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THERMAL AND SPECTROSCOPIC STUDY OF COMPLEXES OF 5,5′-METHYLENEBISTHIOSALICYLIC ACID (MDTSA) AND DIVALENT METALLIC CATIONS

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ABSTRACT

Solid crystalline complexes of 5,5′-methylenebisthiosalicylic acid (MDTSA) and six metallic divalent cations have been obtained and characterized. The stoichiometries were found to be 1 : 1 (MDTSA : Cation) for Cu(II), Pb(II), Mn(II) and Cd(II), and 1 : 2 for Ni(II) and Co(II). The water content of each complex was measured, and the thermal behaviour studied by TG and spectrophotometric techniques.

INTRODUCTION

The ability of *o*-mercaptoacids to form complexes with metallic cations has been studied extensively [1–16]. The complexes formed have a stoichiometry of 2 : 1 (R : C) when the cations are divalent metals. Several of these complexes have been studied in solid state, particularly those formed from thiosalicylic acid [11–16]. The MDTSA reagent synthesized by us forms complexes of stoichiometry 1 : 1 and 1 : 2 (R : C) in aqueous solution with the cations Cu(II), Pb(II), Mn(II), Cd(II), Ni(II) and Co(II).

The aim of the present work was to synthesize complexes of MDTSA and divalent metallic cations and investigate the thermal behaviour of these solids by means of TG, DTG and spectroscopic techniques.

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EXPERIMENTAL

Materials

MDTSA was synthesized by condensation of thiosalicylic acid and formaldehyde in HCl medium [17]. All the chemicals used were of Merck analytical grade. All the MDTSA–divalent cation complexes were prepared according to the same general method. 10 ml of a hot 0.5 M solution of MDTSA were added, with stirring, to 10 ml of a hot 0.1 M solution of the appropriate metallic salt. The precipitate was digested at 50 °C for 1 h and then filtered off, washed with hot alcohol and dried over $CaCl_2$ under vacuum. Analytical data are given in Table 1.

Apparatus

Elemental analyses were carried out at the Instituto de Química Bioorgânica of Barcelona.

The thermal studies were carried out using a Mettler TA 3000 system with a Mettler TG 50 thermobalance and a Mettler differential scanning calorimeter. TG curves were obtained at a heating rate of 10 °C min^{-1} in a static air atmosphere, using samples of weights between 10.809 and 12.937 mg. The temperature ranges studied were 35.5–450 °C in the case of the Cu(II) complex, 35.5–980 °C in the case of the Ni(II) complex, and 35.5–660 °C for the others.

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

RESULTS AND DISCUSSION

The solid MDTSA–metal complexes prepared under the experimental conditions specified have a stoichiometry of 1 : 1 for Cu(II), Pb(II), Mn(II)

TABLE 1

Elemental analysis data

Compound	C (%)		H (%)		S (%)	
	Calc.	Found	Calc.	Found	Calc.	Found
MDTSA	56.35	57.30	3.75	4.03	20.00	19.29
$(C_{15}S_2O_4H_{10})Cu \cdot 2H_2O$	43.11	44.60	3.35	3.13	15.33	15.52
$(C_{15}S_2O_4H_{10})Pb$	34.27	34.80	1.90	1.74	12.19	10.15
$(C_{15}S_2O_4H_{10})Mn \cdot H_2O$	46.04	46.25	3.07	3.02	16.37	15.05
$(C_{15}S_2O_4H_{10})Cd \cdot H_2O$	40.14	40.03	2.68	2.65	14.27	7.06
$(C_{15}S_2O_4H_8)Ni_2 \cdot 3H_2O$	36.93	37.07	2.87	3.36	13.13	8.59
$(C_{15}S_2O_4H_8)Co_2 \cdot 3H_2O$	36.90	39.36	2.87	3.31	13.12	7.05

TABLE 2

TG assignations for dehydration processes

Process	Weight loss (%)		Temperature range (° C)
	Calc.	Found	
$(C_{15}S_2O_4H_{10})Cu \cdot 2H_2O \rightarrow (C_{15}S_2O_4H_{10})Cu$	8.62	8.95	110–160
$(C_{15}S_2O_4H_{10})Mn \cdot H_2O \rightarrow (C_{15}S_2O_4H_{10})Mn$	4.60	5.61	120–220
$(C_{15}S_2O_4H_{10})Cd \cdot H_2O \rightarrow (C_{15}S_2O_4H_{10})Cd$	4.01	3.73	80–170
$(C_{15}S_2O_4H_8)Ni_2 \cdot 3H_2O \rightarrow (C_{15}S_2O_4H_8)Ni_2$	11.10	13.09	80–160
$(C_{15}S_2O_4H_8)Co_2 \cdot 3H_2O \rightarrow (C_{15}S_2O_4H_8)Co_2$	11.10	10.63	70–140

and Cd(II), and 1 : 2 for Ni(II) and Co(II). The Pb(II) complex and MDTSA itself crystallize without water molecules of crystallization or coordination (Table 1).

In the complexes formed between MDTSA and Cd(II), Ni(II) and Co(II), respectively, a difference was found between the percentages of sulphur observed and calculated. This was probably due to the formation of elemental sulphur.

The hydrated complexes undergo a dehydration process between 70 and 220 °C, and the percentage mass losses are in good agreement with the calculated values (Table 2).

The anhydrous complexes are stable within a short range of temperatures, but then undergo strong decomposition in two or more steps (Fig. 1). Table 3 gives the various temperatures at which mass losses occur and the

TABLE 3

TG assignations for the pyrolysis processes

Process	Temperature range (° C)	Residue (%)		$T^{\star}$ [a]
		Calc.	Found	
$(C_{15}S_2O_4H_{10})Cu \rightarrow CuS$	180–260 260–450	23.91	22.34	450
$(C_{15}S_2O_4H_{10})Pb \rightarrow PbO_2$	200–305 360–420 430–570	45.54	46.54	660
$(C_{15}S_2O_4H_{10})Mn \rightarrow MnO_2$	310–475	22.24	24.18	660
$(C_{15}S_2O_4H_{10})Cd \rightarrow CdO$	180–270 370–500	28.63	29.61	660
$(C_{15}S_2O_4H_8)Ni_2 \rightarrow NiO$	240–270 360–410	30.66	28.31	980
$(C_{15}S_2O_4H_8)Co_2 \rightarrow CoO$	210–350 370–450 460–500	30.68	29.62	660

[a] $T^{\star}$, the temperature at which the residues were measured.

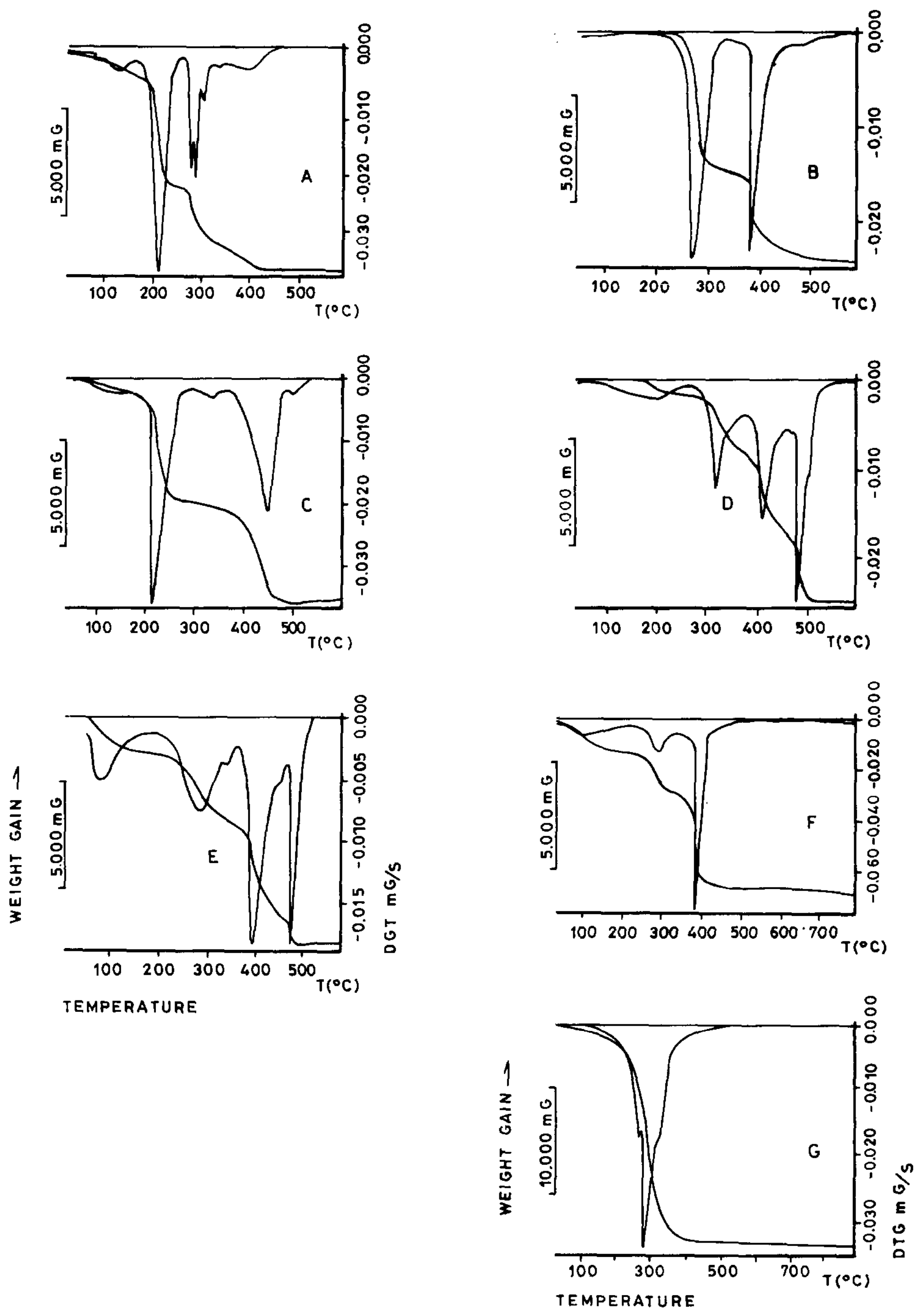


Fig. 1. TG curves of 5,5′-methylenebisthiosalicylic acid complexes of: (A) Cu(II), (B) Pb(II), (C) Cd(II), (D) Mn(II), (E) Co(II), (F) Ni(II); and (G) 5,5′-methylenebisthiosalicylic acid.

TABLE 4

IR absorption bands (cm^{-1})

Compound	OH	SH	C=O	C–O	C–S
MDTSA	3500–3000	2660	1670	1250	695
$(C_{15}S_2O_4H_{10})Cu \cdot 2H_2O$	3600–3500		1610	1400	720
$(C_{15}S_2O_4H_{10})Pb$	[a]		1580	1375	715
$(C_{15}S_2O_4H_{10})Mn \cdot H_2O$	3480–3360		1580	1400	710
$(C_{15}S_2O_4H_{10})Cd \cdot H_2O$	3480–3400		1590	1400	515
$(C_{15}S_2O_4H_8)Ni_2 \cdot 3H_2O$	3600–3000		1595	1400	710
$(C_{15}S_2O_4H_8)Co_2 \cdot 3H_2O$	3500–3200		1595	1400	710

[a] A very broad band without a minimum.

experimental and calculated residues (as percentages) for the assigned decomposition processes.

The Cu(II), Ni(II), Mn(II) and Co(II) complexes have thermal stabilities in accordance with the order proposed by Irving and Williams [18]: Mn < Co < Ni < Cu > Zn.

The masses of the residues of these anhydrous complexes correspond to the formation of the oxide, except in the case of the Cu(II) complex, for which the mass of the residue indicates the formation of copper sulphide. In all cases, the measured residual mass percentages are in good agreement with the calculated values.

MDTSA is stable up to 210 ° C. Pyrolysis is initiated at this temperature, and completed at 400 ° C.

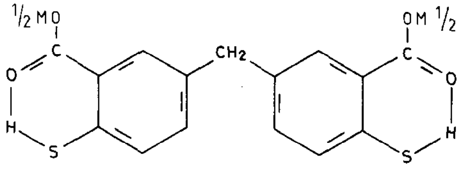
The relevant IR data are given in Table 4. The stretching vibration of S–H bonds (2660 cm^{-1} in free MDTSA) disappears in the IR spectra of the solid complexes, confirming that the sulphur atom is involved in the reaction. In the case of Co(II) and Ni(II), the S–H hydrogen is replaced by the metallic ion to give 2 : 1 (C : R) complexes. In the other cases, it forms a hydrogen bond with other carbonyl groups to give a 1 : 1 complex. These new bonds explain the shift of the C–S stretching band (695 cm^{-1} in free MDTSA) towards greater frequencies (+15–25 cm^{-1}).

The absorptions assigned to the carboxylic groups appear at 1670 and 1260 cm^{-1} in the free acid spectrum. In the metallic complexes, these two bands are clearly shifted, towards slightly lower ($\approx$ 1600 cm^{-1}) and very much higher ($\approx$ 1400 cm^{-1}) frequencies, respectively. These modifications, found for all the complexes studied, can be explained by the formation of a metal–oxygen ionic bond.

The solid complexes all present a broad absorption band between 3500 and 3000 cm^{-1} which is wider and weaker than the corresponding band for the reagent. The absorption in the solid complexes depends on the amount of crystallization water contained in each.

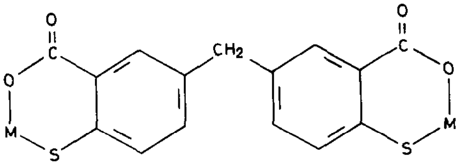
From IR data and elemental analysis, two basic structures for the complexes can be formulated, corresponding to the stoichiometries 1 : 1 and 2 : 1 (cation : MDTSA).

(a) 1 : 1 (cation : MDTSA) complexes



M = Cu, Pb, Mn, Cd

(b) 2 : 1 (cation : MDTSA) complexes



M = Ni, Co

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