT

Solid crystalline complexes of *N*-phenyl-*O*-acetyl-mandelohydroxamic acid (*N*-PAMHA) and seven divalent metallic cations have been obtained and characterised. The stoichiometries were found to be 2:1 (*N*-PAMHA:cation) for Mn^{II}, Cu^{II}, Cd^{II}, Co^{II} and Ni^{II}; 2:1 (*N*-phenylmandelohydroxamic acid : Ba^{II}); and 1 : 1 (*N*-phenylmandelohydroxamic acid : Sr^{II}). The water content of each complex was measured and the thermal behaviour was studied by TG and IR spectroscopic techniques.

INTRODUCTION

The hydroxamic acids are excellent complexing agents for most cations. The complexes formed have the general stoichiometries 2 : 1 (R : C) [1]. The chelation takes place on the carbonylic oxygen and the hydroxamic nitrogen.

A few papers have been published on the TG, DTG and DSC analyses of the complexes obtained from hydroxamic acids and divalent cations as well as on their thermal stabilities in solid state [2–5].

The aim of the present work was to synthesise complexes of *N*-PAMHA and several divalent metallic cations and to investigate the thermal behaviour of these solids by means of TG, DTG and spectroscopic techniques.

EXPERIMENTAL

Materials

All the reagents used were of analytical quality. *N*-PAMHA was synthesised by the reaction between acetylmandelic acid chloride and *N*-phenylhy-

TABLE 1

Elemental analysis data

Compound	C (%)		H (%)		N (%)	
	Calc.	Found	Calc.	Found	Calc.	Found
N-PAMHA	67.35	67.88	5.29	5.34	4.90	4.96
Mn(*N*-PAMHA)$_2$·4H$_2$O	55.26	55.26	5.22	4.41	4.03	4.16
Cu(*N*-PAMHA)$_2$	60.80	60.80	4.46	4.34	4.43	4.45
Cd(*N*-PAMHA)$_2$·H$_2$O	55.00	56.34	4.33	4.36	4.01	4.29
Co(*N*-PAMHA)$_2$·H$_2$O	59.54	61.00	4.68	4.74	4.34	4.64
Ni(*N*-PAMHA)$_2$·H$_2$O	59.56	60.26	4.59	4.67	4.40	4.43
Ba(*N*-PMHA)$_2$ [a]·0.5H$_2$O	55.30	53.55	3.97	3.98	4.44	4.50
SrOH(*N*-PMHA) [a]	48.47	48.77	3.78	4.06	4.04	4.00

[a] *N*-PMHA = *N*-phenylmandelohydroxamic acid.

droxylamine in a bicarbonated medium, according to the general method described by Gupta and Tandon [6].

All the complexes were prepared in the following general way: 10 ml of a 0.1 M solution of the appropriate metallic salt were added with stirring to 10 ml of a hot solution of 0.5 M *N*-PAMHA. The precipitate was immediately filtered off, washed with cold water and dried over calcium chloride under vacuum. Analytical data are given in Table 1.

Apparatus

Elemental analyses were carried out at the Institute de Química Biorgánica de Barcelona.

The thermal studies were carried out on a Mettler TA 3000 System provided with a Mettler TG 50 thermobalance. TG curves were obtained at a heating rate of 10 °C min^{-1} in a static air atmosphere, using samples of weights between 10.00 and 17.92 mg. The studied temperature range was from 40 °C to 600 °C in some cases and from 40 °C to 900 °C in others.

IR spectra were made on a Perkin–Elmer 297 Spectrophotometer using KBr pellets prepared with the solid complexes.

RESULTS AND DISCUSSION

The solid *N*-PAMHA–metallic cation complexes prepared using the conditions specified above, have 2 : 1 stoichiometries for Mn^{II}, Cu^{II}, Cd^{II}, Co^{II} and Ni^{II}. The elemental analysis of the Ba^{II} and Sr^{II} complexes indicate that they are complexes of *N*-phenylmandelohydroxamic acid (*N*-PMHA) of composition Ba(*N*-PMHA)$_2$ and SrOH(*N*-PMHA). These complexes were obtained at pH 10, higher than that for the other complexes; at this pH it is

TABLE 2

TG assignations for dehydration processes

Process	Weight loss (%)		Temperature range (°C)
	Calc.	Found	
Mn(*N*-PAMHA)$_2$·4H$_2$O → Mn(*N*-PAMHA)$_2$	10.4	11.4	85–110
Cd(*N*-PAMHA)$_2$·H$_2$O → Cd(*N*PAMHA)$_2$	2.5	2.2	85–120
Co(*N*-PAMHA)$_2$·H$_2$O → Co(*N*-PAMHA)$_2$	2.8	2.6	85–120
Ni(*N*-PAMHA)$_2$·H$_2$O → Ni(*N*-PAMHA)$_2$	2.8	3.6	85–110
Ba(*N*-PMHA)$_2$·0.5H$_2$O → Ba(*N*-PMHA)$_2$	1.5	1.6	85–120

possible to lose the acetyl group of the reagent. The IR studies confirmed that this had occurred.

The complexes obtained from Cu^{II} and Sr^{II}, as well as *N*-PAMHA itself, crystallise without water of crystallisation or coordination (Table 1).

Hydrated complexes undergo a dehydration process between 85 and 120°C. The percentages of mass loss are in good agreement with the calculated values (Table 2).

Anhydrous complexes are stable within a short temperature interval and generally decompose in two steps (Fig. 1). Table 3 shows the temperature ranges corresponding to the mass losses, and the experimental and calculated residues for the assigned decomposition processes. The first mass loss

TABLE 3

TG assignations for the pyrolysis processes

Process	Temperature range (°C)	Mass loss (%)		Residue (%)	
		Calc.	Found	Calc.	Found
Mn(*N*-PAMHA)$_2$ → Mn(*N*-PAMHA)	120–450	45.8	46.1		
Mn(*N*-PAMHA) → MnO$_2$	450–600			12.5	12.4
Cu(*N*-PAMHA)$_2$ → Cu(O=C=N–O)$_2$	150–380	71.6	72.5		
Cu(O=C=N–O)$_2$ → CuO	380–550			12.6	12.4
Cd(*N*-PAMHA)$_2$ → Cd(O=C=N–O)$_2$	120–450	64.8	67.2		
Cd(O=C=N–O)$_2$ → CdO	450–550			18.4	16.6
Co(*N*-PAMHA)$_2$ → Co(O=C=N–O)$_2$	120–380	70.1	69.5		
Co(O=C=N–O)$_2$ → CoO	380–500			11.6	9.9
Ni(*N*-PAMHA)$_2$ → Ni(O=C=N–O)$_2$	140–400	70.1	67.6		
Ni(O=C=N–O)$_2$ → NiO	400–550			11.5	9.4
Ba(*N*-PMHA)$_2$ → BaCO$_3$	120–580	68.2	72.4		
BaCO$_3$ → BaO	580–900	6.2	6.0	24.3	21.8
SrOH(*N*-PMHA) → SrO	120–900			29.9	30.0

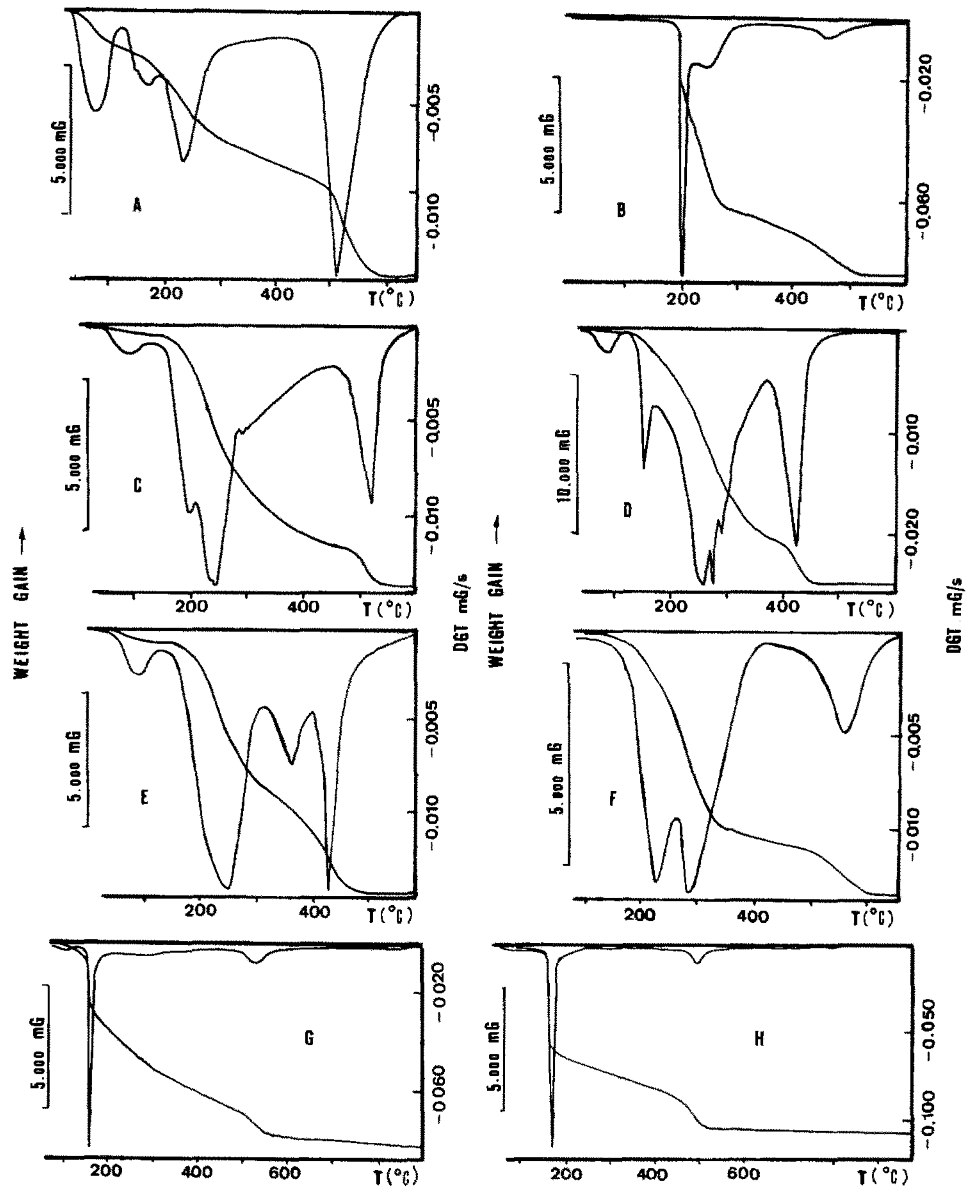

Fig. 1. TG curves of *N*-phenyl-*O*-acetyl-mandelohydroxamic acid (*N*-PAMHA) complexes of: A, Mn^{II}; B, Cu^{II}; C, Cd^{II}; D, Co^{II} and E, Ni^{II}. F, TG curve of *N*-PAMHA. TG curves of *N*-phenylmandelohydroxamic acid complexes of: G, Ba^{II}; and H, Sr^{II}.

of the Cu^{II}, Cd^{II}, Co^{II} and Ni^{II} complexes corresponds to the transformation to $(O{=}C{=}N{-}O)_2$: cation; above 550 °C, the oxides are formed. The 2 : 1 Mn^{II} complex first decomposes to a 1 : 1 complex. In the Ba(*N*-PMHA)$_2$ complex, these is a stage corresponding to carbonate formation before the total oxidation. In all cases, the measured percentages are in good agreement with the calculated values.

TABLE 4

IR absorption bands (cm^{-1})

Compound	O–H	O–H	C=O (acetato)	C=O (amido)	C–N	C–O–C	N–O
N-PAMHA		3180	1740	1640	1380	1225	1020–960
Mn(*N*-PAMHA)$_2 \cdot 4H_2O$	3400		1740	1640	1370	1225	990
Cu(*N*-PAMHA)$_2$	3420		1750	1610	1380	1230	1015–990
Cd(*N*-PAMHA)$_2 \cdot H_2O$	3420		1740	1610	1370	1230	1015–980
Ni(*N*-PAMHA)$_2 \cdot H_2O$	3400		1740	1610	1375	1230	1020–975
Co(*N*-PAMHA)$_2 \cdot H_2O$	3420		1750	1610	1375	1235	1020–985
Ba(*N*-PMHA)$_2 \cdot 0.5H_2O$	3420			1610			1010–985
SrOH(*N*-PMHA)$_2$	3420			1620			1025–990

The thermal stabilities of the complexes of Cu^{II}, Ni^{II}, Co^{II} and Mn^{II} follow the order proposed by Irving and Williams [7]: $Mn < Co < Ni < Cu$. This order has been observed for other complexes of hydroxamic acids [5,8].

The IR data (Table 4) show a strong absorption at 1640 cm^{-1} on the free acid, assigned to C=O stretching, that shifts to lower wavelengths in the complexes studied; another at 3180 cm^{-1} disappears in all the synthesised complexes, indicating the formation of 2 : 1 complexes through the –C=O and –OH of the previously deprotonised hydroxamic acid. Absorption bands corresponding to C=O acetate (1740–1750 cm^{-1}) and C–N (1370–1380 cm^{-1}) can be observed in all cases except the Ba^{II} and Sr^{II} complexes. This confirms the assigned formulae determined from the elemental analyses.

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